

### 13B.1 Wall heat flux for turbulent flow in tubes (approximate)

The integral in Eq. 13.3-6 can be evaluated by making a change of variable. Let

$$\text{Pr}^{1/3} \left( \frac{y v_*}{14.5 \nu} \right) = x$$

Then Eq. 13.3-6 becomes (after setting the upper limit equal to infinity):

$$q_0 \text{Pr}^{-1/3} \left( \frac{v_*}{14.5 \nu} \right)^{-1} \int_0^\infty \frac{dx}{1+x^3} = k(T_0 - \bar{T}_R)$$

The integral may be found in a table of integrals, where we find

$$\int_0^\infty \frac{dx}{1+x^3} = \frac{\pi}{3 \sin \frac{1}{3} \pi} = \frac{\pi}{3 \left( \frac{1}{2} \sqrt{3} \right)} = \frac{2\pi}{3\sqrt{3}}$$

Hence Eq. 13.3-6 becomes

$$q_0 \text{Pr}^{-1/3} \left( \frac{v_*}{14.5 \nu} \right)^{-1} \frac{2\pi}{3\sqrt{3}} = k(T_0 - \bar{T}_R)$$

Then the dimensionless wall heat flux is

$$\frac{q_0 D}{k(T_0 - \bar{T}_R)} = \frac{3\sqrt{3}}{2\pi} \left( \frac{v_*}{14.5 \nu} \right) \text{Pr}^{1/3} D$$

This now has to be written in terms of dimensionless groups:

$$\frac{q_0 D}{k(T_0 - \bar{T}_R)} = \frac{3\sqrt{3}}{2\pi(14.5)} \left( \frac{v_*}{\langle v_z \rangle} \right) \left( \frac{D \langle v_z \rangle \rho}{\mu} \right) \text{Pr}^{1/3} = \frac{3\sqrt{3}}{2\pi(14.5)} \sqrt{\frac{f}{2}} \text{Re Pr}^{1/3}$$

where Eq. 6.1-4a has been used in order to introduce the friction factor. Thus we have obtained Eq. 13.3-7.

### 13B.2 Wall heat flux for turbulent flow in tubes

a. The assumptions are, for the asymptotic solution discussed here (the asymptotic form of the solution is introduced in Eq. 13.4-10):

- i. Fully developed turbulent flow
- ii. Axial heat conduction is presumed to be negligible with respect to axial heat convection
- iii. The turbulent Prandtl number can be taken to be unity (in developing Eq. 13.4-20)
- iv. The modified van Driest equation of Eq. 5.4-7 is used to describe the turbulent velocity profile (in development of Eq. 13.4-20)

b. To get the constant  $C_0$  in Eq. 13.4-10, we use B. C. 2. First we have to get the derivative  $d\Theta/d\xi$  using the Leibniz formula

$$\frac{d\Theta}{d\xi} = 0 + C_0 \frac{I(\xi)}{\xi \left[ 1 + \left( \alpha^{(t)}/\alpha \right) \right]}$$

Then at  $\xi = 1$  (the tube wall), the turbulent thermal diffusivity vanishes, and the dimensionless temperature gradient is unity, so that we get the result in Eq. 13.4-14:

$$1 = C_0 \frac{I(1)}{1[1+0]} \quad \text{or} \quad C_0 = [I(1)]^{-1}$$

The dimensionless wall temperature is obtained from setting  $\xi = 1$  in Eq. 13.4-12 (and setting  $C_1 = 0$ )

$$\Theta_0 = C_0 \zeta + C_0 \int_0^1 \frac{I(\xi)}{\xi \left[ 1 + \left( \alpha^{(t)}/\alpha \right) \right]} d\xi + C_2$$

The dimensionless bulk temperature is obtained using the definition in Eq. 10.8-33, starting with Eq. 13.4-12 (and setting  $C_1 = 0$ ):

$$\Theta_b = \frac{\int_0^1 \phi \Theta \xi d\xi}{\int_0^1 \phi \xi d\xi} = C_0 \zeta + C_0 \frac{1}{I(1)} \int_0^1 \phi \left[ \int_0^\xi \frac{I(\bar{\xi})}{\bar{\xi} \left[ 1 + \left( \alpha^{(t)}/\alpha \right) \right]} d\bar{\xi} \right] \xi d\xi + C_2$$

Then we get the dimensionless temperature difference:

$$\Theta_0 - \Theta_b = C_0 \int_0^1 \frac{I(\xi)}{\xi [1 + (\alpha^{(t)}/\alpha)]} d\xi - C_0 \frac{1}{I(1)} \int_0^1 \phi \left[ \int_0^\xi \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} \right] \xi d\xi$$

Then we exchange the order of integration to get the second line of Eq. 13.4-15:

$$\begin{aligned} \Theta_0 - \Theta_b &= C_0 \int_0^1 \frac{I(\xi)}{\xi [1 + (\alpha^{(t)}/\alpha)]} d\xi \\ &\quad - \frac{C_0}{I(1)} \int_0^1 \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} \left[ \int_0^1 \phi \xi d\xi - \int_0^{\bar{\xi}} \phi \xi d\xi \right] d\bar{\xi} \\ &= C_0 \int_0^1 \frac{I(\xi)}{\xi [1 + (\alpha^{(t)}/\alpha)]} d\xi - \frac{C_0}{I(1)} \int_0^1 \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} [I(1) - I(\bar{\xi})] d\bar{\xi} \\ &= C_0 \int_0^1 \frac{I(\xi)}{\xi [1 + (\alpha^{(t)}/\alpha)]} d\xi - C_0 \int_0^1 \frac{I(\xi)}{\xi [1 + (\alpha^{(t)}/\alpha)]} d\xi \\ &\quad + \frac{C_0}{I(1)} \int_0^1 \frac{[I(\bar{\xi})]^2}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} \end{aligned}$$

The first two terms cancel, and the third term gives Eq. 13.4-16, when the expression for  $C_0$  in Eq. 13.4-14 is used.

c. It is not necessary to find the constant  $C_2$  in this problem because we are interested only in the dimensionless temperature *difference*. In obtaining this difference, the integration constant  $C_2$  cancels out. If, however, we want to find the complete temperature profile, then we need an expression for  $C_2$ .

### 13C.1 Constant wall heat flux for turbulent flow between two parallel walls

a. For slit flow, the analog of Eq. 13.4-6 is

$$\phi \frac{\partial \Theta}{\partial \zeta} = \frac{\partial}{\partial \xi} \left[ \left( 1 + \frac{\alpha^{(t)}}{\alpha} \right) \frac{\partial \Theta}{\partial \xi} \right]$$

with the boundary conditions  $\partial \Theta / \partial \xi = 0$  at  $\xi = 0$ ,  $\partial \Theta / \partial \xi = 1$  at  $\xi = 1$ , and  $\Theta = 0$  at  $\zeta = 0$ . Here the dimensionless variables are defined as:

$$\Theta = \frac{\bar{T} - T_1}{q_0 B / k}; \quad \phi = \frac{\bar{v}_z}{\bar{v}_{z, \max}} \quad \xi = \frac{x}{b} \quad \zeta = \frac{z}{\rho \hat{C}_p \bar{v}_{z, \max} B^2 / k}$$

We now try a solution of the form  $\Theta(\xi, \zeta) = C_0 \zeta + \Psi(\xi)$ , which should be asymptotically correct at distances far down the tube. This leads then directly to the following differential equation

$$C_0 \phi = \frac{d}{d\xi} \left[ \left( 1 + \frac{\alpha^{(t)}}{\alpha} \right) \frac{d\Psi}{d\xi} \right]$$

A first integration then gives

$$\left( 1 + \frac{\alpha^{(t)}}{\alpha} \right) \frac{d\Psi}{d\xi} = C_0 \int_0^\xi \phi(\bar{\xi}) d\bar{\xi} + C_1 = C_0 J(\xi)$$

where we have introduced the abbreviation  $J(\xi) = \int_0^\xi \phi(\bar{\xi}) d\bar{\xi}$  and the constant of integration has been set equal to zero since  $\partial \Theta / \partial \xi = 0$  at the tube axis. Then, since  $\partial \Theta / \partial \xi = 1$  and  $\alpha^{(t)} = 0$  at the tube wall, we find that  $C_0 = 1/J(1)$ . Thus the dimensionless temperature profile is

$$\Theta(\xi, \zeta) = C_0 \zeta + C_0 \int_0^\xi \frac{J(\bar{\xi})}{1 + (\alpha^{(t)}/\alpha)} d\bar{\xi} + C_2$$

in which it is understood that  $\alpha^{(t)}$  is a function of  $\bar{\xi}$ . Next we form

$$\Theta_0 - \Theta_b = C_0 \int_0^1 \frac{J(\bar{\xi})}{1 + (\alpha^{(t)}/\alpha)} d\bar{\xi} - C_0 \frac{\int_0^1 \phi(\xi) \left[ \int_0^\xi \frac{J(\bar{\xi})}{1 + (\alpha^{(t)}/\alpha)} d\bar{\xi} \right] d\xi}{\int_0^1 \phi(\xi) d\xi}$$

Next we exchange the order of integration in the numerator and make use of the definition of  $J$  in the denominator to find

$$\Theta_0 - \Theta_b = C_0 \int_0^1 \frac{J(\bar{\xi})}{1 + (\alpha^{(t)}/\alpha)} d\bar{\xi} - \frac{C_0}{J(1)} \int_0^1 \frac{J(\bar{\xi})}{1 + (\alpha^{(t)}/\alpha)} \left[ \int_{\bar{\xi}}^1 \phi(\xi) d\xi \right] d\bar{\xi}$$

The inner integral of the second term may be written as  $J(1) - J(\bar{\xi})$ , and the  $J(1)$  contribution to the second term of  $\Theta_0 - \Theta_b$  exactly cancels the first term. The final expression for  $\Theta_0 - \Theta_b$  is thus

$$\Theta_0 - \Theta_b = \frac{1}{[J(1)]^2} \int_0^1 \frac{[J(\xi)]^2}{1 + (\alpha^{(t)}/\alpha)} d\xi$$

Then, since  $q_0 B/k(T_0 - T_b) = 1/(\Theta_0 - \Theta_b)$ , Eq. 13C.1-1 follows.

b. For laminar Newtonian flow,  $\phi = 1 - \xi^2$  and  $\alpha^{(t)} = 0$ ; then

$$J(\xi) = \int_0^\xi (1 - \bar{\xi}^2) d\bar{\xi} = \xi - \frac{1}{3} \xi^3 \quad \text{and} \quad J(1) = \frac{2}{3}. \quad \text{Furthermore}$$

$$\int_0^1 [J(\xi)]^2 d\xi = \int_0^1 \left( \xi^2 - \frac{2}{3} \xi^4 + \frac{1}{9} \xi^6 \right) d\xi = \frac{68}{315}$$

Hence, finally, for laminar Newtonian flow (using the mean hydraulic radius in the expression for the Nusselt number)

$$\text{Nu} = \frac{q_0(4B)}{k(T_0 - T_b)} = \frac{140}{17} \quad (\text{see the entry in Table 14.2-2})$$

For plug flow,  $J(\xi) = \int_0^\xi d\bar{\xi} = \xi$ ,  $J(1) = 1$ , and  $\int_0^1 [J(\xi)]^2 d\xi = \int_0^1 \xi^2 d\xi = \frac{1}{3}$ . Hence we finally get  $\text{Nu} = 12$ , which is the entry in Table 14.2-2.

### 13D.1 The temperature profile for turbulent flow in a tube

a. Condition #4 is  $\int_0^1 \Theta(\xi, \zeta) \phi(\xi) \xi d\xi = \zeta$ . Into this, we now substitute the expression for dimensionless temperature of Eq. 13.4-12, in order to get  $C_2$ . We do this term by term:

1st term:  $\int_0^1 C_0 \zeta \phi(\xi) \xi d\xi = C_0 \zeta \int_0^1 \phi(\xi) \xi d\xi = \zeta$  (Eq. 13.4-14 was used)

4th term:  $\int_0^1 C_2 \phi \xi d\xi = C_2 I(1)$

2nd term: 
$$\begin{aligned} \int_0^1 C_0 \left[ \int_0^\xi \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} \right] \phi(\xi) \xi d\xi \\ = C_0 \int_0^1 \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} \left[ \int_{\bar{\xi}}^1 \phi(\xi) \xi d\xi \right] d\bar{\xi} \\ = C_0 \int_0^1 \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} \left[ \int_0^1 \phi(\xi) \xi d\xi - \int_0^{\bar{\xi}} \phi(\xi) \xi d\xi \right] d\bar{\xi} \\ = \int_0^1 \frac{I(\bar{\xi})}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} - \frac{1}{I(1)} \int_0^1 \frac{[I(\bar{\xi})]^2}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} \end{aligned}$$

Substitution into the 4th condition above and solving for  $C_2$  gives

$$C_2 = \int_0^1 \frac{[I(\bar{\xi})/I(1)]^2}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi} - \int_0^1 \frac{[I(\bar{\xi})/I(1)]}{\bar{\xi} [1 + (\alpha^{(t)}/\alpha)]} d\bar{\xi}$$

which is the same as Eq. 13D.1-1.

b. For a Newtonian fluid  $I(\xi) = \int_0^\xi (1 - \bar{\xi}^2) \bar{\xi} d\bar{\xi} = \frac{1}{2} \xi^2 - \frac{1}{4} \xi^4$  and  $I(1) = \frac{1}{4}$ . Then  $[I(\xi)/I(1)] = 2\xi^2 - \xi^4$ ,  $[I(\xi)/I(1)]^2 = 4\xi^4 - 4\xi^6 + \xi^8$ , and

$$C_2 = \int_0^1 (4\xi^3 - 4\xi^5 + \xi^7) d\xi - \int_0^1 (2\xi - \xi^3) d\xi = -\frac{7}{24}$$

### 14A.1 Average heat transfer coefficients.

The total heat transfer rate is:

$$\begin{aligned} Q &= w\hat{C}_p(T_{b2} - T_{b1}) \\ &= (10,000 \text{ lb}_m/\text{hr})(0.6 \text{ Btu}/\text{lb}_m\cdot\text{F})(200 - 100 \text{ F}) \\ &= 600,000 \text{ Btu}/\text{hr} \end{aligned}$$

The total inside surface area of the tubes is:

$$A = \pi DL_{\text{tot}} = (\pi)(1.00 - 2 \times 0.065 \text{ in})(1/12 \text{ ft}/\text{in})(300 \text{ ft}) = 68.3 \text{ ft}^2$$

The various temperature differences between the inner tube surfaces and the oil are:

$$\begin{aligned} (T_0 - T_b)_1 &= 213 - 100 = 113 \text{ F} \\ (T_0 - T_b)_a &= (113 + 13)/2 = 63 \text{ F} \\ (T_0 - T_b)_{\ln} &= (113 - 13)/\ln(113/13) = 46.2 \text{ F} \end{aligned}$$

Insertion of these values into Eqs. 14.1-2,3,4 then gives the heat transfer coefficients:

$$\begin{aligned} h_1 &= (600,000)/(68.3 \times 113) = 78 \text{ Btu}/\text{hr}\cdot\text{ft}^2\cdot\text{F} \\ h_a &= (600,000)/(68.3 \times 63) = 139 \text{ Btu}/\text{hr}\cdot\text{ft}^2\cdot\text{F} \\ h_{\ln} &= (600,000)/(68.3 \times 46.2) = 190 \text{ Btu}/\text{hr}\cdot\text{ft}^2\cdot\text{F} \end{aligned}$$

### 14A.2 Heat transfer in laminar tube flow.

(a) The Prandtl number, based on the property values given, is

$$\text{Pr} = \frac{\hat{C}_p \mu}{k} = \frac{(0.49 \text{ Btu/lb}_m \cdot \text{F})(1.42 \text{ lb}_m/\text{ft} \cdot \text{hr})}{(0.0825 \text{ Btu/hr} \cdot \text{ft} \cdot \text{F})} = 8.43$$

(b) The Reynolds number is

$$\begin{aligned} \text{Re} &= \frac{D \langle v \rangle \rho}{\mu} = \frac{4w}{\pi D \mu} \\ &= \frac{(4)(100 \text{ lb}_m/\text{hr})}{(\pi)(1/12 \text{ ft})(1.42 \text{ lb}_m/\text{ft} \cdot \text{hr})} \\ &= 1076 \end{aligned}$$

(c) From Fig. 14.3-2, at  $L/D = (20 \text{ ft})/(1/12 \text{ ft}) = 240$ , we read

$$\frac{(T_{b2} - T_{b1})}{(T_0 - T_b)_{\ln}} \cdot \left( \frac{D}{4L} \right) \cdot \left( \frac{\hat{C}_p \mu}{k} \right)^{2/3} \left( \frac{\mu_b}{\mu_0} \right)^{-0.14} = 0.0028$$

Now, for uniform  $T_0$ ,

$$\frac{(T_{b2} - T_{b1})}{(T_0 - T_b)_{\ln}} = \ln \left( \frac{T_0 - T_{b1}}{T_0 - T_{b2}} \right)$$

Hence, for this problem,

$$\ln \left( \frac{T_0 - T_{b1}}{T_0 - T_{b2}} \right) = (0.0028)(4 \times 240)(8.43)^{-2/3}(1.0) = 0.649,$$

giving

$$\frac{T_0 - T_{b2}}{T_0 - T_{b1}} = \exp(-0.649) = 0.523$$

Insertion of  $T_0 = 215^\circ\text{F}$  and  $T_{b1} = 100^\circ\text{F}$  gives

$$T_{b2} = 215 - 0.523(215 - 100) = 155^\circ\text{F}$$



### 14A.3 Effect of flow rate on exit temperature from a heat exchanger.

(a) From the solution of Problem 14A.2 we find that  $Re = 10.76w$  and that

$$\frac{T_0 - T_{b2}}{T_0 - T_{b1}} = \exp\left(\frac{-0.649Y}{0.0028}\right) = \exp(-232Y)$$

in which  $w$  is the mass flow rate in  $lb_m/hr$  and  $Y$  is the ordinate of Fig. 14.3-2 at the prevailing Reynolds number. The exit bulk temperature is then

$$T_{b2} = T_{b1} + (T_0 - T_{b1})[1 - \exp(-232Y)]$$

(b) The total heat flow through the tube wall is

$$Q = w\hat{C}_p(T_{b2} - T_{b1})$$

Calculations for (a) and (c) are summarized below:

$w$ , $lb_m/hr$	Re	$Y$	$1 - e^{-232Y}$	$T_{b2} - T_{b1}$ , $^{\circ}F$	$T_{b2}$ , $^{\circ}F$	$Q$ , Btu/hr
100	1076	0.0028	0.478	54.9	154.9	2690
200	2152	0.00185	0.349	40.1	140.1	3930
400	4304	0.0036	0.566	65.1	165.1	12760
800	8608	0.0040	0.605	69.5	169.5	27260
1600	17216	0.0037	0.576	66.3	166.3	51950
3200	34432	0.0033	0.535	61.5	161.5	96460

#### 14A.4 Local heat transfer coefficient for turbulent forced convection in a tube.

Fig. 14.3-2 requires the viscosity values  $\mu_b$  at  $T_b$  and  $\mu_0$  at  $T_0$ . Interpolation in Table 1.1-1, or on page 6-3 of *CRC Handbook of Chemistry and Physics*, 81st Edition (2000-2001) gives  $\mu_b = 1.13 \text{ mPa}\cdot\text{s}$  at  $T_b = 60^\circ\text{F} = 15.56^\circ\text{C}$ , and  $\mu_0 = 0.398 \text{ mPa}\cdot\text{s}$  at  $T_0 = 160^\circ\text{F} = 71.11^\circ\text{C}$ , whence  $(\mu_b/\mu_0) = 2.84$ . The other physical properties in Fig. 14.3-2, including  $\mu$  in the Reynolds and Prandtl numbers, are evaluated at the "film temperature"  $T_f = (T_0 + T_b)/2 = 110^\circ\text{F} = 43.33^\circ\text{C}$ , giving  $\mu = 1.489 \text{ lb}_m/\text{hr}\cdot\text{ft}$ ,  $\hat{C}_p = 4.1792 \text{ J/g}\cdot\text{K} = 0.99885 \text{ Btu/lb}_m\cdot\text{F}$ , and  $k = 0.6348 \text{ W/m}\cdot\text{K} = 0.36679 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F}$ . Then the Prandtl number at  $T_f$  is

$$\frac{\hat{C}_p\mu}{k} = \frac{(0.99885 \text{ Btu/lb}_m\cdot\text{F})(1.489 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F})}{0.36679 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F}} = 4.05$$

and the Reynolds number calculated at  $T_f$  is

$$\begin{aligned} \text{Re} &= \frac{DG}{\mu} = \frac{4w}{\pi D\mu} \\ &= \frac{4 \times (15,000 \text{ lb}_m/\text{hr})}{\pi(2/12 \text{ ft})(1.489 \text{ lb}_m/\text{hr}\cdot\text{ft})} = 7.70 \times 10^4 \end{aligned}$$

From Fig. 14.3-2 at this value of Re, we get the ordinate expression

$$\frac{h_{1n}}{\hat{C}_p G} \left( \frac{\hat{C}_p\mu}{k} \right)^{2/3} \left( \frac{\mu_b}{\mu_0} \right)^{-0.14} = 0.0028 \quad (14A.4-1)$$

in which  $h_{1n}$  can be regarded also as  $h_{loc}$  according to the analysis in Problem 14B.5 and  $G = 4w/\pi D^2 = (4\pi)(15,000 \text{ lb}_m/\text{hr})/(2/12 \text{ ft})^2 = 6.88 \times 10^5 \text{ lb}_m/\text{hr}\cdot\text{ft}^2$ .

Insertion of the foregoing results into Eq. 14A.4-1 then gives

$$\begin{aligned} h_{loc} &= 0.0028 \hat{C}_p G \left( \frac{\hat{C}_p\mu}{k} \right)^{-2/3} \left( \frac{\mu_b}{\mu_0} \right)^{+0.14} \\ &= 0.0028(0.99885 \text{ Btu/lb}_m\cdot\text{F})(6.88 \times 10^5 \text{ lb}_m/\text{hr}\cdot\text{ft}^2)(4.05)^{-2/3}(2.84)^{+0.14} \\ &= 7.8 \times 10^2 \text{ Btu/hr}\cdot\text{ft}^2\cdot\text{F} \end{aligned}$$

as the asymptotic value of the local heat transfer coefficient, and

$$\begin{aligned} q_r|_{r=R} &= -q_0 = h_{loc}(T_b - T_0) \\ &= (7.8 \times 10^2)(60 - 160) = -7.8 \times 10^4 \end{aligned}$$

as the radial heat flux at the inner wall of the pipe.

### 14A.5 Heat transfer from condensing vapors.

(a) The boundaries of the condensate layer are at  $T_0 = 190^\circ\text{F}$  and  $T_d = 212^\circ\text{F}$ ; thus the film temperature  $T_f$  is  $(190 + 212)/2 = 201^\circ\text{F}$ . The physical properties at this temperature are well approximated by the values at  $200^\circ\text{F}$ , given in Ex. 14.7-1:

$$\begin{aligned}\Delta\hat{H}_{\text{vap}} &= 978 \text{ Btu/lb}_m \\ k &= 0.393 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F} \\ \rho &= 60.1 \text{ lb}_m/\text{ft}^3 \\ \mu &= 0.738 \text{ lb}_m/\text{hr}\cdot\text{ft}\end{aligned}$$

The resulting abscissa for Fig. 14.7-2 is:

$$\begin{aligned}& \frac{k\rho^{2/3}g^{1/3}(T_d - T_0)L}{\mu^{5/3}\Delta\hat{H}_{\text{vap}}} \\ &= \frac{(0.393 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F})(60.1 \text{ lb}_m/\text{ft}^3)^{2/3}(4.17 \times 10^8 \text{ ft/hr}^2)^{1/3}(22 \text{ F})(1.0 \text{ ft})}{(0.738 \text{ lb}_m/\text{ft}\cdot\text{hr})^{5/3}(978 \text{ Btu/lb}_m)} \\ &= 168 \text{ Btu}^{-1}\text{hr}^{-1-2/3+5/3}\text{ft}^{1-2+1/3+1+5/3}\text{F}^{-1+1}, \text{ dimensionless}\end{aligned}$$

This value falls in the laminar region of Fig. 14.7-2. Extrapolation of the laminar line with a slope of  $3/4$ , consistent with Eq. 14.7-5, gives

$$\Gamma/\mu = 170(0.168)^{3/4} = 45$$

The heat transfer rate, neglecting subcooling, is

$$\begin{aligned}Q &= \pi D\Gamma\Delta\hat{H}_{\text{vap}} = \pi(1/12 \text{ ft})(45 \times 0.738 \text{ lb}_m/\text{ft}\cdot\text{hr})(978 \text{ Btu/lb}_m) \\ &= 8400 \text{ Btu/hr}.\end{aligned}$$

A similar result is obtainable from Eq. 14.7-5, once the flow is known to be laminar.

(b) Comparison of Eqs. 14.7-5 and 6 gives, for laminar condensate flow:

$$\frac{Q_{\text{hor.}}}{Q_{\text{vert.}}} = \frac{0.725}{0.943} \left(\frac{L}{D}\right)^{1/4}$$

Hence, if the tube were horizontal the heat transfer rate would be:

$$Q_{\text{hor.}} = (8400)(0.725/0.943)(12)^{1/4} = 12,000 \text{ Btu/hr}$$

The assumption of laminar condensate flow on the horizontal tube is clearly reasonable, given the result of (a) and the still smaller value of  $\Gamma/\mu$  in (b).

#### 14A.6 Forced-convection heat transfer from an isolated sphere.

(a) The physical properties of air at 1 atm and  $T_f = \frac{1}{2}(T_0 + T_\infty) = 150^\circ\text{F} = 65.56^\circ\text{C} = 338.7\text{K}$  are:

$$\rho = pM/RT_f = 1.042 \times 10^{-3} \text{ g/cm}^3$$

$$\mu = 0.02023 \text{ cp} = 2.023 \times 10^{-4} \text{ g/cm}\cdot\text{s, from Table 1.1-2}$$

$$\hat{C}_p = 1.008 \text{ J/g}\cdot\text{K} = 1.008 \text{ W}\cdot\text{s/g}\cdot\text{K from CRC Handbook 2000-2001, pp. 6-1,6-2.}$$

$$k = 26.9 \times 10^{-3} \text{ W/m}\cdot\text{K from CRC Handbook 2000-2001, p. 6-185}$$

The Reynolds and Prandtl numbers are

$$\begin{aligned} \text{Re} &= \frac{Dv_\infty\rho}{\mu} \\ &= \frac{(2.54 \text{ cm})(100 \times 12 \times 2.54 \text{ cm/s})(1.042 \times 10^{-3} \text{ g/cm}^3)}{2.023 \times 10^{-4} \text{ g/cm}\cdot\text{s}} \\ &= 3.99 \times 10^4 \\ \text{Pr} &= \frac{\hat{C}_p\mu}{k} \\ &= \frac{(1.008 \text{ W}\cdot\text{s/g}\cdot\text{K})(2.023 \times 10^{-4} \text{ g/cm}\cdot\text{s})}{26.9 \times 10^{-5} \text{ W/cm}\cdot\text{K}} \\ &= 0.703 \end{aligned}$$

Substitution of these values into Eq. 14.4-5 gives

$$\begin{aligned} \text{Nu}_m &= 2 + 0.60(3.99 \times 10^4)^{1/2}(0.703)^{1/3} \\ &= 108.6 \end{aligned}$$

Hence,

$$\begin{aligned} h_m &= 108.6k/D = 108.6(26.9 \times 10^{-5} \text{ W/cm}\cdot\text{K})/(2.54 \text{ cm}) \\ &= 0.01150 \text{ W/cm}^2\cdot\text{K} \end{aligned}$$

and the convective heat loss rate is

$$\begin{aligned} Q &= \pi D^2 h_m (T_0 - T_\infty) \\ &= \pi(2.54^2 \text{ cm}^2)(0.01150 \text{ W/cm}^2\cdot\text{K})([100/1.8] \text{ K}) \\ &= 12.9 \text{ W} = 3.1 \text{ cal/s} \end{aligned}$$

according to Eq. 14.4-5. The radiative loss is about 1.0 W for a perfectly black sphere in a large enclosure with walls at  $100^\circ\text{F}$ , and can be estimated by the methods of §16.5.

(b) For Eq. 14.4-6, we need  $\mu_0 = 0.02144$  cp at  $T_0 = 200^\circ\text{F} = 93.3^\circ\text{C}$  and the following property values at  $T_\infty = 100^\circ\text{F} = 37.8^\circ\text{C} = 310.9$  K:

$$\begin{aligned}\mu_\infty &= 0.01898 \text{ cp} = 1.898 \times 10^{-4} \text{ g/cm}\cdot\text{s} \\ \rho &= pM/RT_\infty = 1.136 \times 10^{-3} \text{ g/cm}^3 \\ \hat{C}_p &= 1.007 \text{ J/g}\cdot\text{K} = 1.007 \text{ W}\cdot\text{s/g}\cdot\text{K} \\ k &= 27.0 \times 10^{-3} \text{ mW/m}\cdot\text{K} = 27.0 \times 10^{-5} \text{ W/cm}\cdot\text{K}\end{aligned}$$

The resulting values of Re and Pr calculated at the upstream state are

$$\begin{aligned}\text{Re} &= \frac{(2.54 \text{ cm})(100 \times 12 \times 2.54 \text{ cm/s})(1.136 \times 10^{-3} \text{ g/cm}^3)}{1.898 \times 10^{-4} \text{ g/cm}\cdot\text{s}} \\ &= 4.63 \times 10^4 \\ \text{Pr} &= \frac{(1.007 \text{ W}\cdot\text{s/g}\cdot\text{K})(1.898 \times 10^{-4} \text{ g/cm}\cdot\text{s})}{27.0 \times 10^{-5} \text{ W/cm}\cdot\text{K}} \\ &= 0.708\end{aligned}$$

Substitution of these values into Eq. 14.4-6 gives

$$\begin{aligned}\text{Nu}_m &= 2 + (0.4 \text{ Re}^{1/2} + 0.06 \text{ Re}^{2/3}) \text{Pr}^{0.4} \left( \frac{\mu_\infty}{\mu_0} \right)^{1/4} \\ &= 2 + 138.1 = 140.1\end{aligned}$$

whence

$$\begin{aligned}h_m &= 140.1 k_\infty / D = 140.1 (27.0 \times 10^{-5} \text{ W/cm}\cdot\text{K}) / (2.54 \text{ cm}) \\ &= 0.0149 \text{ W/cm}^2\cdot\text{K}\end{aligned}$$

and the convective heat loss rate is

$$\begin{aligned}Q &= \pi D^2 h_m (T_0 - T_\infty) \\ &= \pi (2.54 \text{ cm})^2 (0.0149 \text{ W/cm}^2\cdot\text{K}) ([100/1.8] \text{ K}) \\ &= 16.8 \text{ W} = 4.0 \text{ cal/s}\end{aligned}$$

according to Eq. 14.4-6. This result is believed to be more accurate than that found in (a).

### 14A.7 Free-convection heat transfer from an isolated sphere.

For the conditions of this problem, the thermal expansion coefficient  $\beta = 1/T_f$  is (1/338.7 K), and the other physical properties are the same as in part (a) of Problem 14A.6. (Note that, for the correlations in §14.6,  $\beta$  and  $\rho$  are evaluated at  $T_f$  rather than  $\bar{T}$  for calculation of Gr.) Then

$$\begin{aligned}\text{GrPr} &= \left( \frac{D^3 \rho^2 g \beta \Delta T}{\mu^2} \right) \left( \frac{\hat{C}_p \mu}{k} \right) \\ &= \frac{(2.54 \text{ cm})^3 (0.001042 \text{ g/cm}\cdot\text{s})^2 (980.7 \text{ cm/s}^2) (100/[1.8 \times 338.7])}{(2.023 \times 10^{-4} \text{ g/cm}\cdot\text{s})^2} (0.703) \\ &= 4.92 \times 10^4\end{aligned}$$

Eq. 14.6-4 gives

$$\begin{aligned}\text{Nu}_m^{\text{lam}} &= \frac{0.878 \times 0.671}{[1 + (0.492/\text{Pr})^{9/16}]^{4/9}} (\text{GrPr})^{1/4} \\ &= \frac{(0.878)(0.671)}{[1 + (0.492/0.703)^{9/16}]^{4/9}} (4.92 \times 10^4)^{1/4} \\ &= 6.73\end{aligned}$$

Hence,

$$\begin{aligned}h_m &= 6.73k/D = (6.73)(26.9 \times 10^{-5} \text{ W/cm}\cdot\text{K})/(2.54 \text{ cm}) \\ &= 0.000712 \text{ W/cm}^2\cdot\text{K}\end{aligned}$$

and the convective heat loss rate is

$$\begin{aligned}Q &= \pi D^2 h_m (T_0 - T_\infty) \\ &= \pi (2.54 \text{ cm})^2 (0.000712 \text{ W/cm}^2\cdot\text{K}) ([100/1.8] \text{ K}) \\ &= 0.80 \text{ W} = 0.20 \text{ cal/s}\end{aligned}$$

By the methods of §16.5, one can calculate that the rate of heat loss by radiation is of comparable magnitude: 1.0 W for a perfectly black sphere in a large enclosure with walls at 100°F.

**14A.8 Heat loss by free convection from a horizontal pipe immersed in a liquid.**

From the data provided, we find the following values at  $T_f = 32.3^\circ\text{C}$ :

$$\beta = \frac{-1}{\rho} \frac{d\rho}{dT} = -\frac{0.99463 - 0.99528}{0.99496(33.3 - 31.3)}$$

$$= 3.27 \times 10^{-4} \text{ K}^{-1} = 1.815 \times 10^{-4} \text{ F}^{-1}$$

$$\rho = 0.99496 \text{ g/cm}^3 (12 \times 2.54 \text{ cm/ft})^3 / (453.59 \text{ g/lb}_m) = 62.11 \text{ lb}_m/\text{ft}^3$$

$$\hat{C}_p = 0.9986 \text{ cal/g}\cdot\text{C} \approx 0.9986 \text{ Btu/lb}_m\cdot\text{F}$$

$$\mu = 0.7632 \text{ cp} = 1.8463 \text{ lb}_m/\text{hr}\cdot\text{ft}$$

$$k = 0.363 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F}$$

$$\frac{\hat{C}_p \mu}{k} = \frac{(0.9986 \text{ Btu/lb}_m\cdot\text{F})(1.8463 \text{ lb}_m/\text{hr}\cdot\text{ft})}{0.363 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F}} = 5.08$$

Hence,

$$\text{GrPr} = \frac{(0.5 \text{ ft})^3 (62.11 \text{ lb}_m/\text{ft}^3)^2 (4.17 \times 10^8 \text{ ft/hr}^2) (1.815 \times 10^{-4} \times 20)}{(1.8463 \text{ lb}_m/\text{hr}\cdot\text{ft})^2} \quad (5.08)$$

$$= 1.088 \times 10^9$$

Then from Eqs. 14.6-1 to 3 and Table 14.6-1 we get

$$\text{Nu}_m = 0.772 \left( \frac{0.671}{[1 + (0.492/5.08)^{9/16}]^{4/9}} \right) (1.088 \times 10^9)^{1/4}$$

$$= 0.772 \left( \frac{0.671}{1.112} \right) (181.6) = 84.6$$

The heat transfer coefficient is then

$$h_m = \text{Nu} \frac{k}{D} = 84.6 \left( \frac{0.363}{0.5} \right) = 61.4 \text{ Btu/hr}\cdot\text{ft}^2\cdot\text{F}$$

and the rate of convective heat loss per unit length of the pipe is

$$\frac{Q}{L} = \frac{h_m A \Delta T}{L} = h_m \pi D \Delta T$$

$$= (61.4 \text{ Btu/hr}\cdot\text{ft}^2\cdot\text{F})(3.1415)(0.5 \text{ ft})(20^\circ\text{F}) = 1930 \text{ Btu/hr}\cdot\text{ft}$$

### 14B .1 Limiting local Nusselt numbers for plug flow with constant heat flux

(Note: Problem 10B.9-1 should be worked prior to doing this problem)

a. For circular tubes with plug flow, the dimensionless temperature distribution, the dimensionless wall temperature, and the dimensionless bulk temperature are obtainable from Eq. 10B.9-1 on p. 325:

$$\Theta = \frac{k(T - T_1)}{q_0 R} = 2\zeta + \frac{1}{2}\xi^2 - \frac{1}{4} \quad \left(\text{where } \xi = \frac{r}{R} \text{ and } \zeta = \frac{\alpha z}{v_0 R^2}\right)$$

$$\Theta_0 = \Theta|_{\xi=1} = 2\zeta + \frac{1}{4}$$

$$\Theta_b = \frac{\int_0^1 \Theta v_0 \xi d\xi}{\int_0^1 v_0 \xi d\xi} = 2 \int_0^1 \Theta \xi d\xi = 2 \int_0^1 \left(2\zeta + \frac{1}{2}\xi^2 - \frac{1}{4}\right) \xi d\xi = 2\zeta$$

Then the difference between the wall temperature and the bulk temperature is

$$\Theta_0 - \Theta_b = \frac{k(T_0 - T_b)}{q_0 R} = \frac{1}{4}$$

and the Nusselt number is

$$\text{Nu} = \frac{hD}{k} = \frac{q_0(2R)}{k(T_0 - T_b)} = 4 \cdot 2 = 8$$

in agreement with Eq. (J) on p. 430. Note that, by convention, the Nusselt number for tubes is defined using the diameter rather than the radius, and this definition introduces the factor of 2.

b. For the plug flow in a slit of width  $2B$ , we have for the dimensionless temperature, wall temperature, and bulk temperature, all obtainable from the results of part (b) of Problem 10B.9:



$$\Theta = \frac{k(T - T_1)}{q_0 B} = \zeta + \frac{1}{2} \sigma^2 - \frac{1}{6} \quad (\text{where } \sigma = \frac{x}{B} \text{ and } \zeta = \frac{\alpha z}{v_0 B^2})$$

$$\Theta_0 = \Theta|_{\sigma=1} = \zeta + \frac{1}{3}$$

$$\Theta_b = \frac{\int_0^1 \Theta v_0 d\sigma}{\int_0^1 v_0 d\sigma} = \int_0^1 \Theta d\sigma = \int_0^1 \left( \zeta + \frac{1}{2} \sigma^2 - \frac{1}{6} \right) d\sigma = \zeta$$

Then the difference between the wall temperature and the bulk temperature is

$$\Theta_0 - \Theta_b = \frac{k(T_0 - T_b)}{q_0 B} = \frac{1}{3}$$

The Nusselt number is then

$$\text{Nu} = \frac{h(4B)}{k} = \frac{q_0(4B)}{k(T_0 - T_b)} = 3 \cdot 4 = 12$$

in agreement with Eq. (J) on p. 431. Note that the Nusselt number for slits is defined in terms of  $4B$ , and this is the origin of the factor of 4 which appears here (see heading of Tables 14.2-1 and 2, as well as the caption for Figure 14.2-1 on p. 429).

## 14B.2 Local overall heat transfer coefficient.

Let 0 and 1 denote the inner and outer surfaces of the tube, and  $h_0$  and  $h_1$  denote the local heat transfer coefficients on those surfaces at the cross-section where the oil bulk temperature is 150°F. According to the development in §9.6, the temperature drops within a cross-section have the same ratio as the corresponding resistance terms that sum to  $1/(r_0 U_0)$ :

$$\frac{T_1 - 150}{213 - T_1} = \left[ \frac{1}{r_0 h_0} + \frac{\ln(r_1/r_0)}{k_{01}} \right] / \left[ \frac{1}{r_1 h_1} \right]$$

The numerator on the right is

$$\begin{aligned} & \frac{1}{(0.435/12)(190)} + \frac{\ln(0.5/0.435)}{220} \\ & = 0.1452 + 0.0006 = 0.1458 \text{ hr}\cdot\text{ft}\cdot\text{F}/\text{Btu} \end{aligned}$$

in which a thermal conductivity of  $k_{01} = 220 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F}$  has been used for copper at  $T \approx 190^\circ\text{F}$ , based on Tables 9.1-5 and F.3-5. To calculate the denominator, we use Eq. 14.7-3 for the heat transfer coefficient for filmwise condensation on horizontal tubes. Iteration is required, since the temperature difference across the condensate film is unknown. As a first approximation, we choose  $T_1 = 190^\circ\text{F}$ , and use the physical properties at  $200^\circ\text{F}$  from Example 14.7-1:

$$\begin{aligned} \Delta \hat{H}_{\text{vap}} &= 978 \text{ Btu/lb}_m \\ k &= 0.393 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F} \\ \rho &= 60.1 \text{ lb}_m/\text{ft}^3 \\ \mu &= 0.738 \text{ lb}_m/\text{hr}\cdot\text{ft} \end{aligned}$$

Then Eq. 14.7-3 gives

$$\begin{aligned} h_1 = h_m &= 0.725 \left[ \frac{k^3 \rho^2 g \Delta \hat{H}_{\text{vap}}}{\mu D (T_d - T_1)} \right]^{1/4} \\ &= 0.725 \left[ \frac{0.393^3 \rho^2 (4.17 \times 10^8) (978.8)}{(0.738)(0.5/12)(T_d - T_1)} \right]^{1/4} \\ &= 12,500(213 - T_1)^{-1/4} \end{aligned}$$

Equating the heat flow through the numerator and denominator resistances gives

$$(T_1 - 150)/0.1458 = (213 - T_1)r_1 h_1 = (213 - T_1)^{3/4}(0.5/12)(12,500)$$

or

$$213 - T_1 = 0.0000183(T_1 - 150)^{4/3}$$

Successive substitutions of  $T_1$  in the right-hand term give a rapidly converging sequence of left-hand values: to the solution:  $T_1 = 212.9975, 212.9954, 212.9954, \dots$  Thus, the outer-surface temperature of the tubes at this cross-section is  $212.9954^\circ\text{F}$ . The temperature drop through the tube wall is  $0.0006/0.1458(212.995 - 150) = 0.25^\circ\text{F}$ . Thus, the thermal resistances of the tube wall and condensate film are unimportant here, as assumed in Problem 14A.1.

### 14B.3 The hot-wire anemometer

a. The physical properties of interest at  $p = 1$  atm and a film temperature of  $335^\circ\text{F}$  are:

$$\rho = 0.0499 \text{ lb}_m/\text{ft}^3$$

$$\hat{C}_p = 0.242 \text{ Btu}/\text{lb}_m \cdot ^\circ\text{F}$$

$$\mu = 0.0594 \text{ lb}_m/\text{ft} \cdot \text{hr} = 1.64 \times 10^{-5} \text{ lb}_m/\text{ft} \cdot \text{s} \quad (\text{from Eq. 1.4.14})$$

$$k = \left( 0.242 + \frac{5}{4} \left( \frac{1.986}{29} \right) \right) (1.64 \times 10^{-5}) = 5.373 \times 10^{-6} \text{ Btu}/\text{ft} \cdot \text{s} \cdot ^\circ\text{F}$$

(from Eq. 9.3-15)

$$\text{Pr} = 0.74 \quad (\text{from Eq. 9.3-16})$$

$$\text{Also the Reynolds number is } \text{Re} = \frac{(0.01/12)(100)(0.0499)}{(1.64 \times 10^{-5})} = 254$$

Then Eq. 14.4-8 gives

$$\begin{aligned} \text{Nu}_m &= (5.99 + 2.29)(0.905) \\ &\quad + 0.92(-3.54 + 1062)^{-1/3} (6.33)(0.905) = 8.010 \end{aligned}$$

Then we get the heat transfer coefficient from

$$\begin{aligned} h_m &= \frac{\text{Nu}_m k}{D} = \frac{(8.010)(5.373 \times 10^{-6})}{(0.01/12)} = 0.0516 \text{ Btu}/\text{ft}^2 \cdot \text{s} \cdot ^\circ\text{F} \\ &= 186 \text{ Btu}/\text{ft}^2 \cdot \text{hr} \cdot ^\circ\text{F} \end{aligned}$$

Finally, the heat loss from the wire is

$$\begin{aligned} Q &= h_m A \Delta T = h_m \cdot \pi D L \cdot (T_0 - T_\infty) \\ &= (186) \left( \pi \frac{0.01}{12} \frac{0.5}{12} \right) (600 - 70) \text{ Btu}/\text{hr} \\ &= 10.75 \text{ Btu}/\text{hr} = 3.15 \text{ W} = 10.75 \text{ W} \end{aligned}$$

b. For an approach velocity of  $300 \text{ ft}/\text{s}$ ,  $\text{Re} = 762$ . Equation 14.4-8 gives  $\text{Nu}_m = 14.20$ , and  $Q(300)/Q(100) = 14.20/8.010 = 1.77$ . This is very close to  $\sqrt{3} = 1.73$  from King's relation.

#### 14B.4 Dimensional analysis.

(a) The left-hand member of Eq. 14B.4-1 is expressible in terms of integrals of the dimensionless product function  $\overline{\tilde{v}_z \tilde{T}}$  as follows:

$$\frac{T_{b2} - T_{b1}}{T_{b0} - T_{b1}} = \left[ \overline{\langle \tilde{v}_z \tilde{T} |_{\tilde{z}=0} \rangle} - \overline{\langle \tilde{v}_z \tilde{T} |_{\tilde{z}=L/D} \rangle} \right] \quad (\text{A})$$

Here the angle brackets denote cross-sectional averages as in Eqs. 10.8-32 and 33, whereas overlines denote long-term time averages. Thus the averages on the right depend only on Re, Pr, and L/D, when viscous dissipation and radiant energy absorption and emission are neglected in the energy equation. With these assumptions, and the further neglect of axial heat conduction, the quotient  $(T_{b2} - T_{b1})/(T_0 - T_{b1})$  is equal to the time-average of  $Q/(w\hat{C}_p(T_0 - T_{b1}))$ .

(b) The heat transfer coefficients  $h_a$  and  $h_{ln}$  each differ from  $h_1$  only by the ratio of the corresponding  $\Delta T$  definitions given in §14.1. But  $\Delta T_a$  and  $\Delta T_{ln}$  are expressible in terms of  $\Delta T_1$  and  $\Delta T_2$ , so their ratios depend only on Re, Pr, and L/D according to the result in (a). Hence,  $Nu_a$  and  $Nu_{ln}$  are functions of the same arguments as  $Nu_1$ , confirming Eqs. 14.3-12 and 13.

Equation 14.3-14 requires extension of Eq. A to a variable upper limit  $\tilde{z}$ , giving

$$\frac{T_b(z) - T_{b1}}{T_0 - T_{b1}} = \text{a function of } (\text{Re}, \text{Pr}, \tilde{z}) \quad (\text{B})$$

Then, according to Eq. 14.1-18,

$$\begin{aligned} \frac{h_{loc}D}{k} &= \frac{w\hat{C}_p}{\pi Dk} \frac{d \ln(T_0 - T_b)}{d(z/D)} \\ &= \left( \frac{w}{\pi D\mu} \right) \left( \frac{\hat{C}_p\mu}{k} \right) \frac{d \ln(T_0 - T_b)}{d\tilde{z}} \\ &= 4 \text{RePr} \frac{d \ln[(T_0 - T_b)/(T_0 - T_{b1})]}{d\tilde{z}} \end{aligned}$$

Combining this result with Eq. B, we get (for this special case of uniform wall temperature in the heat-exchange section),

$$Nu_{loc} = Nu_{loc} \left( \text{Re}, \text{Pr}, \left( \frac{z}{D} \right) \right)$$

in agreement with Eq. 14.3-14.

### 14B.5 Relation between $h_{loc}$ and $h_{in}$

a. We relate the rate of heat transfer across the increment of surface  $\pi D dz$  to the decrease in the internal energy within the volume element  $\frac{1}{4} \pi D^2$ :

$$h_{loc}(\pi D dz)(T_b - T_0) = -\left(\frac{1}{4} \pi D^2\right) \rho \hat{C}_p \langle v \rangle dT$$

This is really an application of the  $d$ -form of the energy balance discussed in §15.5, and given specifically in Eq. 15.4-4. It is clear from this equation that the kinetic and potential energy changes are being neglected, and that Eq. 15.4-4 has been multiplied through by  $w$ .

The above equation may now be integrated over a length  $L$  of the tube to get, with  $T_0 = \alpha + \beta T_b$ ,

$$\begin{aligned} \int_0^L h_{loc} dz &= -\frac{1}{4} D \rho \hat{C}_p \langle v \rangle \int_{T_b(0)}^{T_b(L)} \frac{dT_b}{T_b - T_0} = -\frac{1}{4} D \rho \hat{C}_p \langle v \rangle \int_{T_b(0)}^{T_b(L)} \frac{dT_b}{T_b(1-\beta) - \alpha} \\ &= -\frac{\frac{1}{4} D \rho \hat{C}_p \langle v \rangle}{1-\beta} \ln [T_b(1-\beta) - \alpha] \Big|_{T_b(0)}^{T_b(L)} \\ &= -\frac{\frac{1}{4} D \rho \hat{C}_p \langle v \rangle}{1-\beta} \left\{ \ln [T_b(L)(1-\beta) - \alpha] - \ln [T_b(0)(1-\beta) - \alpha] \right\} \\ &= -\frac{\frac{1}{4} D \rho \hat{C}_p \langle v \rangle}{1-\beta} \left\{ \ln [T_b(L) - T_0(L)] - \ln [T_b(0) - T_0(0)] \right\} \\ &= -\frac{\frac{1}{4} D \rho \hat{C}_p \langle v \rangle}{1-\beta} \frac{[T_b(L) - T_0(L)] - [T_b(0) - T_0(0)]}{(T_b - T_0)_{ln}} \\ &= -\frac{1}{4} D \rho \hat{C}_p \langle v \rangle \frac{[T_b(L) - (\alpha/(1-\beta))] - [T_b(0) - (\alpha/(1-\beta))]}{(T_b - T_0)_{ln}} \\ &= +\frac{1}{4} D \rho \hat{C}_p \langle v \rangle \frac{T_b(L) - T_b(0)}{(T_0 - T_b)_{ln}} \end{aligned}$$

which agrees with Eq. 15B.5-2.

b. Equation 14.1-14 can be written as

$$h_{\text{in}} = \frac{\frac{1}{4} D \rho \hat{C}_p \langle v \rangle [T_b(L) - T_b(0)]}{L (T_0 - T_b)_{\text{in}}}$$

from which Eq. 14B.5-3 follows at once:

$$h_{\text{in}} = \frac{1}{L} \int_0^L h_{\text{loc}} dz$$

Then, differentiating the integral in Eq. 14B.5-3 using the Leibniz formula in Eq. C.3-2, we get

$$\frac{dh_{\text{in}}}{dL} = -\frac{1}{L^2} (L h_{\text{in}}) + \frac{1}{L} h_{\text{loc}} \Big|_{z=L}$$

or

$$h_{\text{loc}} \Big|_{z=L} = h_{\text{in}} + L \frac{dh_{\text{in}}}{dL}$$

which is Eq. 14B.5-4

### 14B.6 Heat loss by free convection from a pipe

The properties of air at 1 atm and a film temperature of 190°F (or 650° R) are

$$\begin{aligned}\mu &= 0.216 \text{ cp} \\ k &= 0.0173 \text{ Btu/hr} \cdot \text{ft} \cdot ^\circ\text{F} \\ \beta &= 1/650 \text{ (}^\circ\text{R)}^{-1} \\ \hat{C}_p &= 0.242 \text{ Btu/lb}_m \cdot ^\circ\text{F} \\ \text{Pr} &= 0.727\end{aligned}$$

Since the temperature difference is the same in both the original problem (of Example 14.6-1) and the new problem (Problem 14B.6), it suffices to determine the ratio  $h'_m/h_m$ , where the accent indicates the result for the "new" problem.

Next we calculate the ratio of the heat-transfer coefficients:

$$\begin{aligned}\frac{h'_m}{h_m} &= \left(\frac{k'}{k}\right)^{3/4} \left(\frac{\beta'}{\beta} \cdot \frac{\hat{C}_p'}{\hat{C}_p} \cdot \frac{\mu}{\mu'}\right)^{1/4} \left(\frac{[1 + (0.492/\text{Pr})^{9/16}]^{4/9}}{[1 + (0.492/\text{Pr}')^{9/16}]^{4/9}}\right) \\ &= \left(\frac{0.0173}{0.0152}\right)^{3/4} \left(\frac{550}{650} \cdot \frac{0.242}{0.241} \cdot \frac{0.0190}{0.0216}\right)^{1/4} \left(\frac{1.299}{1.299}\right) \\ &= (1.102)(0.930)(1.000) = 1.025\end{aligned}$$

Thus, in the "new" problem, the heat-transfer rate is only slightly greater than in the original problem.

If the thermal conductivity and viscosity had been assumed to vary with temperature by the simple power-law suggested by the simplified kinetic theory of Chapters 9 and 1, then almost no change would have been predicted.

### 14D.1 Heat transfer from an oblate ellipsoid of revolution

a. From Eq. A.7-13 we get (with  $\Sigma = \sinh \xi$ ,  $K = \cosh \xi$ ,  $S = \sin \eta$ ,  $C = \cos \eta$ ,  $s = \sin \psi$ ,  $c = \cos \psi$ )

$$h_\xi^2 = \sum_{i=1}^3 \left( \frac{\partial x_i}{\partial \xi} \right)^2 = a^2 [(\Sigma S c)^2 + (\Sigma S s)^2 + (K C)^2] = a^2 [(\Sigma S)^2 + (K C)^2]$$

$$= a^2 [(K^2 - 1)S^2 + K^2(1 - S^2)] = a^2 (K^2 - S^2) \quad \therefore h_\xi = a\sqrt{K^2 - S^2}$$

$$h_\eta^2 = \sum_{i=1}^3 \left( \frac{\partial x_i}{\partial \eta} \right)^2 = a^2 [(K C c)^2 + (K C s)^2 + (\Sigma S)^2] = a^2 [(K C)^2 + (\Sigma S)^2]$$

$$= a^2 [K^2(1 - S^2) + (K^2 - 1)S^2] = a^2 (K^2 - S^2) \quad \therefore h_\eta = a\sqrt{K^2 - S^2}$$

$$h_\psi^2 = \sum_{i=1}^3 \left( \frac{\partial x_i}{\partial \psi} \right)^2 = a^2 [(K S s)^2 + (K S c)^2] = a^2 K^2 S^2 \quad \therefore h_\psi = aKS$$

These results may be used with the expression for surface elements after Eq. A.7-18 to get

$$S_{\eta\psi} = a^2 \sqrt{\cosh^2 \xi - \sin^2 \eta} (\cosh \xi \sin \eta) d\eta d\psi$$

b. From Eq. A.7-17, we get Laplace's equation as

$$\nabla^2 \Theta = \frac{1}{h_\xi h_\eta h_\psi} \left( \frac{\partial}{\partial \xi} \left( \frac{h_\eta h_\psi}{h_\xi} \frac{\partial \Theta}{\partial \xi} \right) + \dots \right) = 0 \quad \text{or} \quad \frac{d}{d\xi} \left( \cosh \xi \frac{d\Theta}{d\xi} \right) = 0$$

since heat is flowing in the  $\xi$  direction only. This equation may be integrated to give

$$\Theta = K_1 \arctan(\sinh \xi) + K_2$$

with the boundary conditions:  $\Theta(\xi_0) = 0$  and  $\Theta(\infty) = 1$ . This leads to Eq. 14D.1-7.

c. In the limit as  $\xi_0 \rightarrow 0$  (a two-sided disk of radius  $a = R$ ), the result of part (b), namely Eq. 14D.1-7, simplifies to



$$\Theta = 1 - \frac{\frac{1}{2}\pi - \arctan(\sinh \xi)}{\frac{1}{2}\pi - 0} = \frac{2}{\pi} \arctan(\sinh \xi)$$

The normal dimensionless temperature gradient at the surface is then obtained by using Eq. A.7-15, thus:

$$\begin{aligned} \left. \frac{1}{h_\xi} \frac{d\Theta}{d\xi} \right|_{\xi=0} &= \frac{1}{R\sqrt{1-\sin^2 \eta}} \left. \frac{d}{d\xi} \left( \frac{2}{\pi} \arctan(\sinh \xi) \right) \right|_{\xi=0} \\ &= \frac{1}{R\sqrt{1-\sin^2 \eta}} \left( \frac{2}{\pi} \right) \left( \frac{1}{1+\sinh^2 \xi} \cdot \cosh \xi \right) \Big|_{\xi=0} \\ &= \frac{1}{R\sqrt{1-\sin^2 \eta}} \left( \frac{2}{\pi} \right) (\cosh 0) = \left( \frac{2}{\pi} \right) \frac{1}{R\sqrt{1-\sin^2 \eta}} \end{aligned}$$

Then the total heat loss through both sides of the disk is

$$\begin{aligned} Q &= 2 \int (\mathbf{n} \cdot \mathbf{q}) dS = -2k \int (\mathbf{n} \cdot \nabla T) dS \\ &= 2k(T_0 - T_\infty) \cdot \frac{2}{\pi R} \int_0^{2\pi} \int_0^{\pi/2} \frac{1}{\cos \eta} R^2 \cos \eta \sin \eta d\eta d\psi \\ &= 2k(T_0 - T_\infty) \cdot \frac{2}{\pi R} \cdot 2\pi R^2 \int_0^\pi \sin \eta d\eta = 8kR(T_0 - T_\infty) \end{aligned}$$

The heat transfer coefficient is then

$$h_m = \frac{Q}{A\Delta T} = \frac{8kR(T_0 - T_\infty)}{(\pi R^2)(T_0 - T_\infty)} = \frac{8k}{\pi R}$$

and the Nusselt number is

$$\text{Nu}_m = \frac{h_m(2R)}{k} = \frac{8k}{\pi R} \cdot \frac{2R}{k} = \frac{16}{\pi} = 5.09$$

### 15A.1 Heat transfer in double-pipe heat exchangers.

(a) In the absence of heat loss to the surroundings, Eqs. 15.4-7,8 give

$$w_c \hat{C}_{pc}(T_{c2} - T_{c1}) = -w_h \hat{C}_{ph}(T_{h2} - T_{h1})$$

with each flow rate  $w$  expressed from plane 1 toward plane 2. Insertion of the data then gives

$$Q_c = (5000)(1.00)(T_{c2} - 60) = -(-10,000)(0.60)(200 - 100) = 600,000 \text{ Btu/hr}$$

whence

$$T_{c2} = 60 + 120 = 180^\circ\text{F}$$

The log-mean temperature difference is

$$(\Delta T)_{\ln} = (20 - 40) / \ln(20/40) = 28.85\text{F}$$

and the required heat exchange area, from Eq. 15.4-15, is

$$A_0 = \frac{Q_c}{U_0(\Delta T)_{\ln}} = \frac{(600,000 \text{ Btu/hr})}{(200 \text{ Btu/hr}\cdot\text{ft}^2\cdot\text{F})(28.85\text{F})} = 104 \text{ ft}^2$$

(b) Eq. 15B.1-2 gives

$$\begin{aligned} \frac{Q}{A} &= \frac{U_1 \Delta T_2 - U_2 \Delta T_1}{\ln(U_1 \Delta T_2 / U_2 \Delta T_1)} \\ &= \frac{(50 \times 20) - (350 \times 40)}{\ln((50 \times 20) / (350 \times 40))} \\ &= 4926 \text{ Btu/hr}\cdot\text{ft}^2 \end{aligned}$$

The required heat exchange area is then

$$A = \frac{Q}{Q/A} = \frac{600,000}{4926} = 122 \text{ ft}^2$$

(c) The minimum usable flow rate of water to cool the oil to  $100^\circ\text{F}$  in counterflow is

$$w_c = \frac{(10,000)(0.60)(200 - 100)}{(1.00)(200 - 60)} = 4286 \text{ lb}_m/\text{hr}$$

whereas the minimum usable flow rate of water in parallel flow is

$$w_c = \frac{(10,000)(0.60)(200 - 100)}{(1.00)(100 - 60)} = 15,000 \text{ lb}_m/\text{hr}$$

(d) If parallel flow is used, with  $w_c = 15,500 \text{ lb}_m/\text{hr}$  of water, the outlet water temperature will be

$$T_{c2} = 60 + (10,000)(0.60)(200 - 100) / (15,500)(1.00) = 98.71^\circ\text{F}$$

Then  $(\Delta T)_{\ln} = (140 - 1.29) / \ln(140/1.29) = 29.6^\circ\text{F}$  and the required heat exchange area is

$$A = \frac{Q}{U(\Delta T)_{\ln}} = \frac{(10,000)(0.60)(200 - 100)}{(200)(29.6)} = 101 \text{ ft}^2$$

## 15A.2 Adiabatic flow of natural gas in a pipeline.

(a) The density and mass flux at plane 1 are

$$\rho_1 = \frac{p_1 M}{RT} = \frac{(100 \times 144 \text{ lb}_f/\text{ft}^2)(16.04 \text{ lb}_m/\text{lb-mol})}{(1545 \times 530 \text{ ft}\cdot\text{lb}_f/\text{lb-mol})} = 0.2821 \text{ lb}_m/\text{ft}^3$$

$$G := \rho_1 v_1 = (0.2821 \text{ lb}_m/\text{ft}^3)(40 \text{ ft/s}) = 11.28 \text{ lb}_m/\text{ft}^2\cdot\text{s}$$

Re and  $f$  at plane 1 are the same here as in Example 15.4-2, and  $f$  is approximated as constant at 0.0025 along the pipeline, giving

$$e_v = 4fL/D = (4)(0.0025)(52,800/2) = 264.$$

Furthermore,

$$\begin{aligned} p_1 \rho_1 &= (100 \times 144 \text{ lb}_f/\text{ft}^2)(32.2 \text{ lb}_m\text{ft}/\text{lb}_f\cdot\text{s}^2)(0.2821 \text{ lb}_m/\text{ft}^3) \\ &= 1.308 \times 10^5 \text{ lb}_m^2/\text{ft}^4\cdot\text{s}^2. \end{aligned}$$

Eq. 15B3-7 may be rearranged to give

$$\frac{e_v - [(\gamma + 1)/2\gamma] \ln s}{1 - s} - \frac{\gamma - 1}{2\gamma} = \frac{\rho_1 p_1}{G^2}$$

or, for this problem with  $\gamma = 1.3$  for methane,

$$\frac{264 - [2.3/2.6] \ln s}{1 - s} - \frac{0.3}{2.6} = \frac{1.308 \times 10^5}{(11.28)^2} = 1026$$

This equation has the solution  $s = 0.74$ , corresponding to  $\rho_2/\rho_1 = \sqrt{0.74} = 0.86$  and  $\rho_2 = 0.86 \times 0.2821 = 0.243 \text{ lb}_m/\text{ft}^3$ .

(b) Eq. 15B.3-8 and the result of (a) give

$$\begin{aligned} p_2 &= p_1 \frac{\rho_2}{\rho_1} \left[ 1 + \frac{[1 - (\rho_1/\rho_2)^2] G^2}{\rho_1 p_1} \left( \frac{\gamma - 1}{2\gamma} \right) \right] \\ &= (100 \text{ psia})(0.86) \left[ 1 + \frac{[1 - 0.86^{-2}](11.28 \text{ lb}_m/\text{ft}^2\cdot\text{s})^2}{(1.308 \times 10^5 \text{ lb}_m^2/\text{ft}^4\cdot\text{s}^2)} \left( \frac{0.3}{2.6} \right) \right] \\ &= 86 \text{ psia} \end{aligned}$$

(c) The temperature at the compressor inlet is

$$T_2 = T_1(p_2/p_1)(\rho_1/\rho_2) = 530(86/100)/(0.86) = 530^\circ\text{R}$$

Eq. 15.4-22 then gives

$$\begin{aligned}
 \hat{W}_m &= \frac{v_1^2}{2} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right] \\
 &\quad + \frac{RT_2}{M} \frac{\gamma}{\gamma - 1} \left[ \left( \frac{p_1}{p_2} \right)^{(\gamma-1)/\gamma} - 1 \right] \\
 &= \frac{(40)^2}{2} \left[ 1 - \left( \frac{1}{0.86} \right)^2 \right] \\
 &\quad + \frac{(49686 \times 530 \text{ lb}_m \text{ft}^2/\text{s}^2 \cdot \text{lb-mol})}{16.04 \text{ lb}_m/\text{lb-mol}} \frac{1.3}{0.3} \left[ \left( \frac{100}{86} \right)^{0.3/1.3} - 1 \right] \\
 &= (-282 + 2.520 \times 10^5 \text{ ft}^2/\text{s}^2) / (32.2 \text{ lb}_m \text{ft}/\text{s}^2 \cdot \text{lb}_f) = 7817 \text{ ft} \cdot \text{lb}_f/\text{lb}_m
 \end{aligned}$$

and the required compressor power output is

$$\begin{aligned}
 W_m &= w \hat{W}_m = \left( \frac{\pi D^2}{4} \right) G \hat{W}_m \\
 &= \left( \frac{\pi (2 \text{ ft})^2}{4} \right) (11.28 \text{ lb}_m/\text{ft}^2 \cdot \text{s}) (7817 \text{ ft} \cdot \text{lb}_f/\text{lb}_m) = 2.770 \times 10^5 \text{ ft} \cdot \text{lb}_f/\text{s} \\
 &= 504 \text{ hp}
 \end{aligned}$$

### 15A.3 Mixing of two ideal-gas streams.

(a) The right sides of Eqs. 15.3-6, 7 and 10 are

$$\begin{aligned} w &= w_{1a} + w_{1b} = 1000 + 10,000 \\ &= 11,000 \text{ lb}_m/\text{hr} = 3.0556 \text{ lb}_m/\text{s} \end{aligned}$$

$$\begin{aligned} P &= v_{1a}w_{1a} + v_{1b}w_{1b} + p_{1a}S_{1a} + p_{1b}S_{1b} \\ &= v_{1a}w_{1a} + v_{1b}w_{1b} + \frac{RT_{1a}}{M} \frac{w_{1a}}{v_{1a}} + \frac{RT_{1b}}{M} \frac{w_{1b}}{v_{1b}} \\ &= [(1000)(1000/3600) + (100)(10,000/3600) \text{ lb}_m \cdot \text{ft}/\text{s}^2] \\ &\quad + \left( \frac{49686 \times 540}{28.97} \text{ ft}^2/\text{s}^2 \right) \left[ \frac{1000/3600}{1000} + \frac{10,000/3600}{100} \text{ lb}_m/\text{ft} \right] \\ &= 555.6 + 25983.5 = 26539.1 \text{ lb}_m \cdot \text{ft}/\text{s}^2 \end{aligned}$$

With  $\tilde{C}_p = 6.97 \text{ Btu}/\text{lb-mole} \cdot \text{F}$ , hence  $\hat{C}_p = 6.97/28.97 \text{ Btu}/\text{lb}_m \cdot \text{F}$ , the right side of Eq. 15.3-10 becomes

$$\begin{aligned} E &= \hat{C}_p [w_{1a}T_{1a} + w_{1b}T_{1b}] + \frac{1}{2} [w_{1a}v_{1a}^2 + w_{1b}v_{1b}^2] \\ &= (6.97 \times 540/28.97 \text{ Btu}/\text{lb}_m)(25036 \text{ lb}_m \text{ft}^2/\text{s}^2 \cdot \text{Btu}) \left[ \frac{1000}{3600} + \frac{10,000}{3600} \text{ lb}_m/\text{s} \right] \\ &\quad + \frac{1}{2} \left[ \frac{1000}{3600} (1000)^2 + \frac{10,000}{3600} (100)^2 \text{ lb}_m \text{ft}^2/\text{s}^3 \right] \\ &= 9.939 \times 10^6 + 1.390 \times 10^5 = 1.0078 \times 10^7 \text{ lb}_m \text{ft}^2/\text{s}^3 \end{aligned}$$

and  $\gamma = \tilde{C}_p/(\tilde{C}_p - R) = 6.97/(6.97 - 1.9872) = 1.399$ .

Then Eq. 15.3-13 yields the solutions

$$\begin{aligned} v_2 &= \left( \frac{1.399}{2.399} \right) \frac{26539.1}{3.05556} \left[ 1 \pm \sqrt{1 - 2 \left( \frac{1.399^2 - 1}{1.399^2} \right) \frac{3.05556 \times 1.0078 \times 10^7}{(26539.1)^2}} \right] \\ &= 5065[1 \pm 0.97838] = 109.5 \text{ ft/s and } 10020 \text{ ft/s} \end{aligned}$$

the smaller one of which is stable.

Then Eq. 15.3-10 gives the temperature of the mixed stream:

$$\begin{aligned} T_2 &= [E/w - \frac{1}{2}v_2^2]/\hat{C}_p \\ &= \left[ \frac{1.0078 \times 10^7}{3.05556} - \frac{1}{2}(109.5)^2 \text{ ft}^2/\text{s}^2 \right] \frac{28.97}{6.97 \times 25036 \text{ }^\circ\text{R} \cdot \text{s}^2/\text{ft}^2} \\ &= 546.5^\circ\text{R} = 86.5^\circ\text{F} \end{aligned}$$

The cross-sectional area of the mixed stream is

$$\begin{aligned} S_2 &= S_{1a} + S_{1b} = \frac{w_{1a}}{\rho_{1a}v_{1a}} + \frac{w_{1b}}{\rho_{1b}v_{1b}} = \frac{RT_1}{p_1M} \left[ \frac{w_{1a}}{v_{1a}} + \frac{w_{1b}}{v_{1b}} \right] \\ &= \left( \frac{49686 \times 540}{68086 \times 28.97} \text{ ft}^3/\text{lb}_m \right) \left[ \frac{1000/3600}{1000} + \frac{10,000/3600}{100} \text{ lb}_m/\text{ft} \right] \\ &= 0.3816 \text{ ft}^2 \end{aligned}$$

and the pressure  $p_2$  of the mixed stream is obtained from Eq. 15.3-7:

$$\begin{aligned} p_2 &= \frac{P - v_2 w_2}{S_2} \\ &= \left[ \frac{26539.1 - 109.5 \times 11,000/3600}{0.3816} \right] = 6.86 \times 10^4 \text{ lb}_m/\text{ft}\cdot\text{s}^2 = 1.00 \text{ atm} \end{aligned}$$

(b) If the fluid density were treated as constant, Eq. 15.3-6 would give

$$(S_{1a} + S_{1b})v_2 = S_{1a}v_{1a} + S_{1b}v_{1b}$$

whence

$$\begin{aligned} v_2 &= \frac{S_{1a}v_{1a} + S_{1b}v_{1b}}{S_{1a} + S_{1b}} \\ &= \frac{w_{1a}/\rho + w_{1b}\rho}{w_{1a}/\rho v_{1a} + w_{1b}/\rho v_{1b}} \\ &= \frac{w_{1a} + w_{1b}}{w_{1a}/v_{1a} + w_{1b}/v_{1b}} \\ &= \frac{11,000}{1 + 100} = 108.9 \text{ ft/s} \end{aligned}$$

(c) Eq. D of Table 15.3-1 gives, for the conditions of (b),

$$\begin{aligned} \hat{E}_v &= (w_{1a}/w_2) \frac{v_{1a}^2}{2} + (w_{1b}/w_2) \frac{v_{1b}^2}{2} - \frac{v_2^2}{2} \\ &= (1000/11000) \frac{(1000)^2}{2} + (10,000/11000) \frac{(100)^2}{2} - \frac{(109.5)^2}{2} \\ &= 45454.5 + 4545.5 - 5995.1 \text{ ft}^2/\text{s}^2 \\ &= 44004.8 \text{ ft}^2/\text{s}^2 \times 3.1081 \times 10^{-2} \text{ ft}\cdot\text{lb}_f/(\text{lb}_m\text{ft}^2/\text{s}^2) = 1.368 \times 10^3 \text{ ft}\cdot\text{lb}_f/\text{lb}_m \end{aligned}$$

#### 15A.4 Flow through a Venturi tube.

(a) Eq. 15.5-34 requires the calculated values

$$S_0 = (\pi/4)(D_0)^2 = (\pi/4)(3/12 \text{ ft})^2 = 0.04909 \text{ ft}^2,$$

$$\rho_2 = \left(\frac{p_1 M}{RT_1}\right)(p_2/p_1)^{1/\gamma} = \frac{(14.696 \times 144 \text{ lb}_f/\text{ft}^2)(28.97 \text{ lb}_m/\text{lb-mol})}{(1544.3 \times 529.7 \text{ ft}\cdot\text{lb}_f/\text{lb-mol})}(0.75)^{1/1.4}$$

$$= 0.0610 \text{ lb}_m/\text{ft}^3,$$

$$\frac{p_1}{\rho_1} = \frac{RT_1}{M} = \left(\frac{49686 \times 529.7 \text{ lb}_m\cdot\text{ft}^2/\text{s}^2\cdot\text{lb-mol}}{28.97 \text{ lb}_m/\text{lb-mol}}\right) = 9.085 \times 10^5 \text{ ft}^2/\text{s}^2,$$

$$1 - (S_0/S_1)^2(p_2/p_1)^{2/\gamma} = 1 - (D_0/D_1)^4(p_2/p_1)^{2/\gamma} = (3/12)^4(0.75)^{2/1.4} = 0.99990.$$

Substitution of these and known values into Eq. 15.5-34 gives

$$(0.98)(0.0610)(0.04909) \sqrt{2(9.085 \times 10^5)[1.4/0.4][1 - 0.75^{0.4/1.4}]}$$

(b) For isothermal flow,

$$\rho_2 = \frac{p_2 M}{RT_1} = \frac{(0.75 \times 14.696 \times 144 \text{ lb}_f/\text{ft}^2)(28.97 \text{ lb}_m/\text{lb-mol})}{(1544.3 \times 529.7 \text{ ft}\cdot\text{lb}_f/\text{lb-mol})} = 0.0562 \text{ lb}_m/\text{ft}^3,$$

$$1 - (\rho_2 S_0/\rho_1 S_1)^2 = 1 - (p_2/p_1)^2(D_2/D_1)^4 = 1 - (0.75)^2((3/12)^4) = 0.9978,$$

and

$$-\int_1^2 (1/\rho)dp = \frac{RT_1}{M} \ln(p_1/p_2) = \frac{(49686 \times 529.7)}{28.97} \ln(1/0.75) = 2.614 \times 10^5 \text{ ft}^2/\text{s}^2$$

Then Eq. 15.5-33 gives

$$w = (0.98)(0.0562)(0.04909) \sqrt{\frac{2 \times 2.614 \times 10^5}{0.9978}} = 1.96 \text{ lb}_m/\text{s}$$

(c) For constant density at the entering value,

### 15A.5 Free batch expansion of a compressible fluid.

(a) Just after the start of the discharge,  $p_1$  is equal to  $p_0$  and  $p_2/p_1$  attains the critical value given in Eq 15.5-43. Hence,

$$p_2 = p_0 \left( \frac{2}{1.4 + 1} \right)^{1.4/(1.4-1)} = 52.8 \text{ atm}$$

The expansion from  $p_1$  to  $p_2$  satisfies  $p/\rho T = R/M$ , hence

$$\frac{T_2}{T_0} = \frac{p_2 \rho_0}{p_0 \rho_2}$$

Inserting  $\rho_2/\rho_0 = (p_2/p_0)^{1/\gamma}$  according to Eq. 15.5-39, we get

$$\begin{aligned} T_2 &= T_0 (p_2/p_0)^{(\gamma-1)/\gamma} \\ &= T_0 \left[ \left( \frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)} \right]^{(\gamma-1)/\gamma} \\ &= T_0 \left( \frac{2}{\gamma + 1} \right) = 300 \left( \frac{2}{2.4} \right) = 250 \text{ K} \end{aligned}$$

(b) When  $p_2 = p_a = 1 \text{ atm}$ ,  $p_1 = 1/0.528 = 1.893 \text{ atm}$ . Then the temperature within the main part of the tank is

$$T_1 = T_0 \left( \frac{p_1}{p_0} \right)^{(\gamma-1)/\gamma} = 300 \left( \frac{1.893}{100} \right)^{0.4/1.4} = 300 \times 0.5078 = 152 \text{ K}$$

(c) At the state described in (b),  $\rho_1/\rho_0 = (1.893/100)^{1/1.4} = 0.0588$ . The time required to reach this state is computable from Eq. 15.5-46:

$$\begin{aligned} t &= \frac{(V/S_2)}{\sqrt{(\gamma RT_0/M)(2/(\gamma + 1))^{(\gamma+1)/(\gamma-1)}}} \left( \frac{2}{\gamma - 1} \right) \left[ \left( \frac{\rho_1}{\rho_0} \right)^{(1-\gamma)/2} - 1 \right] \\ &= \frac{(10/0.1 \text{ ft})}{\sqrt{(1.4 \times 49686 \times 300 \times 1.8/28.97 \text{ ft}^2/\text{s}^2)(2/2.4)^{2.4/0.4}}} \\ &\quad \cdot \left( \frac{2}{0.4} \right) \left[ (0.0588)^{-0.4/2} - 1 \right] \\ &= 0.58 \text{ s} \end{aligned}$$



### 15A.6 Heating of air in a tube.

For the air contained in the 20-ft length of tube, we write Eq. 15.1-3 with  $\hat{W}_m = 0$  (since this system has no moving surfaces); also we use the approximation  $\Delta(v^2/2)$  of the kinetic energy change from inlet to outlet. This gives the simplified steady-state energy balance

$$\Delta \left( \hat{H} + \frac{1}{2}v^2 \right) = \hat{Q}$$

for horizontal flow, or

$$\frac{1}{M} \int_{T_1}^{T_2} \tilde{C}_p dT + \frac{1}{2}v_1^2 \left[ \left( \frac{p_1 T_2}{p_2 T_1} \right)^2 - 1 \right] = \hat{Q}$$

for horizontal flow of an ideal gas in a tube. Proceeding as in Example 15.3-1, we get the algebraic equation

$$\begin{aligned} & \frac{1}{28.97} [6.39(T_2 - T_1) + \frac{9.8}{2} \times 10^{-4}(T_2^2 - T_1^2) - \frac{8.18}{3} \times 10^{-8}(T_2^3 - T_1^3)] \text{ Btu/lb}_m \\ & + \frac{1}{2} (75 \text{ ft/s})^2 \times 3.9942 \times 10^{-5} \text{ Btu}/(\text{lb}_m \text{ ft}^2/\text{s}^2) \left[ \left( \frac{40T_2}{15T_1} \right)^2 - 1 \right] \\ & = (800 \times 20/185 = 86.4865 \text{ Btu/lb}_m) \end{aligned}$$

Inserting  $T_1 = 5^\circ\text{F}$ , and an initial guess of  $800^\circ\text{R}$  for  $T_2$ , we get the following Newton iteration sequence, converging to  $864^\circ\text{R} \approx 354^\circ\text{F}$ :

Old $T_2$ , $^\circ\text{R}$	LHS, Btu/lb <sub>m</sub>	$f = \text{LHS} - \text{RHS}$	$f' = df/dT_2$ , Btu/lb <sub>m</sub> ·R	$\Delta T_2 = -f/f'$	New $T_2$ , $^\circ\text{R}$
800	82.9245	-3.5620	0.2458	14.49	814.49
814.49	86.5761	+0.0896	0.2474	-0.36	814.12

### 15A.7 Operation of a simple double-pipe heat exchanger.

(a) The two exchangers will work most effectively if connected so as to simulate a single double-pipe exchanger operating in countercurrent flow. That is, the stream to be heated should enter exchanger A through its inner pipe at plane 1, next to the outlet of the twice-cooled hot water stream, and should exit the inner pipe of exchanger B at plane 2, next to the original inlet of the hot-water stream.

(b) The Reynolds and Prandtl numbers for the stream being heated are:

$$\text{Re} = \left( \frac{4w}{\pi D \mu} \right) = \left( \frac{(4)(5400 \text{ lb}_m/\text{hr})}{\pi(0.0875 \text{ ft})(1.09 \text{ lb}_m/\text{hr}\cdot\text{ft})} \right) = 7.21 \times 10^4$$

$$\text{Pr} = \left( \frac{\hat{C}_p \mu}{k} \right) = \left( \frac{(1.00 \text{ Btu}/\text{lb}_m\cdot\text{F})(1.09 \text{ lb}_m/\text{hr}\cdot\text{ft})}{0.376 \text{ Btu}/\text{hr}\cdot\text{ft}\cdot\text{F}} \right) = 2.90$$

At these conditions, with  $\mu_0$  and  $\mu_b$  not distinguished, Fig. 14.3-2 gives

$$\frac{h_{\text{ln}} D}{k} (\text{Re})^{-1} (\text{Pr})^{-1/3} = 0.0028$$

and the insensitivity of  $h_{\text{ln}}$  to  $L/D$  at Re above 8000 gives  $h_{\text{loc}} = h_{\text{ln}}$  according to Eq. 14B.5-4. Hence, the local heat transfer coefficient for the inner pipe wall is

$$\begin{aligned} h_i &= 0.0028 \frac{k}{D_i} (\text{Re})(\text{Pr})^{1/3} \\ &= 0.0028 \frac{(0.376 \text{ Btu}/\text{hr}\cdot\text{ft}\cdot\text{F})}{(0.0875 \text{ ft})} (7.21 \times 10^4)(2.90)^{1/3} \\ &= 1237 \text{ Btu}/\text{hr}\cdot\text{ft}^2\cdot\text{F} \end{aligned}$$

and the local overall coefficient  $U_i$  based on  $D_i$  satisfies

$$\begin{aligned} \frac{1}{D_i U_i} &= \frac{1}{D_i h_i} + \frac{1}{D_i h_{\text{annulus}}} + \text{Wall and deposit resistance based on } D_i \\ &= \frac{1}{(0.0875 \times 1237)} + \frac{1}{(0.0875 \times 2000)} + \frac{0.001}{0.0875} \text{ hr}\cdot\text{ft}\cdot\text{F}/\text{Btu} \end{aligned}$$

or

$$\begin{aligned} \frac{1}{U_i} &= \frac{1}{1237} + \frac{1}{2000} + 0.001 \\ &= 0.000808 + 0.0005 + 0.001 = 0.002308 \text{ hr}\cdot\text{ft}^2\cdot\text{F}/\text{Btu} \end{aligned}$$

Hence,  $U_i = (1/0.002308) \text{ Btu}/\text{hr}\cdot\text{ft}^2\cdot\text{F}$ . Equation 15.4-13 then gives

$$\ln \left( \frac{T_{h1} - T_{c1}}{T_{h2} - T_{c2}} \right) = U_i \left( \frac{1}{w_h \hat{C}_{ph}} + \frac{1}{w_c \hat{C}_{pc}} \right) (\pi D_i L) \quad (15A.7-1)$$

or

$$\ln \left( \frac{T_{h1} - 70}{200 - T_{c2}} \right) = \frac{1}{0.002308} \left( \frac{1}{(5400)(1.00)} + \frac{1}{(-8100)(1.00)} \right) (\pi \times 0.0875 \times 40)$$

$$= 0.2941$$

in which  $L$ ,  $w_h$  and  $w_c$  are measured in the direction of the cold water flow.

The computation of  $T_{c2}$  is summarized below. For each trial value of  $T_{c2}$ , an energy balance with heat capacities of 1.00 Btu/lb<sub>m</sub>·F gives

$$5400(1.00)(T_{c2} - 70) = 8100(1.00)(200 - T_{h1}) \quad (15A.7 - 2)$$

from which the outlet temperature  $T_{h1}$  of the cooled hot water can be calculated for testing against Eq. 15A.7-1. The final  $T_{h1}$  is very close to 136°F.

$T_{c2}$	$T_{h1} = 200 - \frac{2}{3}(T_{c2} - 70)$	$T_{h1} - 70$	$200 - T_{c2}$	$\ln \frac{T_{h1} - 70}{200 - T_{c2}}$
130	160	90	70	0.2513
132	158.667	88.667	68	0.2654
135	156.667	86.667	65	0.2877
136	156	86	64	0.2955
135.8	156.133	86.133	64.2	0.2939

### 15B.1 Performance of a double-pipe heat exchanger with variable overall heat-transfer coefficient

a. We start with Eq. 15.4-12

$$-\frac{d(T_h - T_c)}{(T_h - T_c)} = U \left( \frac{1}{w_h \hat{C}_{ph}} + \frac{1}{w_c \hat{C}_{pc}} \right) (2\pi r_0) dl$$

Since  $U$  is a linear function of  $T_h - T_c$ , we write

$$U = \alpha + \beta(T_h - T_c)$$

and we choose  $\alpha$  and  $\beta$  by requiring that the conditions at planes 1 and 2 are satisfied:

$$\text{At plane 1:} \quad U_1 = \alpha + \beta(T_{h1} - T_{c1})$$

$$\text{At plane 2:} \quad U_2 = \alpha + \beta(T_{h2} - T_{c2})$$

This gives us two equations and for finding the two constants  $\alpha$  and  $\beta$ :

$$\alpha = U_1 - \frac{(U_2 - U_1)(T_{h1} - T_{c1})}{(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})}$$

$$\beta = \frac{(U_2 - U_1)}{(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})}$$

Then the overall heat-transfer coefficient can be written as:

$$\frac{U - U_1}{U_2 - U_1} = \frac{(T_h - T_c) - (T_{h1} - T_{c1})}{(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})} \equiv \frac{\Delta T - \Delta T_1}{\Delta T_2 - \Delta T_1}$$

b. The first equation in (a) may now be written as:

$$-\frac{d\Delta T}{\Delta T} = (\alpha + \beta\Delta T) \left( \frac{1}{w_h \hat{C}_{ph}} + \frac{1}{w_c \hat{C}_{pc}} \right) (2\pi r_0) dl$$

Part of the right side may be rewritten by using Eqs. 15.4-7 and 8:

$$\left( \frac{1}{w_h \hat{C}_{ph}} + \frac{1}{w_c \hat{C}_{pc}} \right) = \left( \frac{T_{h2} - T_{h1}}{-Q_c} + \frac{T_{c2} - T_{c1}}{Q_c} \right)$$

$$= \frac{1}{Q_c} ((T_{h1} - T_{c1}) - (T_{h2} - T_{c2})) = \frac{1}{Q_c} (\Delta T_1 - \Delta T_2)$$

The differential equation now becomes

$$-\frac{d\Delta T}{\Delta T(\alpha + \beta\Delta T)} = \frac{1}{Q_c} (\Delta T_1 - \Delta T_2)(2\pi r_0) dl$$

Integration then gives:

$$-\int_{\Delta T_1}^{\Delta T_2} \frac{d\Delta T}{\Delta T(\alpha + \beta\Delta T)} = \frac{1}{Q_c} (\Delta T_1 - \Delta T_2)(2\pi r_0) \int_0^L dl$$

or

$$+\frac{1}{\alpha} \ln \left| \frac{\alpha + \beta\Delta T}{\Delta T} \right|_{\Delta T_1}^{\Delta T_2} = \frac{A}{Q_c} (\Delta T_1 - \Delta T_2)$$

where  $A$  is the area of the heat-transfer surface. Then, introducing the expression for  $\alpha$  developed in (a), we get

$$Q_c \ln \left( \frac{U_2}{U_1} \cdot \frac{\Delta T_1}{\Delta T_2} \right) = -A [U_1(\Delta T_2 - \Delta T_1) - (U_2 - U_1)\Delta T_1]$$

Finally, solving for  $Q_c$  we find

$$Q_c = A \frac{U_1\Delta T_2 - U_2\Delta T_1}{\ln(U_1\Delta T_2) - \ln(U_2\Delta T_1)}$$

This is the same as Eq. 15B.1-2.

### 15B.2 Pressure drop in turbulent flow in a slightly converging tube

a. We begin with the  $d$ -form of the mechanical energy balance as given in Eq. 15.4-2

$$v dv + g dh + \frac{1}{\rho} dp = d\hat{W} - \frac{1}{2} v^2 \frac{f}{R_h} dz$$

When this is integrated from  $z=0$  to  $z=L$  for flow of an incompressible fluid in a horizontal tube and no mechanical work term, we get (after using Eq. 6.2-16)

$$\frac{1}{2}(v_2^2 - v_1^2) + \frac{1}{\rho}(p_2 - p_1) = -2 \int_0^L \frac{v^2 f}{D} dz$$

b. Since  $w = \rho v S = \rho v (\pi D^2)$  is constant for each cross section, we have  $\rho_1 v_1 D_1^2 = \rho v D^2$  so that, for an incompressible fluid

$$\frac{v}{v_1} = \left( \frac{D_1}{D} \right)^2$$

Furthermore, this result can be used to rewrite the local friction factor thus

$$\begin{aligned} f &= \frac{0.0791}{(Dv/\nu)^{1/4}} = \frac{0.0791}{(D/\nu)^{1/4} (v_1)^{1/4}} \left( \frac{D}{D_1} \right)^{1/2} \\ &= \frac{0.0791}{(D/\nu)^{1/4} (v_1)^{1/4} (D_1/D)^{1/4}} \left( \frac{D}{D_1} \right)^{1/4} = \frac{0.0791}{(D_1 v_1/\nu)^{1/4}} \left( \frac{D}{D_1} \right)^{1/4} \end{aligned}$$

c. Use Eq. 15B.2-1 to make a change of variable in the integral in Eq. 15B.2-3:

$$\int_0^L \frac{v^2 f}{D} dz = \int_{D_1}^{D_2} \frac{v^2 f}{D} \left( \frac{dz}{dD} \right) dD = \frac{L}{D_2 - D_1} \int_{D_1}^{D_2} \frac{v^2 f}{D} dD$$

The limits on the integral over  $D$  are fixed by using Eq. 15B.2-1.

d. When the expressions for the velocity and friction factor in (b) are substituted into the integral in (c), the integration can be performed to get

$$\begin{aligned} \int_0^L \frac{v^2 f}{D} dz &= \frac{0.0791 L v_1^2}{(D_2 - D_1)(D_1 v_1 / \nu)^{1/4}} \int_{D_1}^{D_2} \frac{(D_1/D)^4 (D/D_1)^{1/4}}{D} dD \\ &= \frac{0.0791 L v_1^2}{(D_2 - D_1)(D_1 v_1 / \nu)^{1/4}} \int_1^{D_2/D_1} x^{-19/4} dx \\ &= \frac{\left(\frac{4}{15}\right) 0.0791 L v_1^2}{(D_1 - D_2)(D_1 v_1 / \nu)^{1/4}} \left[ \left(\frac{D_1}{D_2}\right)^{15/4} - 1 \right] \end{aligned}$$

Then Eq. 15B.2-3 becomes

$$\frac{1}{\rho}(p_1 - p_2) = \frac{1}{2} v_1^2 \left[ \left(\frac{D_1}{D_2}\right)^4 - 1 \right] + \frac{\left(\frac{8}{15}\right) 0.0791 L v_1^2}{(D_1 - D_2)(D_1 v_1 / \nu)^{1/4}} \left[ \left(\frac{D_1}{D_2}\right)^{15/4} - 1 \right]$$

e. From Eqs. 6.1-4 and 15B.2-2, we get for  $D_1 = D_2 = D$  and  $v_1 = v_2 = v$

$$\frac{1}{\rho}(p_1 - p_2) = \frac{2L v^2}{D} f = \frac{2L v^2}{D} \frac{0.0791}{(D v \rho / \mu)^{1/4}}$$

We now have to show that the result in (d) simplifies to this result when  $D_1 = D_2 = D$  and  $v_1 = v_2 = v$ . Clearly the first term on the right side of Eq. 15B.2-6 vanishes when  $D_1 = D_2 = D$ . The next term gives 0/0, and hence we have to apply L'Hôpital's rule:

$$\lim_{D_2 \rightarrow D_1} \frac{\left[ \left(D_1/D_2\right)^{15/4} - 1 \right]}{\left(D_1/D_2\right) - 1} = \lim_{x \rightarrow 1} \frac{x^{15/4} - 1}{x - 1} = \lim_{x \rightarrow 1} \frac{\frac{15}{4} x^{11/4}}{1} = \frac{15}{4}$$

This, along with the statements that  $D_1 = D_2 = D$  and  $v_1 = v_2 = v$  completes the proof of equivalence.

### 15B.3 Steady flow of ideal gases in ducts of constant cross section

a, In the absence of work terms associated with moving mechanical parts and for a duct which is horizontal, the second term on the left side of 15.4-2 and the first term on the right side can be omitted. For a circular tube, 4 times the mean hydraulic radius equals the tube diameter, we get for a differential length  $dL$  of the tube

$$v dv + \frac{1}{\rho} dp + 2v^2 \frac{f}{D} dL = 0 \quad \text{or} \quad v dv + \frac{1}{\rho} dp + \frac{1}{2} v^2 de_v = 0$$

b. Use of the product rule for differentiation,

$$d\left(\frac{p}{\rho}\right) = \frac{1}{\rho} dp - \left(\frac{p}{\rho^2}\right) d\rho$$

leads directly from Eq. 15B.3-1 to Eq. 15B.3-2. The  $d$ -form of the mass balance is

$$dw = 0 \quad \text{or} \quad d(\rho v S) = 0 \quad \text{or} \quad \rho dv + v d\rho = 0 \quad \text{or} \quad d\rho = \rho \frac{dv}{v}$$

For an ideal gas,  $p\tilde{V} = RT$  or  $pM\hat{V} = RT$  or  $pM = \rho RT$ . Hence for the isothermal flow of an ideal gas, the second term in Eq. 15B.3-2 is zero, and that equation becomes, after multiplication by  $2/v^2$

$$de_v = -\left(\frac{2}{v^2}\right)v dv - \left(\frac{2}{v^2}\right)\left(\frac{\rho RT}{M}\right)\left(\frac{1}{\rho^2}\right)d\rho$$

Then, combining the last two equations, we get Eq. 15B.3-3.

c. When the result in Eq. 15B.3-3 is integrated from "1" to "2" encompassing a length  $L$  of the pipe, we get

$$\begin{aligned} e_v &= \frac{2RT}{M} \left( \frac{v_2^{-2}}{-2} - \frac{v_1^{-2}}{-2} \right) - 2(\ln v_2 - \ln v_1) = \frac{RT}{Mv_1^2} \left( 1 - \frac{v_1^2}{v_2^2} \right) + \ln \left( \frac{v_1}{v_2} \right)^2 \\ &= \frac{RT\rho_1^2}{M(\rho_1 v_1)^2} \left[ 1 - \left( \frac{p_2}{p_1} \right)^2 \right] + \ln \left( \frac{p_2}{p_1} \right)^2 = \frac{p_1 \rho_1}{G^2} (1 - r) + \ln r \end{aligned}$$



This may be solved for the "mass velocity"  $G$  to give

$$G = \sqrt{\frac{p_1 \rho_1 (1-r)}{e_v - \ln r}}$$

Then

$$\frac{dG^2}{dr} = p_1 \rho_1 \left( \frac{-1}{e_v - \ln r} - \frac{(-1/r)}{(e_v - \ln r)^2} \right) = 0$$

so that the critical value of  $r$  is given by the solution of the equation

$$e_v - \ln r_c = \frac{1-r_c}{r_c}$$

*d.* From Eq. 15.4-4, we find that the right side is zero (for an adiabatic system with no work done by moving parts), and that the ideal gas law makes the fourth term on the left be zero. In addition, since the tube is horizontal, the second term on the left is also zero. Hence we are left with

$$v dv + \hat{C}_p dT = 0 \quad \text{or} \quad v dv + \frac{\tilde{C}_p}{M} dT = 0 \quad \text{or} \quad v dv + \frac{R}{M} \frac{\gamma}{\gamma-1} dT = 0$$

The third expression comes from the use of the ideal-gas expression  $\tilde{C}_p - \tilde{C}_v = R$  and the definition  $\gamma = \tilde{C}_p / \tilde{C}_v$ , which give

$$\frac{\tilde{C}_p}{R} = \frac{\tilde{C}_p}{\tilde{C}_p - \tilde{C}_v} = \frac{(\tilde{C}_p / \tilde{C}_v)}{(\tilde{C}_p / \tilde{C}_v) - 1} = \frac{\gamma}{\gamma-1}$$

Next the energy equation can be integrated to give

$$\frac{1}{2} v^2 + \left( \frac{\gamma}{\gamma-1} \right) \frac{RT}{M} = \text{const} \quad \text{or} \quad \frac{1}{2} v^2 + \left( \frac{\gamma}{\gamma-1} \right) \frac{p}{\rho} = \frac{1}{2} v_1^2 + \left( \frac{\gamma}{\gamma-1} \right) \frac{p_1}{\rho_1}$$

where the ideal gas law has been used to get the second form. Next, after solving the integrated form of the energy equation for  $p/\rho$ , we substitute this expression for  $p/\rho$  into the second and third terms of Eq. 15B.3-2 to get (after multiplying the latter by  $2/v^2$ )

$$2\frac{dv}{v} - 2\left(\frac{\gamma-1}{\gamma}\right)\frac{dv}{v} + \frac{2}{v^2}\left(\frac{p_1}{\rho_1} + \frac{\gamma-1}{\gamma}\frac{1}{2}v_1^2 - \frac{\gamma-1}{\gamma}\frac{1}{2}v^2\right)\frac{d\rho}{\rho} = -de_v$$

Then we use the  $d$ -form of the mass balance ( $\rho dv + v d\rho = 0$ ) to get

$$2\left(\frac{1}{\gamma}\right)\frac{dv}{v} - \frac{2}{v^2}\left(\frac{p_1}{\rho_1} + \frac{\gamma-1}{\gamma}\frac{1}{2}v_1^2 - \frac{\gamma-1}{\gamma}\frac{1}{2}v^2\right)\frac{dv}{v} = -de_v$$

or, when some terms are combined,

$$\left(\frac{\gamma+1}{\gamma}\right)\frac{dv}{v} - \frac{2}{v^3}\left(\frac{p_1}{\rho_1} + \frac{\gamma-1}{\gamma}\frac{1}{2}v_1^2\right)dv = -de_v$$

This equation can be integrated to give

$$\left(\frac{\gamma+1}{\gamma}\right)\ln\frac{v_2}{v_1} + \left(\frac{p_1}{\rho_1} + \frac{\gamma-1}{\gamma}\frac{1}{2}v_1^2\right)\left(\frac{1}{v_2^2} - \frac{1}{v_1^2}\right) = -e_v$$

Using the macroscopic balance,  $v_2/v_1 = \rho_1/\rho_2$ , we get

$$\left(\frac{\gamma+1}{\gamma}\right)\ln\frac{\rho_1}{\rho_2} + \frac{p_1\rho_1}{(\rho_1v_1)^2}\left(\frac{v_1^2}{v_2^2} - 1\right) + \frac{1}{2}\left(\frac{\gamma-1}{\gamma}\right)\left(\frac{v_1^2}{v_2^2} - 1\right) = -e_v$$

We can now solve for  $G = \rho_1v_1$  (using  $s = (\rho_2/\rho_1)^2$ ) to get

$$G = \rho_1v_1 = \sqrt{\frac{\frac{p_1\rho_1}{(\rho_1v_1)^2} - \frac{e_v - [(\gamma+1)/\gamma]\ln s}{1-s}}{\frac{\gamma-1}{2\gamma}}}$$

e. The macroscopic energy balance is

$$\hat{C}_p(T_2 - T_1) + \frac{1}{2}(v_2^2 - v_1^2) = 0$$

Then using the ideal gas law in the first term and the macroscopic mass balance on the second term gives

$$\frac{M\hat{C}_p}{R} \left( \frac{p_2}{\rho_2} - \frac{p_1}{\rho_1} \right) + \frac{1}{2}G^2 \left( \frac{1}{\rho_2^2} - \frac{1}{\rho_1^2} \right) = 0$$

Then, since  $M\hat{C}_p/R = \gamma/(1-\gamma)$ , this equation can be rearranged thus

$$\frac{p_2}{\rho_2} - \frac{p_1}{\rho_1} = \left( \frac{1-\gamma}{2\gamma} \right) \frac{G^2}{\rho_1^2} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right]$$

And this expression can be rearranged further to give Eq. 15B.3-8. Let the right side of the above equation be designated by X and proceed as follows:

$$\frac{p_2}{\rho_1} \frac{p_1}{\rho_2} - \frac{p_1}{\rho_1} = X \quad \text{or} \quad \frac{p_2}{p_1} - \frac{\rho_2}{\rho_1} = \frac{\rho_2}{p_1} X \quad \text{or} \quad \frac{p_2}{p_1} = \frac{\rho_2}{\rho_1} \left( 1 + \frac{\rho_1}{p_1} X \right)$$

Inserting the expression for X will then lead directly to Eq. 15B.3-8.

#### 15B.4 The Mach number in the mixing of two fluid streams

s. Requiring that the radicand in Eq. 15.3-13 be zero is equivalent to the statement that

$$\frac{1}{2} = \left( \frac{\gamma^2 - 1}{\gamma^2} \right) \left( \frac{w}{P} \right)^2 \left( \frac{E}{w} \right)$$

The factor  $(w/P)$  can be obtained from Eq. 15.3-11, and the factor  $(E/w)$  can be obtained from Eq. 15.3-10. This gives

$$\frac{1}{2} = \left( \frac{\gamma^2 - 1}{\gamma^2} \right) \left( v_2 + \frac{RT_2}{Mv_2} \right)^{-2} \left( \hat{C}_p T_2 + \frac{1}{2} v_2^2 \right)$$

We now move the second factor on the right side to the left side, multiply the entire equation by  $v_2^2$ , and replace  $\hat{C}_p$  by  $(R/M)[\gamma/(\gamma - 1)]$  to get

$$\frac{1}{2} \left( v_2^2 + \frac{RT_2}{M} \right)^2 = \left( \frac{\gamma^2 - 1}{\gamma^2} \right) \left[ \frac{R}{M} \left( \frac{\gamma}{\gamma - 1} \right) T_2 + \frac{1}{2} v_2^2 \right] v_2^2$$

We next multiply by 2 and rewrite the equation thus:

$$\left[ v_2^4 + \frac{2RT_2}{M} v_2^2 + \left( \frac{RT_2}{M} \right)^2 \right] = \left( \frac{\gamma + 1}{\gamma} \right) \frac{2RT_2}{M} v_2^2 + \left( \frac{\gamma^2 - 1}{\gamma^2} \right) v_2^4$$

Then we collect terms in the same powers of the velocity at plane "2" to get

$$\left( \frac{1}{\gamma^2} \right) v_2^4 - \frac{2RT_2}{M} \left( \frac{1}{\gamma} \right) v_2^2 + \left( \frac{RT_2}{M} \right)^2 = 0 \quad \text{or} \quad \left( \frac{1}{\gamma} v_2^2 - \frac{RT_2}{M} \right)^2 = 0$$

This equation may be solved for the velocity at plane "2" to give

$$v_2 = \sqrt{\gamma \frac{RT_2}{M}}$$

This is exactly the speed of sound, given in Problem 11C.1(c).

*b.* To describe the behavior of a gas passing through a sudden enlargement, we can set

$$w_{a1} = w_1 \quad \text{and} \quad w_{b1} = 0$$

and also

$$p_{1a} = p_1 \quad T_{1a} = T_1 \quad S_{a1} = S_1 \quad S_{b1} = 0$$

Then when  $w$ ,  $P$ , and  $E$  are defined analogously to the quantities in (a), we find that Eqs. 15.3-11, 12, and 13 remain unchanged.

### 15B.5 Limiting discharge rates for Venturi meters

a. First, we take the square of Eq. 15.5-34

$$w^2 = C_d^2 \rho_1^2 S_0^2 \left( \frac{2p_1}{\rho_1} \right) \left( \frac{\gamma}{\gamma - 1} \right) \left[ \frac{(\rho_2/\rho_1)^2 (1 - r^{(\gamma-1)/\gamma})}{1 - \beta r^{2/\gamma}} \right]$$

in which  $\beta = (S_0/S_1)^2$  and  $r = p_2/p_1$ . Next we set  $dw^2/dr = 0$  to get

$$\frac{d}{dr} \left[ \frac{r^{2/\gamma} (1 - r^{(\gamma-1)/\gamma})}{1 - \beta r^{2/\gamma}} \right] = 0$$

and, performing the differentiation, we have

$$\frac{(2/\gamma)r^{(2/\gamma)-1} - ((1/\gamma) + 1)r^{1/\gamma}}{1 - \beta r^{2/\gamma}} - \frac{r^{2/\gamma} (1 - r^{(\gamma-1)/\gamma}) - \beta(2/\gamma)r^{(2/\gamma)-1}}{(1 - \beta r^{2/\gamma})^2} = 0 \quad \text{or}$$

$$\left[ (2/\gamma)r^{(2/\gamma)-1} - ((1/\gamma) + 1)r^{1/\gamma} \right] (1 - \beta r^{2/\gamma}) - r^{2/\gamma} (1 - r^{(\gamma-1)/\gamma}) \left[ -\beta(2/\gamma)r^{(2/\gamma)-1} \right] = 0$$

When this is multiplied out, two terms cancel, and the remaining terms are:

$$\frac{2}{\gamma} r^{(2/\gamma)-1} + \beta \left( \frac{1}{\gamma} + 1 \right) r^{3/\gamma} - \left( \frac{1}{\gamma} + 1 \right) r^{1/\gamma} - \beta \frac{2}{\gamma} r^{3/\gamma} = 0$$

Multiplication by  $\gamma r^{-3/\gamma}$  finally yields

$$\beta(\gamma - 1) + \frac{2}{r^{(1/\gamma)+1}} - \frac{(1 + \gamma)}{r^{2/\gamma}} = 0$$

This is equivalent to Eq. 15B.5-1.

b. First we solve Eq. 15B.5-1 for  $\beta = 0$  and get

$$r = \left( \frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)}$$

We substitute this expression for  $r$  into the first equation above in (a) in for  $\beta = 0$  and then rearrange it as follows:

$$\begin{aligned} w_{\max} &= C_d p_1 S_0 \sqrt{2 \frac{\rho_1}{p_1} \left( \frac{\gamma}{\gamma-1} \right) r^{2/\gamma} \left( 1 - r^{(\gamma-1)/\gamma} \right)} \\ &= C_d p_1 S_0 \sqrt{2 \frac{M}{RT_1} \left( \frac{\gamma}{\gamma-1} \right) \left( \frac{2}{\gamma+1} \right)^{2/(\gamma-1)} \left( 1 - \frac{2}{\gamma+1} \right)} \\ &= C_d p_1 S_0 \sqrt{2 \frac{M}{RT_1} \left( \frac{\gamma}{\gamma+1} \right) \left( \frac{2}{\gamma+1} \right)^{2/(\gamma-1)}} \\ &= C_d p_1 S_0 \sqrt{\frac{\gamma M}{RT_1} \left( \frac{2}{\gamma+1} \right)^{(\gamma+1)/(\gamma-1)}} \end{aligned}$$

in agreement with Eq. 15B.5-2.

c. For isothermal flow, we get from Eq. 15.5-33

$$\begin{aligned} w &= C_d \rho_2 S_0 \sqrt{\frac{-2 \int_{p_1}^{p_2} (RT/pM) dp}{1 - (p_2 S_0 / p_1 S_1)^2}} = C_d \rho_2 S_0 \sqrt{\frac{(2RT/M) \ln(p_1/p_2)}{1 - (p_2 S_0 / p_1 S_1)^2}} \\ &= C_d \rho_1 S_0 r \sqrt{\frac{(2RT/M) \ln(1/r)}{1 - \beta r^2}} \end{aligned}$$

in which  $r = p_2/p_1$  and  $\beta = (S_0/S_1)^2$ .

Now for negligibly small  $\beta$ , we can find the maximum discharge rate by setting  $dw^2/dr = 0$  which gives

$$\frac{d}{dr} \left( r^2 \ln \frac{1}{r} \right) = 2r \ln \frac{1}{r} - 1 = 0$$

This gives the value of  $r$  for the maximum discharge rate as

$$r = \frac{p_2}{p_1} = \frac{1}{\sqrt{e}}$$

Then

$$w_{\max} = C_d \rho_1 S_0 \frac{1}{\sqrt{e}} \sqrt{\frac{2RT}{M} \cdot \frac{1}{2}} = C_d \rho_1 S_0 \sqrt{\frac{RT}{eM}} = C_d p_1 S_0 \sqrt{\frac{M}{eRT}}$$

It is interesting to compare the results for air ( $\gamma = 1.4$ ) for the two cases. For adiabatic flow, we get

$$\begin{aligned} \frac{w_{\max}}{C_d p_1 S_0 \sqrt{M/RT_1}} &= \sqrt{\gamma \left( \frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)}} = \sqrt{1.4 \left( \frac{2}{2.4} \right)^{2.4/0.4}} = \sqrt{1.4} (0.8333)^3 \\ &= (1.183)(0.5787) = 0.6846 \end{aligned}$$

For isothermal flow, we have

$$\frac{w_{\max}}{C_d p_1 S_0 \sqrt{M/RT}} = \frac{1}{\sqrt{e}} = \frac{1}{\sqrt{2.718}} = 0.6065$$

The ratio of these two results is 1.13.

We estimate that this ratio will almost never be greater than 25%. Thus, the simpler isothermal expressions are frequently useful for preliminary estimates of flow behavior



### 15B.6 Flow of a compressible fluid through a convergent-divergent nozzle

a. From Eq. 15.2-2 with no work done by moving parts and with viscous heating neglected, we get for the assumption of flat velocity profiles:

$$\frac{1}{2}(v_2^2 - v_1^2) + \int_1^2 \frac{1}{\rho} dp = 0$$

Then, we set  $v_1 = 0$  and, assuming adiabatic flow, we can use Eq. 15.2-5 to evaluate the integral. This results in

$$\frac{1}{2}v_2^2 + \frac{p_1}{\rho_1} \frac{\gamma}{\gamma - 1} \left[ \left( \frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right] = 0$$

Then the ideal gas law may be used to rewrite this expression as

$$\frac{1}{2}v_2^2 = \frac{RT_1}{M} \frac{\gamma}{\gamma - 1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} \right]$$

b. We may start with Eq. 15.5-34 with  $S_1$  considered to be very large, and  $S_0$  replaced by  $S_2$

$$w = C_d \rho_2 S_2 \sqrt{2 \left( \frac{p_1}{\rho_1} \right) \left( \frac{\gamma}{\gamma - 1} \right) \left[ 1 - \left( \frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} \right]}$$

We next replace  $\rho_2$  by  $\rho_1 (p_2/p_1)^{1/\gamma}$  and solve for  $S_2$ , assuming that  $C_d = 1$ . This gives, with  $r = p_2/p_1$

$$S_2 = \frac{w}{\rho_1 \sqrt{2 \left( \frac{p_1}{\rho_1} \right) \left( \frac{\gamma}{\gamma - 1} \right) (r^{2/\gamma} - r^{(\gamma+1)/\gamma})}}$$

The minimum cross-section for given values of  $w$ ,  $p_1$ , and  $\rho_1$  will occur when

$$\frac{dS_2^2}{dr} = 0 = \frac{d}{dr} \left( r^{2/\gamma} - r^{(\gamma+1)/\gamma} \right)^{-1} = \frac{(-1) \left[ (2/\gamma)r^{2/\gamma} - ((\gamma+1)/\gamma)r^{(\gamma+1)/\gamma} \right]}{r \left( r^{2/\gamma} - r^{(\gamma+1)/\gamma} \right)^2}$$

When this equation is solved for  $r$ , we get

$$r = \frac{p_2}{p_1} = \left( \frac{2}{\gamma+1} \right)^{\gamma/(\gamma-1)}$$

which is Eq. 15B.6-2.

c. Combining the results from (a) and (b) we get

$$\frac{1}{2}v_2^2 = \frac{RT_1}{M} \frac{\gamma}{\gamma-1} \left[ 1 - \frac{2}{\gamma+1} \right] = \frac{RT_1}{M} \frac{\gamma}{\gamma-1} \left( \frac{\gamma-1}{\gamma+1} \right) = \frac{RT_1}{M} \frac{\gamma}{\gamma+1}$$

Then, from Eq. 11.4-56 and Eq. 15B.6-2, we find

$$T_1 = T_2 \left( \frac{p_1}{p_2} \right)^{(\gamma-1)/\gamma} = T_2 \left( \frac{\gamma+1}{2} \right)$$

From the last two equations we get

$$\frac{1}{2}v_2^2 = \frac{RT_2}{M} \left( \frac{\gamma}{2} \right) \quad \text{or} \quad v_2 = \sqrt{\frac{\gamma RT_2}{M}}$$

Therefore, the velocity at surface "2" is sonic (cf. Eq. 9.4-4). It is clear that this problem is very similar to that in Problem 15B.5. Here, however, we are considering the effect of varying  $S_2$ , whereas in Problem 15B.5 the reverse procedure was used.

d. Since we now want to get the velocity as a function of the local pressure, we have to replace the first equation in (a) by

$$\frac{1}{2}(v^2 - v_1^2) + \int_{p_1}^p \frac{1}{\rho} dp = 0$$

We then use the fact that  $v_1 = 0$ , and perform the integration to get the velocity at any value of the local pressure for an ideal gas in adiabatic flow

$$\begin{aligned}\frac{1}{2}v^2 &= -\int_{p_1}^p \frac{1}{\rho} dp = -\int_{p_1}^p \left( \frac{p_1^{1/\gamma}}{\rho_1} \right) p^{-1/\gamma} dp = -\left( \frac{p_1^{1/\gamma}}{\rho_1} \right) \left( \frac{\gamma}{\gamma-1} \right) \left( p^{(\gamma-1)/\gamma} - p_1^{(\gamma-1)/\gamma} \right) \\ &= +\left( \frac{p_1^{1/\gamma}}{\rho_1} \right) \left( \frac{\gamma}{\gamma-1} \right) p_1^{(\gamma-1)/\gamma} \left[ 1 - \left( \frac{p}{p_1} \right)^{(\gamma-1)/\gamma} \right] \\ &= \left( \frac{p_1}{\rho_1} \right) \left( \frac{\gamma}{\gamma-1} \right) (1 - r^{(\gamma-1)/\gamma})\end{aligned}$$

where  $r = p/p_1$  (!). Then taking the square root and using the ideal gas law, we get

$$v = \sqrt{\frac{2RT_1}{M} \left( \frac{\gamma}{\gamma-1} \right) (1 - r^{(\gamma-1)/\gamma})}$$

The cross-section at any value of the local pressure can then be obtained from (with  $r = p/p_1$ ):

$$\begin{aligned}w &= \rho S \sqrt{2 \left( \frac{p_1}{\rho_1} \right) \left( \frac{\gamma}{\gamma-1} \right) \left[ 1 - \left( \frac{p}{p_1} \right)^{(\gamma-1)/\gamma} \right]} \\ &= \rho_1 S r^{1/\gamma} \sqrt{2 \left( \frac{RT_1}{M} \right) \left( \frac{\gamma}{\gamma-1} \right) (1 - r^{(\gamma-1)/\gamma})}\end{aligned}$$

Then, solving for the cross-section  $S$ , we get

$$S = \frac{w/\rho_1}{r^{1/\gamma} \sqrt{2 \left( \frac{RT_1}{M} \right) \left( \frac{\gamma}{\gamma-1} \right) (1 - r^{(\gamma-1)/\gamma})}}$$

Next, for the conditions of the problem given in part (d) of the problem, we have

$$R = (1544)(32.17) = \text{ft}^2 \text{lb}_m / \text{lb - mole} \cdot \text{s}^2 \cdot \text{R}$$

$$RT_1/M = (1544)(32.17)(560)/29 = 9.592 \times 10^5 \text{ ft}^2/\text{s}^2$$

$$\sqrt{\frac{2RT_1}{M} \left( \frac{\gamma}{\gamma-1} \right)} = \sqrt{(9.592 \times 10^5) \frac{2(1.4)}{0.4}} = 2591 \text{ ft/s}$$

$$w = (10 \text{ lb - mol / s})(29 \text{ lb}_m / \text{lb - mol})$$

$$\rho_1 = \frac{p_1 M}{RT_1} = \frac{(10 \text{ atm})(6.8087 \times 10^4 \text{ (lb}_m / \text{ft} \cdot \text{s}^2) \text{ per atm.)}}{(4.9686 \times 10^4 \text{ lb}_m \text{ft}^2 / \text{s}^2 \cdot \text{lb - mol} \cdot \text{K})(560^\circ \text{K})}$$

$$= 0.710 \text{ lb}_m / \text{ft}^3$$

We may now summarize the calculations of  $v$ ,  $T$ , and  $S$  thus:

$$v = 2591 \sqrt{1 - r^{0.286}}; \quad T = 560 r^{0.286}; \quad S = \frac{0.157 r^{-0.714}}{\sqrt{1 - r^{0.286}}}$$

$p$ (atm)	$r$	$r^{0.286}$	$v$	$T$	$S$
10	1.0	1.000	0000	560	$\infty$
9	0.9	0.970	449	543	0.977
8	0.8	0.938	645	525	0.739
7	0.7	0.903	807	506	0.650
6	0.6	0.864	956	484	0.613
5.28*	0.528	0.833	1058	466	0.606
5	0.5	0.820	1099	459	0.607
4	0.4	0.769	1245	431	0.628
3	0.3	0.709	1398	397	0.688
2	0.2	0.631	1574	353	0.816
1	0.1	0.518	1798	290	1.171
0	0.0	0.000	2591	0	$\infty$

\*Pressure at the minimum cross-section

### 15B.7 Transient thermal behavior of a chromatographic device

We start with the energy equation of Eq. 15.1-2, which we apply to the gas inside the chromatographic column. We are concerned only with the change in time (and not distance) within the column. Since there are no moving mechanical parts, the equation simplifies to

$$\frac{d}{dt}U_{\text{tot}} = Q = UA(T_g - T)$$

in which the total kinetic and potential energy in the system are considered constant, and  $U$  is the overall heat transfer coefficient between the external gas stream and the gas within the chromatographic device.

From thermodynamics we can write

$$d\hat{U} = \left( \frac{\partial \hat{U}}{\partial T} \right)_{\hat{V}} dT + \left( \frac{\partial \hat{U}}{\partial \hat{V}} \right)_T d\hat{V} = \hat{C}_V dT + \left[ -p + T \left( \frac{\partial p}{\partial T} \right)_{\hat{V}} \right] d\hat{V}$$

The quantity inside the brackets is zero for an ideal gas and is neglected here. Then  $\hat{U} - \hat{U}^\circ = \hat{C}_V(T - T^\circ)$ , where the superscripts  $^\circ$  stand for the reference state, and

$$U_{\text{tot}} = \int \rho \hat{U} dV = \rho \hat{U}^\circ V_{\text{tot}} + \rho \hat{C}_V (T - T^\circ) V_{\text{tot}}$$

where the density and heat capacity are taken to be constants. The energy balance becomes

$$\rho \hat{C}_V V_{\text{tot}} \frac{dT}{dt} = UA(T_g - T) \quad \text{or} \quad \frac{dT}{dt} = \frac{UA}{\rho \hat{C}_V V_{\text{tot}}} \left[ T_{g0} \left( 1 + \frac{t}{t_0} \right) - T \right]$$

We now introduce the dimensionless temperature  $\Theta = T/T_{g0}$  and the dimensionless time  $\tau = t/t_0$  and rewrite the energy balance as

$$\frac{d\Theta}{d\tau} = B[(1 + \tau) - \Theta] \quad \text{with} \quad B = UA t_0 / \rho \hat{C}_V V_{\text{tot}}$$

This differential equation can be put into the form

$$\frac{d\Theta}{d\tau} + B\Theta = B(1 + \tau) \quad \text{with} \quad \Theta = 1 \text{ at } \tau = 0$$

This is a linear first-order differential equation (see Eq. C.1-2), which with the indicated initial condition has the solution

$$\Theta = \left(1 + \tau - \frac{1}{B}\right) + \frac{1}{B}e^{-B\tau}$$

This is probably the simplest solution that can be offered for this problem. We are now in a position to answer the questions in the problem:

a. The difference between the external gas temperature and the temperature within the chromatographic device is

$$T_g - T = T_{g0}(1 - \tau) - T_{g0}\left(1 + \tau - \frac{1}{B} + \frac{1}{B}e^{-B\tau}\right) = T_{g0}\left(\frac{1}{B} - \frac{1}{B}e^{-B\tau}\right)$$

b. The limiting value of the temperature difference will be

$$(\Delta T)_\infty = T_{g0} \frac{1}{B}$$

c. The time required for the temperature difference to be within 1% of the limiting value is given by the solution of the equation  $e^{-B\tau} = 0.01$  or  $\tau = (2.303)(2)/B$ .

d. Constant physical properties; no dependence of temperature as a function of distance down the column; the neglecting of potential energy and kinetic energy effects.

e. All the quantities that are contained in  $B$ .

### 15B.8 Continuous heating of a slurry in an agitated tank

a. The starting point is Eq. 15.1-1 or 2. On the left side the potential energy term  $\Phi_{\text{tot}}$  is omitted because for a full tank the  $\Phi_{\text{tot}}$  is a constant. Similarly  $K_{\text{tot}}$  is time-independent and can be omitted. The term  $U_{\text{tot}} = \int_V \rho \hat{U} dV$  will be retained. Since  $\hat{U} = \hat{H} - (p/\rho)$ , and  $p$  and  $\rho$  are time-independent, we can replace the internal energy by enthalpy, which is given by Eq. 9.8-8, the second term on the right side of that equation being negligible. Furthermore, since the heat capacity is considered constant, Eq. 9.8-8 becomes simply

$$\hat{H} = \hat{H}_i + \hat{C}_p (T - T_i)$$

where the inlet slurry temperature  $T_i$  has been chosen to the datum plane for the enthalpy.

On the right side of Eq. 15.1-1, the mechanical work term and the kinetic energy and potential energy terms can be disregarded. But the heat addition term  $Q$  and the outlet enthalpy term must be retained. Therefore, Eq. 15.1-1 becomes

$$\frac{d}{dt} U_{\text{tot}} = -\hat{H}_2 w + Q$$

or

$$\rho \hat{C}_p V \frac{dT}{dt} = -w \hat{C}_p (T - T_i) + UA(T_s - T)$$

which is Eq. 15B.8-1.

b. When the system has attained steady state operation, the left side of the above equation becomes zero, and the slurry temperature has leveled off to  $T_\infty$ . This quantity is then defined by the equation

$$0 = -w \hat{C}_p (T_\infty - T_i) + UA(T_s - T_\infty)$$

or (with the definition that  $UA/w\hat{C}_p = \Omega$ ):

$$T_{\infty} = \frac{T_i + (UA/w\hat{C}_p)T_s}{1 + (UA/w\hat{C}_p)} = \frac{T_i + \Omega T_s}{1 + \Omega}$$

From the last equation we may also get the relation

$$\frac{T_s - T_{\infty}}{T_i - T_{\infty}} = -\frac{w\hat{C}_p}{UA} = -\frac{1}{\Omega}$$

which is needed presently.

Now the differential equation can be rewritten in terms of the dimensionless variables given in Eqs. 15B.8-2,3:

$$\begin{aligned} \frac{d}{d\tau} \left( \frac{T - T_{\infty}}{T_i - T_{\infty}} \right) &= \Omega \left( \frac{T_s - T}{T_i - T_{\infty}} \right) - \left( \frac{T - T_i}{T_i - T_{\infty}} \right) \\ &= \Omega \left( \frac{(T_s - T_{\infty}) - (T - T_{\infty})}{T_i - T_{\infty}} \right) - \left( \frac{(T - T_{\infty}) - (T_i - T_{\infty})}{T_i - T_{\infty}} \right) \\ &= \Omega \left( -\frac{1}{\Omega} - \Theta \right) - (\Theta - 1) = -\Theta(1 + \Omega) \end{aligned}$$

Hence the differential equation in dimensionless form is

$$\frac{d\Theta}{d\tau} = -\Theta(1 + \Omega)$$

c. This equation is solved to give

$$\int_1^{\Theta} \frac{d\Theta}{\Theta} = -(1 + \Omega) \int_0^{\tau} d\tau \quad \text{or} \quad \Theta = e^{-(1+\Omega)\tau}$$

This is just the dimensionless form of the solution given in the text.

d. When the solution is written in the dimensionless form, it is easy to see that it satisfies the differential equation and initial condition. It is also evident that  $\Theta \rightarrow 0$  (or  $T \rightarrow T_{\infty}$ ), which is to be expected.



### 15C.1 Parallel-counterflow heat exchangers

a. From Eq. 15.1-3, with only the enthalpy terms contributing, and Eq. 9.3-8 with only the first term being important (and the heat capacity constant), we get for the region between  $a$  and  $b$

$$w_B \hat{C}_{pB} (T_B - T_{B2}) - w_A \hat{C}_{pA} (T_A^{\text{II}} - T_A^{\text{I}}) = 0$$

from which Eq. 15C.1-1 follows.

b. Then the application of Eq. 15.4-4 gives, for the region between the dashed lines in Fig. 15C.1, three differential energy balances over the heat-transfer surface  $dA$ :

$$w_A \hat{C}_{pA} dT_A^{\text{I}} = \frac{1}{2} U (T_B - T_A^{\text{I}}) dA$$

$$w_A \hat{C}_{pA} dT_A^{\text{II}} = -\frac{1}{2} U (T_B - T_A^{\text{II}}) dA$$

$$w_B \hat{C}_{pB} dT_B = \left[ \frac{1}{2} U (T_A^{\text{I}} - T_B) + \frac{1}{2} U (T_A^{\text{II}} - T_B) \right] dA$$

Then introducing the ratio  $R$ , and the dimensionless differential area  $d\alpha$  (defined in the problem statement) leads directly to Eqs. 15C.1-2, 3, and 4.

c. First we differentiate Eq. 15C.1-4 with respect to  $\alpha$  to get

$$\frac{1}{R} \frac{d^2 T_B}{d\alpha^2} + \frac{dT_B}{d\alpha} - \frac{1}{2} \left( \frac{dT_A^{\text{I}}}{d\alpha} + \frac{dT_A^{\text{II}}}{d\alpha} \right) = 0$$

Then using Eqs. 15C.1-2 and 3 this becomes

$$\frac{1}{R} \frac{d^2 T_B}{d\alpha^2} + \frac{dT_B}{d\alpha} - \frac{1}{4} (T_B - T_A^{\text{I}}) - \frac{1}{4} (T_A^{\text{II}} - T_B) = 0$$

Next use Eq. 15C.1-1 to rewrite this as

$$\frac{d^2 T_B}{d\alpha^2} + R \frac{dT_B}{d\alpha} - \frac{1}{4} (T_B - T_{B2}) = 0 \quad \text{or} \quad \frac{d^2 \Theta}{d\alpha^2} + R \frac{d\Theta}{d\alpha} - \frac{1}{4} \Theta = 0$$

In the second equation we have used the dimensionless temperature. This differential equation may be solved (see Eq. C.1-7a) as follows:

$$\Theta = C_1 \exp\left[-\frac{1}{2}(R - \sqrt{R^2 - 1})\alpha\right] + C_2 \exp\left[-\frac{1}{2}(R + \sqrt{R^2 - 1})\alpha\right]$$

$$\equiv C_1 e^{m_- \alpha} + C_2 e^{m_+ \alpha}$$

Application of the boundary conditions gives two equations for the integration constants:

$$1 = C_1 + C_2$$

$$0 = C_1 e^{m_- \alpha_T} + C_2 e^{m_+ \alpha_T}$$

The integration constants are therefore:

$$C_1 = -\frac{e^{m_+ \alpha_T}}{e^{m_- \alpha_T} - e^{m_+ \alpha_T}} = \frac{1}{1 - e^{(m_- - m_+) \alpha_T}} = \frac{1}{1 - e^{\sqrt{R^2 - 1} \alpha_T}}$$

$$C_2 = +\frac{e^{m_- \alpha_T}}{e^{m_- \alpha_T} - e^{m_+ \alpha_T}} = \frac{1}{1 - e^{(m_+ - m_-) \alpha_T}} = \frac{1}{1 - e^{-\sqrt{R^2 - 1} \alpha_T}}$$

d. Next we obtain  $d\Theta/d\alpha$ :

$$\frac{d\Theta}{d\alpha} = \frac{m_- e^{m_- \alpha}}{1 - e^{\sqrt{R^2 - 1} \alpha_T}} + \frac{m_+ e^{m_+ \alpha}}{1 - e^{-\sqrt{R^2 - 1} \alpha_T}}$$

Then evaluate this at  $\alpha = 0$  to get

$$\frac{1}{T_{B1} - T_{B2}} \left. \frac{dT_B}{d\alpha} \right|_{\alpha=0} = \frac{m_-}{1 - e^{\sqrt{R^2 - 1} \alpha_T}} + \frac{m_+}{1 - e^{-\sqrt{R^2 - 1} \alpha_T}}$$

Then eliminate the derivative by use of Eq. 15C.1-4 (also evaluated at  $\alpha = 0$ ) to obtain:

$$\frac{R}{T_{B1} - T_{B2}} \left[ -T_{B1} + \frac{1}{2}(T_{A1} + T_{A2}) \right] = \frac{m_-}{1 - e^{\sqrt{R^2 - 1}\alpha_T}} + \frac{m_+}{1 - e^{-\sqrt{R^2 - 1}\alpha_T}} \quad (*)$$

We now replace the denominator on the left side by using Eq. 15C.1-1, and then we have to manipulate the left side in such a way as to obtain the ratio  $\Psi$  defined after Eq. 15C.1-8; thus the left side becomes:

$$\begin{aligned} \frac{\frac{1}{2}(T_{A1} - T_{B1}) + \frac{1}{2}(T_{A2} - T_{B1})}{T_{A2} - T_{A1}} &= \frac{(T_{A1} - T_{B1}) + \frac{1}{2}(T_{A2} - T_{B1} - T_{A1} + T_{B1})}{T_{A2} - T_{A1}} \\ &= -\frac{T_{B1} - T_{A1}}{T_{A2} - T_{A1}} + \frac{1}{2} = -\frac{1}{\Psi} + \frac{1}{2} \equiv C \end{aligned}$$

With this substitution Eq. (\*) gives  $\Psi$  as a function of  $\alpha_T$ . But we would like to have  $\alpha_T$  as a function of  $\Psi$ . That is, we have to solve the following equation for  $x$ :

$$C = \frac{A}{1-x} + \frac{B}{1-(1/x)} \quad \text{with } A = m_-, \quad B = m_+, \quad x = e^{\sqrt{R^2 - 1}\alpha_T}$$

But this is just a quadratic equation, which can be solved by the standard method, which yields two solutions:

$$x = 1 \quad \text{and} \quad x = \frac{C - A}{C - B}$$

The solution  $x = 1$  is physically uninteresting. The other solution gives

$$e^{\sqrt{R^2 - 1}\alpha_T} = \frac{\left(-\frac{1}{\Psi} + \frac{1}{2}\right) - m_-}{\left(-\frac{1}{\Psi} + \frac{1}{2}\right) - m_+} = \frac{(-2 + \Psi) - 2\Psi m_-}{(-2 + \Psi) - 2\Psi m_+} = \frac{2 - \Psi(1 - 2m_-)}{2 - \Psi(1 - 2m_+)} \quad \text{or}$$

$$e^{\sqrt{R^2 - 1}\alpha_T} = \frac{2 - \Psi(1 - 1 + R - \sqrt{R^2 + 1})}{2 - \Psi(1 - 1 + R + \sqrt{R^2 + 1})}$$

Taking the logarithm of this equation gives Eq. 15C.1-8.

### 15D.1 The macroscopic entropy balance

a. First rewrite Eq. 11D.1-3 as

$$\begin{aligned}\frac{\partial}{\partial t}\rho\hat{S} &= -(\nabla \cdot \rho\mathbf{v}\hat{S}) - \frac{1}{T}(\nabla \cdot \mathbf{q}) - \frac{1}{T}(\boldsymbol{\tau}:\nabla\mathbf{v}) \\ &= -(\nabla \cdot \rho\mathbf{v}\hat{S}) - \left(\nabla \cdot \frac{1}{T}\mathbf{q}\right) - \frac{1}{T^2}(\mathbf{q} \cdot \nabla T) - \frac{1}{T}(\boldsymbol{\tau}:\nabla\mathbf{v})\end{aligned}$$

We now integrate this over the entire macroscopic flow system, which is presumed to have some moving parts in it so that the volume and surface of the system are time dependent:

$$\begin{aligned}\int_{V(t)} \frac{\partial}{\partial t}\rho\hat{S}dV &= - \int_{V(t)} (\nabla \cdot \rho\mathbf{v}\hat{S})dV - \int_{V(t)} \left(\nabla \cdot \frac{1}{T}\mathbf{q}\right)dV \\ &\quad - \int_{V(t)} \frac{1}{T}[(\mathbf{q} \cdot \nabla \ln T) + (\boldsymbol{\tau}:\nabla\mathbf{v})]dV\end{aligned}$$

Since the last term is the integral of the entropy production terms in Eq. 11D.1-4, we can label this term  $g_{S,\text{tot}}$ . We may now use the Leibniz rule to move the time-derivative operator to the left of the integral sign and the Gauss divergence theorem to transform the volume integral into a surface integral:

$$\int_{V(t)} \frac{\partial}{\partial t}\rho\hat{S}dV = \frac{d}{dt} \int_{V(t)} \rho\hat{S}dV + \int_{S(t)} (\mathbf{n} \cdot \rho\mathbf{v}_S\hat{S})dS = \frac{d}{dt}S_{\text{tot}} + \int_{S(t)} (\mathbf{n} \cdot \rho\mathbf{v}_S\hat{S})dS$$

When this is inserted into the preceding equation and the Gauss theorem applied to the integrals containing divergences, we get:

$$\frac{d}{dt}S_{\text{tot}} = - \int_{S(t)} (\mathbf{n} \cdot \rho(\mathbf{v} - \mathbf{v}_S)\hat{S})dS - \int_{S(t)} \left(\mathbf{n} \cdot \frac{1}{T}\mathbf{q}\right)dS + g_{S,\text{tot}}$$

We now divide the surface into four parts:  $S(t) = S_1 + S_2 + S_f + S_m$ , the cross-section of the entrance (1), the cross-section of the exit (2), the fixed solid surfaces ( $f$ ), and the moving surfaces ( $m$ ). The first surface integral above will contribute only at 1 and 2:

$$-\int_{S(t)} (\mathbf{n} \cdot \rho(\mathbf{v} - \mathbf{v}_s) \hat{S}) dS = \rho_1 v_1 \hat{S}_1 S_1 - \rho_2 v_2 \hat{S}_2 S_2 = w_1 \hat{S}_1 - w_2 \hat{S}_2$$

The second surface integral will, however, contribute at all four surfaces:

$$-\int \left( \mathbf{n} \cdot \frac{1}{T} \mathbf{q} \right) dS = \frac{q_1 S_1}{T} - \frac{q_2 S_2}{T} - \int \left( \mathbf{n} \cdot \frac{1}{T} \mathbf{q} \right) dS = \frac{w_1 q_1}{T} - \frac{w_2 q_2}{T} + Q_s$$

Hence the macroscopic entropy balance becomes:

$$\frac{d}{dt} S_{\text{tot}} = \left( \hat{S}_1 + \frac{q_1}{\rho_1 v_1 T_1} \right) w_1 - \left( \hat{S}_2 + \frac{q_2}{\rho_2 v_2 T_2} \right) w_2 + Q_s + g_{S,\text{tot}}$$

which is Eq. 15D.1-1.

b. The macroscopic energy balances states that the increase in the total entropy of the system results from (1) the convection of entropy in and out of the system ( $w_1 \hat{S}_1 - w_2 \hat{S}_2$ ); (2) the entropy transport at the inlet and outlet of the system by heat conduction ( $(q_1 S_1 / T_1) - (q_2 S_2 / T_2)$ )--presumably very small compared with the entropy convection terms; (3) the entropy transport through the walls of the system, and (4) the entropy production within the system, which consists of a term involving the heat flux and a term involving the momentum flux. Entropy is thus produced by the dissipative effects of heat conduction and viscous flow. These terms are positive for linear flux laws.

c. The term in the entropy production term involving the stress tensor can be written

$$-\int_{V(t)} \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) dV \doteq -\frac{1}{T_{\text{avg}}} \int_{V(t)} (\boldsymbol{\tau} : \nabla \mathbf{v}) dV = \frac{E_v}{T_{\text{avg}}}$$

if the temperature variation throughout the system is not too large with respect to the absolute temperature. Then the integral is indeed the energy dissipation by viscous heating divided by the average temperature.

## 15D.2 Derivation of the macroscopic energy balance

When Eq. (N) of Table 11.4-1 is integrated over the entire volume of the flow system we get:

$$\int_{V(t)} \frac{\partial}{\partial t} \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) dV = - \int_{V(t)} \left( \nabla \cdot \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) \mathbf{v} \right) dV \\ - \int_{V(t)} (\nabla \cdot \mathbf{q}) dV - \int_{V(t)} (\nabla \cdot p \mathbf{v}) dV - \int_{V(t)} (\nabla \cdot [\boldsymbol{\tau} \cdot \mathbf{v}]) dV$$

We now apply the Leibniz formula to the integral on the left side of the equation to get

$$\int_{V(t)} \frac{\partial}{\partial t} \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) dV \\ = \frac{d}{dt} \int_{V(t)} \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) dV + \int_{S(t)} \left( \mathbf{n} \cdot \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) \mathbf{v}_s \right) dS \\ = \frac{d}{dt} (K_{\text{tot}} + U_{\text{tot}} + \Phi_{\text{tot}}) + \int_{S(t)} \left( \mathbf{n} \cdot \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) \mathbf{v}_s \right) dS$$

This is now substituted into the preceding equation (in which the volume integrals have been converted into surface integrals by using the Gauss divergence theorem) to get:

$$\frac{d}{dt} (K_{\text{tot}} + U_{\text{tot}} + \Phi_{\text{tot}}) = - \int_{S(t)} \left( \mathbf{n} \cdot \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) (\mathbf{v} - \mathbf{v}_s) \right) dS \\ - \int_{S(t)} (\mathbf{n} \cdot \mathbf{q}) dS - \int_{S(t)} (\mathbf{n} \cdot p \mathbf{v}) dS - \int_{S(t)} (\mathbf{n} \cdot [\boldsymbol{\tau} \cdot \mathbf{v}]) dS$$

We now divide the surface into four parts:  $S(t) = S_1 + S_2 + S_f + S_m$ , the cross-section of the entrance (1), the cross-section of the exit (2), the fixed solid surfaces ( $f$ ), and the moving surfaces ( $m$ ). The first surface integral above will contribute only at 1 and 2:

$$- \int_{S(t)} \left( \mathbf{n} \cdot \left( \frac{1}{2} \rho v^2 + \rho \hat{U} + \rho \hat{\Phi} \right) (\mathbf{v} - \mathbf{v}_s) \right) dS \\ = \left( \frac{1}{2} \rho_1 \langle v_1^3 \rangle + \rho_1 \hat{U}_1 \langle v_1 \rangle + \rho_1 \hat{\Phi}_1 \langle v_1 \rangle \right) S_1 - \left( \frac{1}{2} \rho_2 \langle v_2^3 \rangle + \rho_2 \hat{U}_2 \langle v_2 \rangle + \rho_2 \hat{\Phi}_2 \langle v_2 \rangle \right) S_2$$

The contribution of the second surface integral at 1 and 2 is presumed to be negligible with respect to the convective energy transport, but will in general have a nonzero value on the surfaces; we call this  $Q$ . The third integral will contribute both at "1" and "2" and on the moving surfaces:

$$- \int_{S(t)} (\mathbf{n} \cdot p\mathbf{v}) dS = +p_1 \langle v_1 \rangle S_1 - p_2 \langle v_2 \rangle S_2 + W_m^{(p)}$$

where  $W_m^{(p)}$  is the pressure contribution to the work done on the system by the via the moving surfaces. The fourth integral will be:

$$- \int_{S(t)} (\mathbf{n} \cdot [\boldsymbol{\tau} \cdot \mathbf{v}]) dS + W_m^{(\tau)}$$

which is the stress contribution to the work done on the system by the via the moving surfaces. Of course there are also contributions at 1 and 2, but these are considered to be negligible to the pressure forces. When all of the above contributions are assembled, we get

$$\begin{aligned} \frac{d}{dt} (K_{\text{tot}} + U_{\text{tot}} + \Phi_{\text{tot}}) = & \\ & \left( \frac{1}{2} \rho_1 \langle v_1^3 \rangle + \rho_1 \hat{U}_1 \langle v_1 \rangle + \rho_1 \hat{\Phi}_1 \langle v_1 \rangle \right) S_1 - \left( \frac{1}{2} \rho_2 \langle v_2^3 \rangle + \rho_2 \hat{U}_2 \langle v_2 \rangle + \rho_2 \hat{\Phi}_2 \langle v_2 \rangle \right) S_2 \\ & + Q + p_1 \langle v_1 \rangle S_1 - p_2 \langle v_2 \rangle S_2 + W_m^{(p)} + W_m^{(\tau)} \end{aligned}$$

which is the macroscopic energy balance given in Eq. 15.1-1.

### 15D.5 The classical Bernoulli equation

For an isentropic flow,

$$d\hat{U} = -pd\hat{V} = -pd\frac{1}{\rho} \quad \text{or} \quad \nabla\hat{U} = -p\nabla\hat{V} = -p\nabla\frac{1}{\rho}$$

Then Eq. (E) of Table 11.4-1, with the heat and momentum fluxes set equal to zero, becomes for a steady-state system

$$\rho(\mathbf{v} \cdot \nabla \frac{1}{2}v^2) + \rho(\mathbf{v} \cdot (-p\nabla\rho^{-1})) = -(\nabla \cdot p\mathbf{v}) + \rho(\mathbf{v} \cdot \mathbf{g})$$

Using  $\mathbf{g} = -g\nabla h$  and some standard vector identities

$$\rho(\mathbf{v} \cdot \nabla \frac{1}{2}v^2) + p\rho^{-1}(\mathbf{v} \cdot \nabla\rho) = -p(\nabla \cdot \mathbf{v}) - (\mathbf{v} \cdot \nabla p) - \rho(\mathbf{v} \cdot \nabla h)$$

The second term on the left and the second term on the right can be shown to be equal, using the equation of continuity (appropriately simplified for steady-state flow). Next, consider that the del operators are acting only along a streamline, so that  $\nabla = (\mathbf{v}/v)(d/ds)$ , and hence we get

$$\rho v \frac{d}{ds} \left( \frac{1}{2}v^2 \right) = -\frac{\rho v}{\rho} \frac{d}{ds} p - \rho v g \frac{d}{ds} h$$

When this equation is divided through by  $\rho v$ , we get Eq. 3.5-11. Then Eq. 3.5-12 follows at once.



**16A.1 Approximation of a black body by a hole in a sphere**  
Use Eq. 16.2-12

$$e_{\text{hole}} = \frac{e}{e + f(1 - e)}$$

or

$$f = \frac{e(1 - e_{\text{hole}})}{e_{\text{hole}}(1 - e)}$$

Into this we insert the values  $e = 0.57$  and  $e_{\text{hole}} = 0.99$  and get

$$f = \frac{0.57(1 - 0.99)}{0.99(1 - 0.57)} = \frac{0.57(0.01)}{0.99(0.43)} = \frac{0.0057}{0.4257} = 0.01339$$

Then using the definition of  $f$  we write

$$f = 0.01339 = \frac{\pi r_{\text{hole}}^2}{4\pi(3^2)}$$

Then solving for the hole radius we get

$$r_{\text{hole}} = 2\sqrt{0.01339(3)} = 0.69 \text{ in.}$$

## 16A.2 Efficiency of a solar engine

The area of the mirror is  $(\pi R^2) = 25\pi \text{ ft}^2$ . Since the solar constant (heat flux entering the earth's atmosphere) is, according to Example 16.4-1,  $430 \text{ Btu/hr} \cdot \text{ft}^2$ , the energy input to the solar device is

$$(430 \text{ Btu/hr} \cdot \text{ft}^2)(25\pi \text{ ft}^2)(3.93 \times 10^{-4} \text{ hp/Btu} \cdot \text{hr}^{-1}) = 13.3 \text{ hp}$$

Therefore the efficiency of the solar device is

$$\text{Efficiency} = \frac{2}{13.3} = 0.150 = 15\%$$

### 16A.3 Radiant heating requirements

The heat required is the sum of the radiant heat-transfer rates between the floor and each of the other surfaces. Since no pertinent data are supplied for its estimation, the convective heat transfer will be neglected. It can be expected to be appreciable, however.

The total radiant heat-transfer rate is then

$$Q_{\text{rad}} = \sigma A_{\text{floor}} (T_{\text{floor}}^4 - T_{\text{walls}}^4) \sum F_i$$

$$\text{Floor to ceiling:} \quad F_1 = 0.49$$

$$\text{Floor to large walls:} \quad F_2 = F_3 = 0.17$$

$$\text{Floor to small walls:} \quad F_4 = F_5 = 0.075$$

Summing the contributions, we get:

$$\sum F_i = 0.49 + 2(0.17) + 2(0.075) = 0.49 + 0.34 + 0.15 = 0.98$$

Alternatively, we may consider the floor to be completely surrounded by black surfaces. From that point of view we know that the sum of the  $F_i$  should be 1.00. A cumulative error of 2% has thus resulted from considering each of the cold surfaces separately. Then we get

$$\begin{aligned} Q_{\text{rad}} &= (1.712 \times 10^{-9} \text{ Btu/hr} \cdot \text{ft}^2 \text{R}^4)(450 \text{ft}^2) \\ &\quad \cdot [(75 + 460)^4 - (-10 + 460)^4] \text{R}^4 \\ &= (1.712 \times 10^{-9})(450)(8.19 \times 10^{10} - 4.10 \times 10^{10}) \\ &= 3.15 \times 10^4 \text{ Btu/hr} \end{aligned}$$

Here we have used the value of the Stefan-Boltzmann constant given on p. 867.

#### 16A.4 Steady-state temperature of a roof

Since June 21 is (conveniently) very close to the summer solstice, the angle of incidence of the sun's rays on a flat roof may be calculated quite simply. We know that the earth's axis is tilted at an angle of about 23.5 degrees. Thus the angle of incidence of a flat roof at 45 degrees north latitude will be about  $45 - 23.5 = 21.5$  degrees, and the heat received by the roof will be given by the solar constant multiplied by the cosine of the angle of incidence and then further multiplied by the absorptivity of the surface:  $(430)(\cos 21.5^\circ)a = (430)(0.9304)a$ , in units of Btu/hr.ft<sup>2</sup>. We now equate the radiant energy received from the sun by the roof to the radiant energy emitted by the roof plus the heat lost by convective heat transfer for the two cases given in parts (a) and (b):

$$(430)(0.9304)a = h(T_{\text{roof}} - T_{\text{air}}) + \sigma e T_{\text{roof}}^4$$

*a.* For a perfectly black roof, we have

$$(430)(0.9304)(1.00) = 2.0(T_{\text{roof}} - 560) + (1.712 \times 10^{-9})(1.00)T_{\text{roof}}^4$$

This equation may be solved by trial and error to get about 625°R or 165°F.

*b.* For the flat roof with  $a = 0.3$  and  $e = 0.07$  we get

$$(430)(0.9304)(0.3) = 2.0(T_{\text{roof}} - 560) + (1.712 \times 10^{-9})(0.07)T_{\text{roof}}^4$$

which may be solved by trial and error to give 610°R or 150°F.

## 16A.5 Radiation errors in temperature measurements

Assume that the thermocouple behaves as a gray body in a large black enclosure, and equate the net radiation loss to the convective heat input:

$$e\sigma(T_{\text{th}}^4 - T_{\text{wall}}^4) = h(T_{\text{gas}} - T_{\text{th}})$$

in which  $T_{\text{th}}$  is the thermocouple junction temperature.

For the conditions of this problem

$$(0.8)(1.712 \times 10^{-9})[(960)^4 - (760)^4] = (50)(T_{\text{gas}} - 960)$$

Solving this for  $T_{\text{gas}}$  we get

$$T_{\text{gas}} = 960 + \frac{705}{50} = 971^\circ\text{R} = 514^\circ\text{F}$$

There is thus a  $14^\circ\text{F}$  difference between the calculated gas temperature and the thermocouple reading.

## 16A.6 Surface temperatures on Earth's moon.

(a) A quasi-steady-state energy balance on a lunar surface element that directly faces the sun gives

$$I_0 a = e \sigma T_{s,\max}^4$$

in which  $I_0$  is the solar constant,  $T_{s,\max}$  is the temperature of that surface element, and  $a$  and  $e$  are its total absorptivity and emissivity. Setting  $a = e$  for a gray surface, and using the value calculated in Example 16.4-1 for the solar constant, we obtain the quasi-steady-state estimate

$$T_{s,\max} = (I_0 \sigma)^{1/4} = (430/1.7124 \times 10^{-9})^{1/4} = 708^\circ\text{R}$$

of the maximum temperature on the moon.

(b) For a spherical lunar surface, receiving radiation from the sun only, the local intensity of incident radiation is

$$I(\theta) = \begin{cases} I_0 \cos \theta, & \text{for } 0 \leq \theta \leq \pi/2; \\ 0 & \text{for } \pi/2 \leq \theta \leq \pi, \end{cases}$$

when the sun is treated as an infinitely distant point radiator. Here  $\theta$  is the angular displacement from the surface location nearest the sun. Replacement of  $I_0$  by  $I(\theta)$  in the result of (a) gives the quasi-steady-state temperature prediction

$$T(\theta) = \begin{cases} T_{s,\max} \cos^{1/4}(\theta) & \text{for } 0 \leq \theta \leq \pi/2; \\ 0 & \text{for } \pi/2 \leq \theta \leq \pi \end{cases}$$

This prediction becomes less accurate in the partially shadowed region (penumbra), given by  $|\theta - \pi| \approx 0.0046$  for a spherical lunar surface and the solar dimensions shown in Fig. 16.4-1. Transient energy transport and shadows cast by the rugged lunar topography also become important in this region, and radiation emitted and reflected from Earth and the other planets become significant on the dark side of the moon.

### 16B.1 Reference temperature for effective emissivity

By the assumption of linear variation of emissivity with temperature we write

$$e = a + bT$$

where  $a$  and  $b$  are constants. Then

$$e_1 - e^\circ = b(T_1 - T^\circ) \quad \text{and} \quad e_2 - e^\circ = b(T_2 - T^\circ)$$

and

$$(e_1 - e^\circ)T_1^4 = b(T_1 - T^\circ)T_1^4$$

$$(e_2 - e^\circ)T_2^4 = b(T_2 - T^\circ)T_2^4$$

However

$$(e_1 - e^\circ)T_1^4 = (e_2 - e^\circ)T_2^4$$

and therefore

$$T_1^5 - T_1^4 T^\circ = T_2^5 - T_2^4 T^\circ$$

This may be solved for the reference temperature to give

$$T^\circ = \frac{T_1^5 - T_2^5}{T_1^4 - T_2^4}$$

This is the same as Eq. 16B.1-2.

### 16B.2 Radiation across an annular gap

The system in this problem is very similar that depicted in Fig. 16.5-1 and described in Eq. 16.5-9. Since all the radiation leaving the inner surface ("1") of the annulus is directly intercepted by the outer surface ("2"), we know from the interpretation of  $F_{12}$  after Eq. 16.4-11 that  $F_{12} = 1$ . Then

$$\begin{aligned} Q_{12} &= \frac{\sigma(T_1^4 - T_2^4)}{\frac{1-e_1}{e_1 A_1} + \frac{1}{A_1} + \frac{1-e_2}{e_2 A_2}} \\ &= \frac{\sigma(T_1^4 - T_2^4)}{\frac{1}{e_1 A_1} - \frac{1}{A_1} + \frac{1}{A_1} + \frac{1}{e_2 A_2} - \frac{1}{A_2}} \\ &= \frac{\sigma(T_1^4 - T_2^4)}{\frac{1}{e_1 A_1} + \frac{1}{A_2} \left( \frac{1}{e_2} - 1 \right)} \end{aligned}$$

Note that if, in Eq. 16.5-9 we had replaced  $A_1 F_{12}$  by  $A_2 F_{21}$ , then we cannot set  $F_{21} = 0$  in this problem, inasmuch as light leaving surface "2" is not all intercepted by surface "1". In fact, it is not difficult to show that  $F_{21} = A_1/A_2$ . Then if the inner cylindrical surface is only slightly smaller than the outer cylindrical surface, then  $F_{21}$  will be just slightly smaller than 1, and if the inner cylinder shrinks to a wire, then  $F_{21}$  will approach zero.



### 16B.3 Multiple radiation shields.

(a) Equation 16.5-1 gives the radiant heat flow between successive planes in the series as

$$Q_{i,i+1} = \frac{\sigma(T_i^4 - T_{i+1}^4)}{[1/e_i + 1/e_{i+1} - 1]} = \frac{\sigma(T_i^4 - T_{i+1}^4)}{R_{i,i+1}}$$

in which

$$R_{i,i+1} = [1/e_i + 1/e_{i+1} - 1] / A_i$$

Summing the thermal resistances  $R_{i,i+1}$  from  $i = 1$  to  $i = n - 1$ , and equating the heat flows through all of them, gives

$$Q \sum_{i=1}^{i=n-1} R_{i,i+1} = \sigma(T_1^4 - T_n^4)$$

whence

$$Q = \frac{\sigma(T_1^4 - T_n^4)}{\sum_{i=1}^{i=n-1} R_{i,i+1}}$$

(b) The ratio of the radiant heat flow through  $n$  identical sheets to that between two is

$$\frac{Q(n \text{ sheets})}{Q(2 \text{ sheets})} = \frac{R_{1,2}}{(n-1)R_{1,2}} = \frac{1}{n-1}$$

(c) The ratio of the heat flow with three non-identical sheets to the heat flow without the middle sheet is

$$\frac{R_{1,3}}{R_{1,2} + R_{2,3}} = \frac{[1/e_1 + 1/e_3 - 1]}{[1/e_1 + 1/e_2 - 1] + [1/e_2 + 1/e_3 - 1]}$$

in agreement with the result of Example 16.5-1.

### 16B.4 Radiation and conduction through absorbing media

a. We begin by combining Eqs. 16.6-5 and 6 to get

$$0 = -\frac{d}{dz} q_z^{(r)} - m_a q_z^{(r)}$$

This may be integrated to give

$$\ln q_z^{(r)} = -m_a z + C$$

The constant of integration may be obtained from the boundary condition at  $z = 0$ , so that

$$q_z^{(r)} = q_0^{(r)} e^{-m_a z} \quad \text{and (from Eq. 16.6-6)} \quad \mathcal{Q} = m_a q_0^{(r)} e^{-m_a z}$$

Next, use Eq. 16.6-4 to get

$$0 = k \frac{d^2 T}{dz^2} + m_a q_0^{(r)} e^{-m_a z}$$

Integration twice with respect to  $z$  gives

$$T(z) = -\frac{q_0^{(r)}}{m_a k} e^{-m_a z} + C_1 z + C_2$$

Next we apply the boundary conditions that  $T(0) = T_0$  and  $T(\delta) = T_\delta$  to get

$$T(z) - T_0 = \frac{q_0^{(r)}}{m_a k} (1 - e^{-m_a z}) + \left[ (T_\delta - T_0) - \frac{q_0^{(r)}}{m_a k} (1 - e^{-m_a \delta}) \right] \frac{z}{\delta}$$

b. The conductive heat flux is given by Fourier's law:

$$q_z = -k \frac{dT}{dz} = -q_0^{(r)} e^{-m_a z} + k \frac{T_\delta - T_0}{\delta} - \frac{q_0^{(r)}}{m_a \delta} (1 - e^{-m_a \delta})$$

For very large values of  $m_a$ , the first and third terms become negligibly small, and we are left with

Very large  $m_a$ : 
$$q_z \approx -k \frac{T_0 - T_\delta}{\delta}$$

For very small values of  $m_a$  we can expand the first and third terms in a Taylor series and get:

Very small  $m_a$ : 
$$\begin{aligned} q_z &= -q_0^{(r)}(1 - m_a z + \dots) - k \frac{T_0 - T_\delta}{\delta} \\ &\quad - \frac{q_0^{(r)}}{m_a \delta} (1 - 1 + m_a \delta - \dots) \\ &\approx -k \frac{T_0 - T_\delta}{\delta} \end{aligned}$$

Thus in both limits, the conductive heat flux is virtually unaffected by the radiation.

### 16B.5 Cooling of a black body in vacuo

An energy balance over the black body in the enclosure is

$$\frac{d}{dt}U_{\text{tot}} = Q \quad \text{or} \quad \rho \hat{C}_p V \frac{dT}{dt} = Aq_b^{(e)}$$

When the Stefan-Boltzmann law is inserted, we get

$$\rho \hat{C}_p V \frac{dT}{dt} = A\sigma(T_2^4 - T^4)$$

This separable, first-order equation may be integrated as follows

$$\int_{T_1}^T \frac{dT}{T_2^4 - T^4} = \frac{A\sigma}{\rho \hat{C}_p V} \int_0^t dt$$

The integral on the left side may be integrated with the help of an integral table to give

$$\left( \frac{1}{4T_2^3} \ln \left| \frac{T_2 + T}{T_2 - T} \right| + \frac{1}{2T_2^3} \arctan \frac{T}{T_2} \right) \Bigg|_{T_1}^T = \frac{A\sigma t}{\rho \hat{C}_p V}$$

Therefore the temperature-time relation is

$$\ln \left| \frac{T_2 + T}{T_2 - T} \right| - \ln \left| \frac{T_2 + T_1}{T_2 - T_1} \right| + 2 \arctan \frac{T}{T_2} - 2 \arctan \frac{T_1}{T_2} = \frac{4A\sigma T_2^3 t}{\rho \hat{C}_p V}$$

The left side gives  $T = T_2$  as  $t$  goes to infinity, and  $T = T_1$  as  $t$  goes to zero.

The left side is dimensionless, and the right side is also, as can be seen by using the table of notation given on pp. 872 et seq.

$$\frac{(L^2) \left( \frac{M}{t^3 T^4} \right) (T^3) (t)}{\left( \frac{M}{L^3} \right) \left( \frac{L^2}{t^2 T} \right) (L^3)} = \text{dimensionless}$$

### 16B.6 Heat loss from an insulated pipe.

(a) Eq. 10.6-29 gives for this problem,

$$Q_0^{(\text{cond})}/L = \frac{2\pi(T_0 - T_2)}{\frac{\ln(r_1/r_0)}{k_{01}} + \frac{\ln(r_2/r_1)}{k_{12}}}$$

with  $r_0 = 1.0335$  in.,  $r_1 = 1.0335 + 0.154 = 1.1875$  in., and  $r_2 = 1.1875 + 2 = 3.1875$  in. With the given thermal conductivity values, we then obtain

$$\begin{aligned} Q_0^{(\text{cond})}/L &= \frac{2\pi(T_0 - T_a)}{\frac{\ln(1.1875/1.0335)}{26} + \frac{\ln(3.1875/1.1875)}{0.35}} \\ &= \frac{2\pi(250 - T_a)}{0.0053 + 2.8} \\ &= \begin{cases} 334 \text{ Btu/hr}\cdot\text{ft} & \text{if } T_0 = 100^\circ\text{F}; \\ 0 & \text{if } T_2 = 250^\circ\text{F} \end{cases} \end{aligned}$$

(b) The net radiative heat loss is given by Eq. 16.5-3. Setting  $e = a = 0.05$  for the aluminum foil, we get

$$\begin{aligned} Q^{(\text{rad})}/L &= \sigma\pi D_2(0.05)(T_0^4 - T_a^4) \\ &= 0.1712 \times 10^{-8} \pi (2 \times 3.1875)(0.05)(T_0^4 - 540^4) \\ &= \begin{cases} 23 \text{ Btu/hr}\cdot\text{ft} & \text{if } T_0 = 100^\circ\text{F} = 560^\circ\text{R}; \\ 290 \text{ Btu/hr}\cdot\text{ft} & \text{if } T_0 = 250^\circ\text{F} = 710^\circ\text{R} \end{cases} \end{aligned}$$

The free-convective heat loss is predictable as in §14.6. For  $T_a = 100^\circ\text{F}$ , Example 14.6-1 gives

$$Q^{(\text{conv})}/L = 18 \text{ Btu/hr}\cdot\text{ft}$$

For  $T_a = 250^\circ\text{F}$ , Eqs. 14.6-4,5 and Tables 14.6-1,2 give

$$Nu_m^{\text{lam}} = 0.772(0.515)(\text{GrPr})^{1/4} = 0.398(\text{GrPr})^{1/4}$$

The needed properties of air at  $T_f = (80 + 250)/2 = 165^\circ\text{F} = 74^\circ\text{C}$  are obtained from the ideal gas law, from Table 1.1-2, and from *CRC Handbook of Chemistry and Physics*, 81st Ed., 2001-2002, pp. 6-1, 6-2, and 6-185.

$$\begin{aligned} \mu &= 0.0206 \text{ mPa}\cdot\text{s} = 0.0498 \text{ lb}_m/\text{ft}\cdot\text{hr} \\ \rho &= pM/RT = 1.017 \times 10^{-3} \text{ g/cm}^3 = 0.0634 \text{ lb}_m/\text{ft}^3 \\ \hat{C}_p &= 1.012 \text{ J/g}\cdot\text{K} = 0.2420 \text{ Btu/lb}_m/\text{cdotR} \\ k &= 29.5 \text{ mW/m}\cdot\text{K} = 0.0170 \text{ Btu/hr}\cdot\text{ft}\cdot\text{F} \\ \beta &= 1/T_f = (1/625)\text{R}^{-1} \end{aligned}$$

Hence,

$$\begin{aligned}\text{GrPr} &= \left( \frac{(2 \times 3.1875/12)^3 (0.0634)^2 (4.17 \times 10^8) (170/625)}{(0.0498)^2} \right) \left( \frac{(0.2420)(0.0498)}{(0.0170)} \right) \\ &= (2.76 \times 10^7)(0.709) = 1.96 \times 10^7\end{aligned}$$

and

$$\begin{aligned}\text{Nu}_m &= (0.398)(\text{GrPr})^{1/4} \\ &= (0.398)(1.96 \times 10^7)^{1/4} = 26.5\end{aligned}$$

Therefore,

$$\begin{aligned}Q^{(\text{conv})}/L &= h_m \pi D (T_0 - T_a) = (\text{Nu}_m k/D)(\pi D)(T_0 - T_a) \\ &= \text{Nu}_m \pi k (T_0 - T_a) \\ &= (26.5)\pi(0.0170)(250 - 80) = 241 \text{ Btu/hr}\cdot\text{ft}\end{aligned}$$

giving

$$\frac{Q^{(\text{cond})} - Q^{(\text{rad})} - Q^{(\text{conv})}}{L} = \begin{cases} 334 - 23 - 18 = 293 \text{ Btu/hr}\cdot\text{ft} & \text{if } T_0 = 100^\circ\text{F}; \\ 0 - 290 - 241 = -531 \text{ Btu/hr}\cdot\text{ft} & \text{if } T_0 = 250^\circ\text{F}. \end{cases}$$

(c) Linear interpolation to zero heat accumulation at the outer surface gives the steady-state values

$$T_0 = 100 + 293/824(250 - 100) = 153^\circ\text{F}$$

$$Q^{(\text{cond})}/L = Q^{(\text{rad})+(\text{conv})}/L = 334 + (293/824)(0 - 334) = 215 \text{ Btu/hr}\cdot\text{ft}$$

### 17A.1 Prediction of a low-density binary diffusivity.

(a) We begin by looking up the needed properties of the species from Table E.1:

Species	$M$ , g/g-mol	$T_c$ , K	$p_c$ , atm
A: CH <sub>4</sub>	16.04	191.1	45.8
B: C <sub>2</sub> H <sub>6</sub>	30.07	305.4	48.2

Equation 17.2-1 then gives the following prediction of  $D_{AB}$  for methane-ethane (treated here as a nonpolar gas-pair) at  $p = 1$  atm and  $T = 293$ K:

$$\begin{aligned}
 D_{AB} &= a \left( \frac{T}{\sqrt{T_{cA}T_{cB}}} \right)^b (p_{cA}p_{cB})^{1/3} (T_{cA}T_{cB})^{5/12} (1/M_A + 1/M_B)^{1/2} / p \\
 &= 2.745 \times 10^{-4} \left( \frac{293}{\sqrt{191.1 \times 305.4}} \right)^{1.823} \\
 &\quad \cdot (45.8 \times 48.2)^{1/3} (191.1 \times 305.4)^{5/12} (1/16.04 + 1/30.07)^{1/2} / 1 \text{ atm} \\
 &= 0.152 \text{ cm}^2/\text{s}
 \end{aligned}$$

(b) Equation 17.2-3 gives

$$\begin{aligned}
 (cD_{AB})_c &= 2.96 \times 10^{-6} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \frac{(p_{cA}p_{cB})^{1/3}}{(T_{cA}T_{cB})^{1/12}} \\
 &= 2.96 \times 10^{-6} \left( \frac{1}{16.04} + \frac{1}{30.07} \right)^{1/2} \frac{(45.8 \times 48.2)^{1/3}}{(191.1 \times 305.4)^{1/12}} \\
 &= 4.78 \times 10^{-6} \text{ g-mol/cm-s}
 \end{aligned}$$

The reduced conditions for Fig. 17.2-1 for this problem, calculated as described on page 522, are

$$\begin{aligned}
 T_r &= \frac{T}{\sqrt{T_{cA}T_{cB}}} = \frac{293}{\sqrt{191.1 \times 305.4}} = 1.21 \\
 p_r &= \frac{p}{\sqrt{p_{cA}p_{cB}}} = \frac{1.0}{\sqrt{45.8 \times 48.2}} = 0.021
 \end{aligned}$$

At this reduced state, Fig. 17.2-1 gives  $(cD_{AB})_r = 1.20$ . Hence, the predicted value of  $cD_{AB}$  is  $1.20(cD_{AB})_c = 5.74 \times 10^{-6}$ . Dividing this result by the ideal-gas prediction  $c = p/RT = 4.16 \times 10^{-5}$  g-mol/cm<sup>-3</sup> at this low-density condition gives  $D_{AB} = 0.138$  cm<sup>2</sup>/s.

(c) Equations 17.3-14 and 15 give the binary interaction parameters

$$\sigma_{AB} = (3.780 + 4.388)/2 = 4.084 \text{ \AA} \quad \text{and} \quad \epsilon_{AB}/K = \sqrt{154 \times 232} = 189 \text{ K}$$

when the Lennard-Jones parameters of Table E.1 are used for the individual species. Then, at  $kT/\varepsilon_{AB} = 293/189 = 1.550$ , Table E.2 gives  $\Omega_{\mathcal{D},AB} = 1.183$ , and Eq. 17.3-12 gives the prediction

$$\begin{aligned} \mathcal{D}_{AB} &= 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p\sigma_{AB}^2 \Omega_{calD,AB}}} \\ &= 0.0018583 \sqrt{(293)^3 \left( \frac{1}{16.04} + \frac{1}{30.07} \right) \frac{1}{(1)(4.084)^2 (1.183)}} \\ &= 0.146 \text{ cm}^2/\text{s} \end{aligned}$$

(d) Use of Eqs. 1.4-11a,c with the combining rules of Eqs. 17.3-14,15 gives the estimates

$$\begin{aligned} \varepsilon_{AB}/K &= 0.77 \sqrt{191.1 \times 305.4} = 186.0 \text{ K} \\ \sigma_{AB} &= \frac{2.44}{2} \left[ \left( \frac{T_{cA}}{p_{cA}} \right)^{1/3} + \left( \frac{T_{cB}}{p_{cB}} \right)^{1/3} \right] = 4.222 \text{ \AA} \end{aligned}$$

Then at  $kT/\varepsilon_{AB} = 293/186.0 = 1.575$ , Table E.2 gives  $\Omega_{\mathcal{D},AB} = 1.1755$ , whereupon Eq. 17.3-12 gives

$$\begin{aligned} \mathcal{D}_{AB} &= 0.0018583 \sqrt{(293)^3 \left( \frac{1}{16.04} + \frac{1}{30.07} \right) \frac{1}{(1)(4.222)^2 (1.1755)}} \\ &= 0.138 \text{ cm}^2/\text{s} \end{aligned}$$



### 17A.2 Extrapolation of binary diffusivity to a very high temperature.

(a) Equation 17.2-1 in the nonpolar form gives

$$\mathcal{D}_{AB}|_{1500\text{K}} = \mathcal{D}_{AB}|_{293\text{K}} (1500/293)^{1.823} = 2.96 \text{ cm}^2/\text{s}$$

(b) Equation 17.3-10, with  $n = p/kT$ , predicts  $\mathcal{D}_{AB} \propto T^{3/2}$ , thus giving

$$\mathcal{D}_{AB}|_{1500\text{K}} = \mathcal{D}_{AB}|_{293\text{K}} (1500/293)^{1.5} = 1.75 \text{ cm}^2/\text{s}$$

(c) Equation 17.3-12 and Table E.2, with  $\varepsilon_{AB} = 135.8$  from Table E.1 and Eq. 17.3-15, gives

$$\mathcal{D}_{AB}|_{1500\text{K}} = \mathcal{D}_{AB}|_{293\text{K}} (1500/293)^{3/2} \left( \frac{\Omega_{\mathcal{D},AB}|_{293\text{K}/\varepsilon_{AB}}}{\Omega_{\mathcal{D},AB}|_{1500\text{K}/\varepsilon_{AB}}} \right) = 2.51 \text{ cm}^2/\text{s}$$

The superior agreement of Method (c) with the experimental value of 2.45  $\text{cm}^2/\text{s}$  illustrates the wider range provided by the Chapman-Enskog theory when combined with the Lennard-Jones potential-energy model.

$$D_{AA^*} = \frac{kT}{2\pi\mu_A} \left( \frac{\tilde{N}_A}{\tilde{V}_A} \right)^{1/3}$$

or in cgs units,

$$D_{AA^*} = \frac{(1.38066 \times 10^{-16} \text{ erg/K})(T, \text{K})}{2\pi(\mu_A, \text{g/cm}\cdot\text{s})} \left( \frac{6.02214 \times 10^{23} \text{ molecules/g}\cdot\text{mol}}{(200.61 \text{ g/g}\cdot\text{mol})(\hat{V}_A, \text{cm}^3/\text{g})} \right)^{1/3}$$

Insertion of the values tabulated for this problem, with  $\mu(\text{cp})$  divided by 100 to get  $\mu_A, \text{g/cm}\cdot\text{s}$ , gives the following results:

$T(\text{K})$	$D_{AA^*}, \text{obs.}$	$D_{AA^*}, \text{pred.}$	Ratio, pred./obs.
275.7	$1.52 \times 10^{-5}$	$1.24 \times 10^{-5}$	0.82
289.6	$1.68 \times 10^{-5}$	$1.40 \times 10^{-5}$	0.84
364.2	$2.57 \times 10^{-5}$	$2.16 \times 10^{-5}$	0.84

The predicted self-diffusivities are about 5/6 of the measured values.

### 17A.4 Schmidt numbers for binary gas mixtures at low density.

We begin by tabulating the needed molecular parameters for species  $A$  and  $B$  from Table E.1, and estimating the binary parameters  $\sigma_{AB}$  and  $\epsilon_{AB}/K$  from Eqs. 17.3-14 and 15:

Species	$M$ , g/g-mol	$\sigma$ , Å	$\epsilon/K$ , K
A: H <sub>2</sub>	2.016	2.915	38.0
B: CCl <sub>2</sub> F <sub>2</sub>	120.92	5.116	280.
AB:		4.0155	103.15

Equation 17.3-11 and Table E.2 then give the following prediction of  $c\mathcal{D}_{AB}$  for binary mixtures of H<sub>2</sub> and Freon-12 at  $T = 25^\circ\text{C} = 298.15\text{ K}$ :

$$\begin{aligned} c\mathcal{D}_{AB} &= 2.2646 \times 10^{-5} \sqrt{T \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{\sigma_{AB}^2 \Omega_{\mathcal{D},AB}}} \\ &= 2.2646 \times 10^{-5} \sqrt{298.15 \left( \frac{1}{2.016} + \frac{1}{120.92} \right) \frac{1}{(4.0155)^2 (0.9597)}} \\ &= 1.794 \times 10^{-5} \text{ g-mol/cm}\cdot\text{s} \end{aligned}$$

With this prediction of  $c\mathcal{D}_{AB}$  and the viscosity data of Problem 1A.4, the Schmidt number can then be calculated as

$$\text{Sc} = \frac{\mu}{\rho \mathcal{D}_{AB}} = \frac{\mu}{M c \mathcal{D}_{AB}} = \frac{\mu}{(x_A M_A + x_B M_B) c \mathcal{D}_{AB}}$$

in accordance with Eqs. G and L of Table 17.7-1. Results are as follows:

$x_A = x_{\text{H}_2}$	0.00	0.25	0.50	0.75	1.00
$\mu$ , g/cm·s	$124.0 \times 10^{-6}$	$128.1 \times 10^{-6}$	$131.9 \times 10^{-6}$	$135.1 \times 10^{-6}$	$88.4 \times 10^{-6}$
$M$ , g/g-mol	120.92	91.194	61.468	31.742	2.016
Sc	0.057	0.078	0.120	0.237	2.44

We see that the Schmidt number depends strongly on the composition when  $M_A$  and  $M_B$  differ greatly. This fact is also illustrated in Table 17.3-1.

### 17A.5 Estimation of diffusivity for a binary mixture at high density.

The following properties of  $N_2$  and  $C_2H_6$  for this problem are obtained from Table E.1:

Species	$M$ , g/g-mol	$T_c$ , K	$p_c$ , atm
A: $N_2$	28.01	126.2	33.5
B: $C_2H_6$	30.07	305.4	48.2

(a) The measured value  $\mathcal{D}_{AB} = 0.148 \text{ cm}^2/\text{s}$  at  $T = 298.2 \text{ K}$  permits calculation of an experimentally-based value of  $(c\mathcal{D}_{AB})_c$ . The reduced conditions for this measurement are

$$T_r = \frac{T}{\sqrt{T_{cA}T_{cB}}} = \frac{298.2}{\sqrt{126.2 \times 305.4}} = 1.52;$$

$$p_r = \frac{p}{\sqrt{p_{cA}p_{cB}}} = \frac{1.0}{\sqrt{33.5 \times 48.2}} = 0.025$$

On Fig. 17.2-1, this state lies essentially at the low-pressure limit, with  $(c\mathcal{D}_{AB})_r = 1.47$ . Accordingly expressing  $c$  by the ideal gas law, we find

$$\begin{aligned} c\mathcal{D}_{AB} &= \frac{p}{RT} \mathcal{D}_{AB} \\ &= \frac{1 \text{ atm}}{(82.06 \times 298.2 \text{ cm}^3 \cdot \text{atm}/\text{g-mol})} (0.148 \text{ cm}^2/\text{s}) \\ &= 6.05 \times 10^{-6} \text{ g-mol}/\text{cm} \cdot \text{s} \end{aligned}$$

Hence, the critical  $c\mathcal{D}_{AB}$  value is

$$(c\mathcal{D}_{AB})_c = c\mathcal{D}_{AB}/(c\mathcal{D}_{AB})_r = 6.05 \times 10^{-6}/1.47 = 4.12 \times 10^{-6} \text{ g-mol}/\text{cm} \cdot \text{s}$$

Now, the reduced conditions for the desired prediction are

$$T_r = \frac{T}{\sqrt{T_{cA}T_{cB}}} = \frac{288.2}{\sqrt{126.2 \times 305.4}} = 1.47;$$

$$p_r = \frac{p}{\sqrt{p_{cA}p_{cB}}} = \frac{40}{\sqrt{33.5 \times 48.2}} = 0.995$$

at which state Fig. 17.2-1 gives  $(c\mathcal{D}_{AB})_r = 1.42$ . The resulting prediction is then

$$\begin{aligned} c\mathcal{D}_{AB} &= (c\mathcal{D}_{AB})_c (c\mathcal{D}_{AB})_r \\ &= (4.12 \times 10^{-6})(1.42) = 5.8 \times 10^{-6} \text{ g-mol}/\text{cm} \cdot \text{s}. \end{aligned}$$

(b) Equation 17.2-3 gives the predicted critical value

$$\begin{aligned} (c\mathcal{D}_{AB})_c &= 2.96 \times 10^{-6} \left( \frac{1}{28.01} + \frac{1}{30.07} \right)^{1/2} \frac{(33.5 \times 48.2)^{1/3}}{(126.2 \times 305.4)^{1/12}} \\ &= 3.78 \times 10^{-6} \text{ g-mol}/\text{cm} \cdot \text{s}. \end{aligned}$$

Multiplication by  $(c\mathcal{D}_{AB})_r = 1.42$  as in (a) gives

$$c\mathcal{D}_{AB} = (3.78 \times 10^{-6})(1.42) = 5.4 \times 10^{-6} \text{ g-mol}/\text{cm} \cdot \text{s}.$$

## 17A.6 Diffusivity and Schmidt number for chlorine-air mixtures.

(a) We begin by tabulating molecular parameters for chlorine and air from

Table E.1 and Table E.2

14 and 15:

Species	$M$ , g/g-mol	$\sigma$ , Å	$\epsilon/K$ , K
A: Cl <sub>2</sub>	70.91	4.115	357.
B: Air	28.97	3.617	97.0
AB:		3.866	186.1

Equation 17.3-12 and Table E.2 then give the following prediction of  $\mathcal{D}_{AB}$  for chlorine-air mixtures at  $T = 75^\circ\text{F} = 23.89^\circ\text{C} = 297.04\text{ K}$ :

$$\begin{aligned}\mathcal{D}_{AB} &= 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p \sigma_{AB}^2 \Omega_{\mathcal{D},AB}}} \\ &= 0.0018583 \sqrt{(297.04)^3 \left( \frac{1}{28.97} + \frac{1}{70.91} \right) \frac{1}{(1)(3.866)^2(1.169)}} \\ &= 0.120 \text{ cm}^2/\text{s}\end{aligned}$$

(b) Equation 17.2-1 needs the following values from Table E.1:

Component	$M$ , g/g-mol	$T_c$ , K	$p_c$ , atm
A: Cl <sub>2</sub>	70.91	417.	76.1
B: Air	28.97	132.	36.4

The nonpolar version of Eq. 17.2-1 then gives the prediction

$$\begin{aligned}\mathcal{D}_{AB} &= 2.745 \times 10^{-4} \left( \frac{297.04}{\sqrt{417. \times 132.}} \right)^{1.823} \\ &\cdot (76.1 \times 36.4)^{1/3} (417. \times 132.)^{5/12} (1/70.91 + 1/28.97)^{1/2} / 1 \text{ atm} \\ &= 0.123 \text{ cm}^2/\text{s}\end{aligned}$$

$x_{Cl_2}$	0.00	0.25	0.50	0.75	1.00
$\mu$ , g/cm·s	0.000183	0.000164	0.000150	0.000139	0.000131
$M$ , g/g-mol	28.97	39.455	49.94	60.425	70.91
Sc	1.28	0.84	0.61	0.47	0.375

We see that the Schmidt number depends strongly on the composition when  $M_A$  and  $M_B$  differ greatly. This fact is also illustrated in Table 17.3-1 and in Problem 17A.4.

### 17A.7 The Schmidt number for self-diffusion

(a) Equation 1.3-1b, written for non-tracer species A, gives

$$\mu_c = 7.70 \times 10^{-6} M_A^{1/2} p_{cA}^{2/3} T_{cA}^{-1/6}$$

for the critical viscosity in g/cm·s. Here  $M_A$  is in g/g-mol,  $p_{cA}$  in atm and  $T_{cA}$  in K. Eq. 17.2-2 gives

$$(c\mathcal{D}_{AA^*})_c = 2.96 \times 10^{-6} \left( \frac{1}{M_A} + \frac{1}{M_{A^*}} \right)^{1/2} p_{cA}^{1/3} T_{cA}^{-1/6}$$

The resulting critical Schmidt number for self-diffusion with  $M_A \approx M_{A^*}$  is

$$\left( \frac{\mu}{M_A c \mathcal{D}_{AA^*}} \right)_c = \frac{7.70}{2.96\sqrt{2}} = 1.84$$

(b) Figs. 1.3-1 and 17.2-1, with the result in (a) for  $M_A \approx M_{A^*}$ , give Sc for self-diffusion as the following function of  $T_r$  and  $p_r$ :

$$Sc_{AA^*} = 1.84 \frac{\mu_r(T_r, p_r)}{(c\mathcal{D}_{AA^*})_r(T_r, p_r)}$$

Calculations from this formula are summarized below:

Phase→	Gas	Gas	Gas	Liquid	Gas	Gas
$T_r$	0.7	1.0	5.0	0.7	1.0	2.0
$p_r$	0.0	0.0	0.0	sat.	1.0	1.0
$\mu_r$	0.32	0.45	1.62	7.8	1.00	0.94
$(c\mathcal{D}_{AA^*})_r$	0.72	1.01	3.65	0.37	1.03	1.83
$Sc_{AA^*}$	0.82	0.82	0.82	39	1.79	0.94

### 17A.8 Correction of high-density diffusivity for temperature.

The following properties of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> for this problem are obtained from Table E.1:

Species	<i>M</i> , g/g-mol	<i>T<sub>c</sub></i> , K	<i>p<sub>c</sub></i> , atm
A: CH <sub>4</sub>	16.04	191.1	45.8
B: C <sub>2</sub> H <sub>6</sub>	30.07	305.4	48.2

The reduced conditions (State 1) for the given  $c\mathcal{D}_{AB}$  value, calculated as described on page 522, are

$$T_r = \frac{313}{\sqrt{191.1 \times 305.4}} = 1.30; \quad p_r = \frac{136}{\sqrt{45.8 \times 48.2}} = 2.89$$

and Fig. 17.2-1 gives  $(c\mathcal{D}_{AB})_r = 1.27$  at this state. The reduced conditions (State 2) for the desired prediction are

$$T_r = \frac{351}{\sqrt{191.1 \times 305.4}} = 1.45; \quad p_r = \frac{136}{\sqrt{45.8 \times 48.2}} = 2.89$$

and Fig. 17.2-1 gives  $(c\mathcal{D}_{AB})_r = 1.40$  at this state. The prediction of  $c\mathcal{D}_{AB}$  is then obtained as follows:

$$\begin{aligned} (c\mathcal{D}_{AB})|_{\text{State 2}} &= (c\mathcal{D}_{AB})|_{\text{State 1}} \frac{(c\mathcal{D})_r|_{\text{State 2}}}{(c\mathcal{D})_r|_{\text{State 1}}} \\ &= 6.0 \times 10^{-6} \frac{1.40}{1.27} = 6.6 \times 10^{-6} \text{ g-mol/cm}\cdot\text{s} \end{aligned}$$

The observed  $c\mathcal{D}_{AB}$  value at State 2 is  $6.3 \times 10^{-6}$  g-mol/cm·s, in fair agreement with this prediction.



### 17A.9 Prediction of critical $cD_{AB}$ values.

(a) Equation 17A.9-1 gives  $kT/\varepsilon_{AA^*} = 1/0.77 = 1.2987$  at  $T = T_{cA}$ , and Table E.2 gives  $\Omega_{D,AA^*} = 1.2746$  at this argument value. Insertion of this result, along with Eq. 17A.9-2, into Eq. 17A.9-1 gives

$$\begin{aligned}(cD_{AA^*})_c &= \frac{2.2646 \times 10^{-5}}{1.01} \sqrt{T_{cA} \left( \frac{1}{M_A} + \frac{1}{M_{A^*}} \right)} \frac{1}{(2.44(T_{cA}/p_{cA})^{1/3})^2 (1.2746)} \\ &= 2.955 \times 10^{-6} \left( \frac{1}{M_A} + \frac{1}{M_{A^*}} \right)^{1/2} \frac{p_{cA}^{2/3}}{T_{cA}^{1/6}}\end{aligned}$$

which verifies Eq. 17.2-2, within the uncertainty of the coefficient 1.01 determined from low-density self-diffusion data.

(b) Evaluation of the component parameters in Eqs. 17A.9-4,5 according to Eqs. 1.4-11a,c gives

$$\sigma_{AB} = 2.44 \sqrt{\left( \frac{T_{cA}}{p_{cA}} \right)^{1/3} \left( \frac{T_{cB}}{p_{cB}} \right)^{1/3}} = 2.44 \left( \frac{T_{cA} T_{cB}}{p_{cA} p_{cB}} \right)^{1/6}$$

and

$$\frac{\varepsilon_{AB}}{K} = 0.77 \sqrt{T_{cA} T_{cB}}$$

Replacement of  $A^*$  by  $B$  and  $T_{cA}$  by  $\sqrt{T_{cA} T_{cB}}$  in Eq. 17A.9-1 gives

$$(cD_{AB})_c = \frac{2.2646 \times 10^{-6}}{1.01} \sqrt{T_{cA} T_{cB} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{\sigma_{AB}^2 \Omega_{D,AB}}$$

Evaluation of  $\sigma_{AB}$  and  $\varepsilon_{AB}/K$  according to Eqs. 17A.9-6,7 then gives

$$(cD_{AB})_c = 2.955 \times 10^{-6} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \frac{(p_{cA} p_{cB})^{1/3}}{(T_{cA} T_{cB})^{1/6}}$$

by a procedure analogous to that given in part (a). This result reproduces Eq. 17.2-3 within the uncertainty of the empirical coefficient 1.01.

### 17A.10 Estimation of liquid diffusivities.

(a) We begin by evaluating the solvent properties  $\psi_B = 2.6$ ,  $M_B = 18.016$ , and the dilute-solution viscosity  $\mu = 1.22$  cp at  $12.5^\circ\text{C}$  from a plot of the data for liquid water in Table 1.1-2. The solute, acetic acid, has a molecular weight  $M_A = 60.052$ , and its molar volume  $\tilde{V}_A = M_A/\rho$  at its normal boiling point is  $60.052/0.937 = 64.1$  cm<sup>3</sup>/g-mole. The Wilke-Chang formula, Eq. 17.4-8, then gives the following prediction at  $12.5^\circ\text{C}$ :

$$\begin{aligned} \mathcal{D}_{AB} &= 7.4 \times 10^{-8} \frac{\sqrt{\psi_B M_B T}}{\mu \tilde{V}_A^{0.6}} \\ &= 7.4 \times 10^{-8} \frac{\sqrt{(2.6)(18.016)(273.15 + 12.5)}}{(1.22)(64.1)^{0.6}} \\ &= 9.8 \times 10^{-6} \end{aligned}$$

(b) For a given composition, Eq. 17.4-8 predicts  $\mathcal{D}_{AB}$  to be proportional to  $T/\mu$ . Let  $T_1 = 15^\circ\text{C} = 288.15\text{K}$ , and  $T_2 = 100^\circ\text{C} = 373.15\text{K}$ . Then, the predicted viscosity for a dilute aqueous solution of methanol at  $T_2$  is

$$\begin{aligned} \mathcal{D}_{AB}|_{T_2} &= \frac{(\mathcal{D}_{AB}\mu)|_{T_1} T_2}{\mu|_{T_2} T_1} \\ &= (1.28 \times 10^{-5} \text{ cm}^2/\text{s}) \left( \frac{1.14 \text{ cp}}{0.2821 \text{ cp}} \right) \left( \frac{373.15\text{K}}{288.15\text{K}} \right) \\ &= 6.7 \times 10^{-6} \text{ cm}^2/\text{s} \end{aligned}$$

### 17B.1 Interrelation of composition variables in mixtures

a.. To get Eq. (H), use Eqs. (A) and (D)

$$c_\alpha = \frac{\text{moles of } \alpha}{\text{volume}} = \frac{\rho_\alpha}{M_\alpha} = \frac{(\text{mass of } \alpha) / \text{volume}}{(\text{mass of } \alpha) / (\text{moles of } \alpha)}$$

and Eq. (I) follows immediately.

To get Eq. (J), use Eqs. (F) and (E)

$$\sum_{\alpha=1}^N x_\alpha = \frac{1}{c} \sum_{\alpha=1}^N c_\alpha = \frac{c}{c} = 1$$

Equation (K) may be obtained similarly.

To get Eq. (L), use Eqs. (F), (J), and (B) thus

$$\sum_{\alpha=1}^N x_\alpha M_\alpha = \frac{1}{c} \sum_{\alpha=1}^N c_\alpha M_\alpha = \frac{1}{c} \sum_{\alpha=1}^N \rho_\alpha = \frac{\rho}{c} = M$$

and Eq. (M) may be obtained in a similar way.

To derive Eq (N), we use Eqs. (F), (H), and (C) to get

$$x_\alpha = \frac{c_\alpha}{c} = \frac{(\rho_\alpha / M_\alpha)}{\sum_{\beta=1}^N (\rho_\beta / M_\beta)} = \frac{(\rho_\alpha / M_\alpha)(1/\rho)}{\sum_{\beta=1}^N (\rho_\beta / M_\beta)(1/\rho)} = \frac{(\omega_\alpha / M_\alpha)}{\sum_{\beta=1}^N (\omega_\beta / M_\beta)}$$

The derivation of Eq. (O) is done in like manner.

b. To get Eq. (P') from Eq. (P),

$$\begin{aligned} \nabla x_A &= -\frac{M^2}{M_A} \left[ \frac{1}{M} + \omega_A \left( \frac{1}{M_B} - \frac{1}{M_A} \right) \right] \nabla \omega_B \\ &= \frac{M^2}{M_A} \left[ \left( \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} \right) + \left( \frac{\omega_A}{M_B} - \frac{\omega_A}{M_A} \right) \right] \nabla \omega_A = \frac{M^2}{M_A M_B} \nabla \omega_A \\ &= \frac{1}{M_A M_B} \nabla \omega_A = \frac{1}{M_A M_B \left( \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} \right)^2} \nabla \omega_A \end{aligned}$$

In going from line 1 to line 2, we used Eq. (M) and then Eq. (K). To get line 3, we used Eq. (K) again. The same method is used to get Eq. (Q') from Eq. (Q).

c. First we must write the binary equivalent of Eq. (N) in such a way that only one variable appears on the right side (we have to keep in mind that the two mass fractions cannot be varied independently):

$$x_A = \frac{\frac{\omega_A}{M_A}}{\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}} = \frac{\frac{\omega_A}{M_A}}{\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}}$$

Then to get Eq. (P'), we differentiate

$$\begin{aligned} \nabla x_A &= \frac{\frac{1}{M_A}}{\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}} \nabla \omega_A - \frac{\frac{\omega_A}{M_A}}{\left(\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}\right)^2} \left(\frac{1}{M_A} - \frac{1}{M_B}\right) \nabla \omega_A \\ &= \frac{\frac{1}{M_A} \left(\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}\right) - \frac{\omega_A}{M_A} \left(\frac{1}{M_A} - \frac{1}{M_B}\right)}{\left(\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}\right)^2} \nabla \omega_A \\ &= \frac{\frac{1}{M_A} \left(\frac{1 - \omega_A}{M_B}\right) + \frac{\omega_A}{M_A} \left(\frac{1}{M_B}\right)}{\left(\frac{\omega_A}{M_A} + \frac{1 - \omega_A}{M_B}\right)^2} \nabla \omega_A \\ &= \frac{\frac{\omega_A + \omega_B}{M_A M_B}}{\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)^2} \nabla \omega_A = \frac{1}{M_A M_B} \frac{1}{\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)^2} \nabla \omega_A \end{aligned}$$

The derivation of Eq. (Q') from Eq. (O) proceeds similarly.

## 17B.2 Relations among the fluxes in multicomponent systems

a. To verify Eq. (K) of Table 17.8-1, we proceed as follows:

$$\begin{aligned}\sum_{\alpha=1}^N \mathbf{j}_{\alpha} &= \sum_{\alpha=1}^N \rho_{\alpha} (\mathbf{v}_{\alpha} - \mathbf{v}) = \sum_{\alpha=1}^N \rho_{\alpha} \mathbf{v}_{\alpha} - \sum_{\alpha=1}^N \rho_{\alpha} \mathbf{v} \\ &= \rho \sum_{\alpha=1}^N \omega_{\alpha} \mathbf{v} - \mathbf{v} \sum_{\alpha=1}^N \rho_{\alpha} \\ &= \rho \mathbf{v} - \mathbf{v} \rho = 0\end{aligned}$$

In the second line, we have used Eq. (C) of Table 17.7-1, and to get the third line we used Eq. (B) of the same table as well as Eq. (B) of

The proof of Eq. (O) of Table 17.8-1 proceeds analogously.

b. The verification of Eq. (T) of Table 17.8-1 follows directly from the definitions of the fluxes:

$$\mathbf{j}_{\alpha} = \rho_{\alpha} (\mathbf{v}_{\alpha} - \mathbf{v}) \quad \text{and} \quad \mathbf{n}_{\alpha} = \rho_{\alpha} \mathbf{v}_{\alpha}$$

Substitution of these definitions into Eq. (T) gives

$$\rho_{\alpha} (\mathbf{v}_{\alpha} - \mathbf{v}) = \rho_{\alpha} \mathbf{v}_{\alpha} - \omega_{\alpha} \sum_{\beta=1}^N \rho_{\beta} \mathbf{v}_{\beta}$$

This can be rewritten as

$$\rho_{\alpha} \mathbf{v}_{\alpha} - \rho_{\alpha} \mathbf{v} = \rho_{\alpha} \mathbf{v}_{\alpha} - \rho \omega_{\alpha} \sum_{\beta=1}^N (\rho_{\beta} / \rho) \mathbf{v}_{\beta}$$

or, making use of Eq. (C) of Table 17.7-1,

$$-\rho_{\alpha} \mathbf{v} = -\rho_{\alpha} \sum_{\beta=1}^N \omega_{\beta} \mathbf{v}_{\beta}$$

Then, use of Eq. (B) of Table 17.7-2 completes the verification.

### 17B.3 Relations between the fluxes in binary systems

The expressions for the fluxes are

$$\begin{aligned} \mathbf{j}_A &= \rho_A (\mathbf{v}_A - \mathbf{v}) \\ \mathbf{J}_A^* &= c_A (\mathbf{v}_A - \mathbf{v}^*) \quad \text{or} \quad M_A \mathbf{J}_A^* = \rho_A (\mathbf{v}_A - \mathbf{v}^*) \end{aligned}$$

Next form the difference between the above expressions, and then repeat for species B

$$\mathbf{j}_A - M_A \mathbf{J}_A^* = \rho_A (\mathbf{v} - \mathbf{v}^*) \quad \text{and} \quad \mathbf{j}_B - M_B \mathbf{J}_B^* = \rho_B (\mathbf{v} - \mathbf{v}^*)$$

Then eliminate  $\mathbf{v} - \mathbf{v}^*$  between these two equations to get

$$\frac{\mathbf{j}_A}{\rho_A} - \frac{M_A \mathbf{J}_A^*}{\rho_A} = \frac{\mathbf{j}_B}{\rho_B} - \frac{M_B \mathbf{J}_B^*}{\rho_B}$$

Then use Eqs. (K) and (O) of Table 17.8-1 to eliminate the fluxes with subscripts B and then rearrange to get

$$\mathbf{j}_A \left( \frac{1}{\rho_A} + \frac{1}{\rho_B} \right) = \mathbf{J}_A^* \left( \frac{M_A}{\rho_A} + \frac{M_B}{\rho_B} \right) \quad \text{or} \quad \mathbf{j}_A \left( \frac{1}{\rho_A} + \frac{1}{\rho_B} \right) = \mathbf{J}_A^* \left( \frac{1}{c_A} + \frac{1}{c_B} \right)$$

whence

$$\mathbf{j}_A \left( \frac{\rho_A + \rho_B}{\rho_A \rho_B} \right) = \mathbf{J}_A^* \left( \frac{c_A + c_B}{c_A c_B} \right)$$

where Eq. (H) of Table 17.7-1 has been used. Next use Eqs. (B), (C), (E), and (F) to get Eq. 17B.3-1.

#### 17B.4 Equivalence of various forms of Fick's law for binary mixtures

(Note: Problem 17B.3 should be worked prior to Problem 17B.4)

a. To get Eq. (B) of Table 17.8-2, we start by rewriting Eq. (A) by using Eq. 17B.3-1 and Eqs. (Q') and (L) of Table 17.7-1:

$$\mathbf{J}_A^* \frac{\rho \omega_A \omega_B}{c x_A x_B} = -\rho \mathcal{D}_{AB} \frac{M_A M_B}{M^2} \nabla x_A$$

Next, use of Eq. (G) of Table 17.7-1 allows us to rewrite this as

$$\mathbf{J}_A^* = -\frac{c x_A x_B}{\rho \omega_A \omega_B} \rho \mathcal{D}_{AB} \frac{M_A M_B}{(\rho/c)^2} \nabla x_A$$

Then we note that Eqs. (C), (F), and (H) of Table 17.7-1 give

$$\frac{x_A}{\omega_A} = \frac{c_A}{c} \frac{\rho}{\rho_A} = \frac{\rho}{c} \frac{1}{M_A}$$

so that

$$\mathbf{J}_A^* = -\frac{c}{\rho} \left( \frac{\rho}{c} \frac{1}{M_A} \cdot \frac{\rho}{c} \frac{1}{M_B} \right) \rho \mathcal{D}_{AB} \frac{M_A M_B}{(\rho/c)^2} \nabla x_A = -c \mathcal{D}_{AB} \nabla x_A$$

Equation (D) of Table 17.8-2 follows at once from Eq. (B) of Table 17.8-2 and Eq. (V) of Table 17.8-1:

$$\mathbf{N}_A = c_A \mathbf{v}^* + \mathbf{J}_A^* = c_A \mathbf{v}^* - c \mathcal{D}_{AB} \nabla x_A$$

Equation (F) of Table 17.8-2 is obtained by writing Eq. (C) of the same table for both species A and B after using Eq. (I) of Table 17.8-1:

$$c_A (\mathbf{v}_A - \mathbf{v}^*) = -c \mathcal{D}_{AB} \nabla x_A \quad \text{and} \quad c_B (\mathbf{v}_B - \mathbf{v}^*) = -c \mathcal{D}_{AB} \nabla x_B = +c \mathcal{D}_{AB} \nabla x_A$$

These equations may be rewritten as

$$(\mathbf{v}_A - \mathbf{v}^*) = -\frac{1}{x_A} \mathcal{D}_{AB} \nabla x_A \quad \text{and} \quad (\mathbf{v}_B - \mathbf{v}^*) = +\frac{1}{x_B} \mathcal{D}_{AB} \nabla x_A$$

Subtraction of these equations eliminates the molar average velocity, and we get

$$\mathbf{v}_A - \mathbf{v}_B = -\left(\frac{1}{x_A} + \frac{1}{x_B}\right) \mathcal{D}_{AB} \nabla x_A = -\frac{\mathcal{D}_{AB}}{x_A x_B} \nabla x_A$$

b. To get the first equation, we use is Eq. (Q') of Table 17.7-1

$$\mathbf{j}_\alpha = -\rho \mathcal{D}_{AB} \nabla \rho_A = -\rho \mathcal{D}_{AB} \frac{M_A M_B}{M^2} \nabla x_A$$

From this equation, we conclude that the expressions written in a mixture of molar and mass quantities are more complex than those written entirely in molar quantities alone or mass quantities alone.

To get the second equation, we start with Eq. (B) of Table 17.9-2 (which we have seen in (a) and obtained from Eq. (A))

written for species A and B

$$\mathbf{J}_A^* = -c \mathcal{D}_{AB} \nabla x_A$$

$$\mathbf{J}_B^* = -c \mathcal{D}_{AB} \nabla x_B = +c \mathcal{D}_{AB} \nabla x_A$$

Then we rewrite these equations in terms of the combined molar



Subtracting the second equation from the first then gives Eq. 17B,4-2 after use has been made of Eq. (J) of Table 17.7-1

$$x_A \mathbf{N}_B - x_B \mathbf{N}_A = c \mathcal{D}_{AB} \nabla x_A$$

This equation contains no reference to the mass average velocity or the molar average velocity. That is true also of Eq. (E) of Table 17.8-2, which can be derived in analogous fashion from Eq. (A) of the same table.

c. We start by rewriting Eq. (F) in the following form

$$\mathbf{v}_A - \mathbf{v}_B = -\mathcal{D}_{AB} \frac{1}{x_A x_B} \nabla x_A = -\mathcal{D}_{AB} \left( \frac{x_B + x_A}{x_A x_B} \right) \nabla x_A$$

This may also be written as

$$\mathbf{v}_A - \mathbf{v}_B = -\mathcal{D}_{AB} \left( \frac{1}{x_A} + \frac{1}{x_B} \right) \nabla x_A = -\mathcal{D}_{AB} \left( \frac{\nabla x_A}{x_A} - \frac{\nabla x_B}{x_B} \right)$$

Then, finally

$$\mathbf{v}_A - \mathbf{v}_B = -\mathcal{D}_{AB} (\nabla \ln x_A - \nabla \ln x_B) = -\mathcal{D}_{AB} \nabla \ln \frac{x_A}{x_B}$$

### 17C.1 Mass flux with respect to the volume average velocity

a. Using the definitions of  $\mathbf{j}_A^\blacksquare$  and  $\mathbf{j}_A$  we get

$$\mathbf{v}^\blacksquare = c_A \bar{V}_A \mathbf{v}_A + c_B \bar{V}_B \mathbf{v}_B = c_A \bar{V}_A \left( \frac{\mathbf{j}_A}{\rho} + \mathbf{v} \right) + c_B \bar{V}_B \left( \frac{\mathbf{j}_B}{\rho} + \mathbf{v} \right)$$

Using the relation just after Eq. 17C.1-3 the above result gives the relation between the volume average velocity and the mass average velocity

$$\mathbf{v}^\blacksquare - \mathbf{v} = \left( \frac{\bar{V}_A}{M_A} - \frac{\bar{V}_B}{M_B} \right) \mathbf{j}_A$$

If we now subtract Eq. (E) of Table 17.8-1 from Eq. 17C.1-2 we get

$$\mathbf{j}_A^\blacksquare - \mathbf{j}_A = -\rho_A (\mathbf{v}^\blacksquare - \mathbf{v}) = -\rho_A \left( \frac{\bar{V}_A}{M_A} - \frac{\bar{V}_B}{M_B} \right) \mathbf{j}_A$$

Then, using the relation just after Eq. 17C.1-3 we get

$$\mathbf{j}_A^\blacksquare = \mathbf{j}_A \left( 1 - \rho_A \frac{\bar{V}_A}{M_A} + \rho_A \frac{\bar{V}_B}{M_B} \right) = \mathbf{j}_A \left( \rho_A \frac{\bar{V}_A}{M_A} + \rho_B \frac{\bar{V}_B}{M_B} - \rho_A \frac{\bar{V}_A}{M_A} + \rho_A \frac{\bar{V}_B}{M_B} \right)$$

and this leads to Eq. 17C.1-3

$$\mathbf{j}_A^\blacksquare = \mathbf{j}_A \left( \rho_B \frac{\bar{V}_B}{M_B} + \rho_A \frac{\bar{V}_B}{M_B} \right) = \mathbf{j}_A \rho \frac{\bar{V}_B}{M_B}$$

b. Starting from Eq. 17C.1-3 we have

$$\begin{aligned} \mathbf{j}_A^\blacksquare &= \mathbf{j}_A \rho \frac{\bar{V}_B}{M_B} = (-\rho \mathfrak{D}_{AB} \nabla \omega_A) \rho \left( \frac{c_B \bar{V}_B}{c_B M_B} \right) \\ &= -\rho \mathfrak{D}_{AB} \left( \frac{1}{\rho} \nabla \rho_A + \rho_A \nabla \frac{1}{\rho} \right) \rho \left( \frac{1 - c_A \bar{V}_A}{c_B M_B} \right) \end{aligned}$$

$$\begin{aligned}
&= -\rho \mathfrak{D}_{AB} \left( \frac{1}{\rho} \nabla \rho_A - \frac{\rho_A}{\rho^2} \nabla \rho \right) \left( \frac{\rho_A}{M_B} + \frac{\rho_B}{M_B} \right) \left( \frac{1 - c_A \bar{V}_A}{c_B} \right) \\
&= -\mathfrak{D}_{AB} \nabla \rho_A - (\mathfrak{D}_{AB} \nabla \rho_A) \left( \frac{\rho_A}{M_B} \frac{c_B \bar{V}_B}{c_B} - \frac{\rho_B}{M_B} \frac{c_A \bar{V}_A}{c_B} \right) \\
&\quad + \left( \frac{\rho_A}{\rho} \mathfrak{D}_{AB} \nabla \rho \right) \left( \frac{\rho}{M_B} \right) \left( \frac{c_B \bar{V}_B}{c_B} \right) \\
&= -\mathfrak{D}_{AB} \nabla \rho_A - (\mathfrak{D}_{AB} \nabla \rho_A) \left( \frac{\rho_A}{\rho_B} c_B \bar{V}_B - c_A \bar{V}_A \right) \\
&\quad + \left( \frac{\rho_A}{\rho_B} \mathfrak{D}_{AB} \nabla (\rho_A + \rho_B) \right) c_B \bar{V}_B \\
&= -\mathfrak{D}_{AB} \nabla \rho_A + c_A \bar{V}_A \mathfrak{D}_{AB} \nabla \rho_A + c_B \bar{V}_B \frac{\rho_A}{\rho_B} \mathfrak{D}_{AB} \nabla \rho_B \\
&= -\mathfrak{D}_{AB} \nabla \rho_A + \rho_A \mathfrak{D}_{AB} (\bar{V}_A \nabla c_A + \bar{V}_B \nabla c_B)
\end{aligned}$$

Since the second term on the right side is zero, we get Eq. 17C.1-4.

To get the equation just after Eq. 17C.1-4, we proceed thus. The definitions of the partial molar volumes enable us to write

$$dV = \bar{V}_A dn_A + \bar{V}_B dn_B$$

Since the volume is a homogeneous function of order 1, we get from Euler's theorem:

$$V = n_A \bar{V}_A + n_B \bar{V}_B, \text{ or by dividing by } V: \quad 1 = c_A \bar{V}_A + c_B \bar{V}_B \quad (\#)$$

Forming the differential of  $V$  from this equation gives

$$dV = n_A d\bar{V}_A + \bar{V}_A dn_A + n_B d\bar{V}_B + \bar{V}_B dn_B$$

Comparing this with the first equation gives

$$n_A d\bar{V}_A + n_B d\bar{V}_B = 0, \text{ or by dividing by } V: \quad c_A d\bar{V}_A + c_B d\bar{V}_B = 0 \quad (*)$$

Differentiating (#) and subtracting (\*) gives the desired result.

## 17C.2 Mass flux with respect to the solvent velocity

a. First we rewrite Eq. 17C.2-1 as

$$\mathbf{j}_\alpha^N = \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}) - \rho_\alpha(\mathbf{v}_N - \mathbf{v})$$

Then we modify the terms on the right side as follows

$$\mathbf{j}_\alpha^N = \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}) - \left(\frac{\rho_\alpha}{\rho_N}\right)\rho_N(\mathbf{v}_N - \mathbf{v}) = \mathbf{j}_\alpha - \left(\frac{\rho_\alpha}{\rho_N}\right)\mathbf{j}_N$$

Here we have used the definition in Eq. H of Table 17.8-1.

b. Application of Eq. 17C.2-2 to a binary system with  $N = B$  gives

$$\mathbf{j}_A^N = \mathbf{j}_A - \left(\frac{\rho_A}{\rho_B}\right)\mathbf{j}_B$$

Then we make use of Eq. (K) of Table 17.8-1 and Eq. (A) of Table 17.8-2 to get

$$\begin{aligned}\mathbf{j}_A^B &= \mathbf{j}_A - \left(\frac{\rho_A}{\rho_B}\right)(-\mathbf{j}_A) = \mathbf{j}_A \left(1 + \frac{\rho_A}{\rho_B}\right) \\ &= \mathbf{j}_A \left(\frac{\rho_A + \rho_B}{\rho_B}\right) = \mathbf{j}_A \left(\frac{\rho}{\rho_B}\right) = -\left(\frac{\rho}{\rho_B}\right)\rho\mathcal{D}_{AB}\nabla\omega_A\end{aligned}$$

c. For a very dilute solution of A in B, we know that  $\rho_B \approx \rho$ , so that

$$\mathbf{j}_A^B = -\rho\mathcal{D}_{AB}\nabla\omega_A$$

### 17C.3 Determination of Lennard-Jones parameters from diffusivity data for a binary mixture.

(a) Computational software is preferable to graphical methods for treatment of this statistical problem. The results shown below were obtained by Dr. Mike Caracotsios, using Athena Visual Workbench, a Windows package for formulation and solution of chemical process models. The problem formulation and results are displayed fully at [www.AthenaVisual.com /transportphenomena](http://www.AthenaVisual.com/transportphenomena), a website provided by Stewart & Associates Engineering Software, Inc.

In the following table, PAR(1) (the first adjustable parameter), denotes  $\sigma_{AB}$ , and PAR(2) (the second adjustable parameter), denotes  $\epsilon_{AB}/K$ . The values in the "Last PAR(I)" column, with status "Estimated", are the recommended parameter values in the sense of maximum posterior probability density based on the data provided. The individual uncertainty of each parameter is reported as "95% Marginal HPD Interval" (the interval of highest posterior density containing 95% of the posterior probability distribution for that parameter; we prefer this Bayesian interpretation to the notion of a "confidence interval", which invokes a hypothetical population of alternative sets of data). The two columns labeled DYDPAR(1:NPAR) are the parametric sensitivities of the predicted diffusivities to the individual parameters. Further documentation of this problem and the modeling capabilities of Athena Visual Workbench are provided at the website named above.

#### NONLINEAR SINGLE-RESPONSE ESTIMATION STATISTICS SUMMARY

SUM OF SQUARES OF RESIDUALS..... 3.15638D-05  
 RESIDUAL DEGREES OF FREEDOM..... 6  
 MODEL PARAMETERS ESTIMATED..... 2

RMS VALUE OF WEIGHTED RESIDUALS..... 2.29361D-03  
 T(0.025)-STUDENT DISTRIBUTION VALUE..... 2.447

ADJ. PARS	Last PAR(I)	Status	95% Marginal HPD Interval
PAR( 1)	3.313569E+00	Estimated	3.313569E+00 +- 4.080E-02
PAR( 2)	8.024473E+01	Estimated	8.024473E+01 +- 1.205E+01

EVENT	OBSERVED	PREDICTED	RESIDUAL	ERROR(%)	DYDPAR(1:NPAR)-->
1	4.7000E-01	4.7273E-01	-2.7282E-03	-0.58	-2.8533E-01 -1.2242E-03
2	6.9000E-01	6.9072E-01	-7.2080E-04	-0.10	-4.1690E-01 -1.6487E-03
3	9.4000E-01	9.3925E-01	7.5217E-04	0.08	-5.6691E-01 -2.1090E-03
4	1.2200E+00	1.2161E+00	3.8625E-03	0.32	-7.3404E-01 -2.6078E-03
5	1.5200E+00	1.5198E+00	2.2434E-04	0.01	-9.1731E-01 -3.1524E-03
6	1.8500E+00	1.8489E+00	1.0664E-03	0.06	-1.1160E+00 -3.7483E-03
7	2.2000E+00	2.2026E+00	-2.6318E-03	-0.12	-1.3295E+00 -4.3978E-03
8	2.5800E+00	2.5801E+00	-5.1116E-05	0.00	-1.5573E+00 -5.1009E-03

NUMBER OF MODEL CALLS..... 13  
 NUMBER OF ITERATIONS..... 4

### 18A.1 Evaporation rate.

Let  $A$  denote chloropicrin and  $B$  denote air; then Eq. 18.2-14 gives, for constant total pressure  $p$  and ideal gas behavior,

$$\begin{aligned} N_{Az}|_{z=z_1} &= \frac{cD_{AB}}{(z_2 - z_1)} \ln \left( \frac{x_{B2}}{x_{B1}} \right) \\ &= \frac{p}{RT} \frac{D_{AB}}{(z_2 - z_1)} \ln \left( \frac{p_{B2}}{p_{B1}} \right) \end{aligned}$$

Inserting the values  $T = 15^\circ\text{C} = 298.15\text{K}$ ,  $p_{B2} = p = 770 \text{ mm Hg}$  and  $p_{B1} = 770 - 23.81 = 746.19 \text{ mm Hg}$ , we get

$$\begin{aligned} N_{Az}|_{z=z_1} &= \frac{(770/760) \text{ atm}}{(82.06 \times 298.15) \text{ cm}^3 \text{ atm/g-mol}} \frac{(0.088 \text{ cm}^2/\text{s})}{(11.14 \text{ cm})} \ln \left( \frac{770}{746.19} \right) \\ &= 1.03 \times 10^{-8} \text{ g-mol/cm}^2 \cdot \text{s} \end{aligned}$$

Finally, the evaporation rate in g/hr is

$$\begin{aligned} W_A &= N_{Az} M_A S \\ &= (1.03 \times 10^{-8} \text{ g-mol/cm}^2 \cdot \text{s})(164.4 \text{ g/g-mol})(2.29 \text{ cm}^2)(3600 \text{ s/hr}) \\ &= 0.0139 \text{ g/hr} \end{aligned}$$

## 18A.2 Sublimation of small iodine spheres in still air.

(a) From Table E.1 and Eqs. 17.3-14,15, we get the following values for the system I<sub>2</sub>-air:

Species	<i>M</i>	$\sigma$ , Å	$\epsilon/K$ , K
A: I <sub>2</sub>	253.81	4.982	550.
B: air	28.97	3.617	97.0
AB		4.2995	231.0

Thus, at  $T = 40^\circ\text{C} = 313.15\text{K}$ , we get the argument value

$$kT/\epsilon_{AB} = 313.15/231.0 = 1.356,$$

at which Table E.2 gives  $\Omega_{D,AB} = 1.251$ . Equation 17.3-12 then gives

$$\begin{aligned} \mathcal{D}_{AB} &= 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p\sigma^2\Omega_{D,AB}}} \\ &= 0.0018583 \sqrt{(313.15)^3 \left( \frac{1}{253.81} + \frac{1}{28.97} \right) \frac{1}{(747/760)(4.2995)^2(1.251)}} \\ &= 0.0888 \text{ cm}^2/\text{s} \end{aligned}$$

(b) Equation 18.2-27, with  $r_2 \rightarrow \infty$ , gives

$$\begin{aligned} W_A &= 4\pi r_1 c \mathcal{D}_{AB} \ln \left( \frac{1 - x_{A2}}{1 - x_{A1}} \right) \\ &= 4\pi r_1 \frac{p \mathcal{D}_{AB}}{RT} \ln \left( \frac{p}{p - p_{A,\text{vap}}} \right) \\ &= 4\pi (0.5 \text{ cm}) \frac{(747/760 \text{ atm})(0.0888 \text{ cm}^2/\text{s})}{(82.06 \times 313.15 \text{ cm}^3 \text{ atm/g-mol})} \ln \left( \frac{747}{747 - 1.03} \right) \\ &= 2.95 \times 10^{-8} \text{ g-mol/s} \times 3600 \text{ s/hr} \\ &= 1.06 \times 10^{-4} \text{ g-mol/hr} \end{aligned}$$

### 18A.3 Estimating the error in calculating the absorption rate.

Equation 18.5-18 gives

$$W_A = K c_{A0} \sqrt{D_{AB}}$$

in which  $K$  is a product of known quantities. Then the error in  $W_A$  resulting from small errors  $\Delta c_{A0}$  and  $\Delta D_{AB}$  is

$$\begin{aligned} \Delta W_A &= \left( \frac{\partial W_A}{\partial c_{A0}} \right) \Delta c_{A0} + \left( \frac{\partial W_A}{\partial D_{AB}} \right) \Delta D_{AB} \\ &= K \sqrt{D_{AB}} \Delta c_{A0} + \frac{K c_{A0}}{2 \sqrt{D_{AB}}} \Delta D_{AB} \end{aligned}$$

Division by  $W_A$  then gives the fractional error expression

$$\frac{\Delta W_A}{W_A} \approx \frac{\Delta c_{A0}}{c_{A0}} + \frac{1}{2} \frac{\Delta D_{AB}}{D_{AB}}$$

Hence, the maximum absolute percentage error in the calculation of  $W_A$  under the given conditions is

$$\left| 100 \frac{\Delta W_A}{W_A} \right|_{\max} = 5\% + \frac{1}{2}(10\%) = 10\%$$



#### 18A.4 Chlorine absorption in a falling film.

The absorption rate is predicted by Eq. 18.5-18, which may be rewritten in terms of the average film velocity by use of Eq. 2.2-20:

$$W_A = 2\pi RLc_{A0} \sqrt{\frac{6D_{AB}\langle v_z \rangle}{\pi L}}$$

The solubility is

$$\begin{aligned} c_{A0} &= \rho\omega_{A0}/M_A \\ &\approx (0.998 \text{ g soln/cm}^3)(0.00823 \text{ g Cl}_2/\text{g soln})/(70.91 \text{ g Cl}_2/\text{g-mol Cl}_2) \\ &= 1.16 \times 10^{-4} \text{ g-mol Cl}_2/\text{cm}^3 \end{aligned}$$

Then the predicted absorption rate is

$$\begin{aligned} W_A &= 2\pi(1.4 \times 13 \text{ cm}^2)(1.16 \times 10^{-4} \text{ g-mol Cl}_2/\text{cm}^3) \\ &\quad \times \sqrt{\frac{6(1.26 \times 10^{-5} \text{ cm}^2/\text{s})(17.7 \text{ cm/s})}{(\pi)(13 \text{ cm})}} \\ &= 7.58 \times 10^{-5} \text{ g-mol/s} = 0.273 \text{ g-mol/hr} \end{aligned}$$

### 18A.5 Measurement of diffusivity by the point-source method.

(a) Directly downstream of the source, the distance  $s$  from the source reduces to  $z$ ; hence, Eq. 18C.1-3 takes the form

$$c_A = \frac{W_A}{4\pi\mathcal{D}_{AB}z}$$

Therefore, the injection rate  $W_A$  required to produce a mole fraction  $x_A \approx 0.01$  at  $p = 1$  atm and  $T = 800^\circ\text{C} = 1073\text{K}$  at a point 1 cm downstream of the source is

$$\begin{aligned} W_A &= 4\pi\mathcal{D}_{AB}(0.01c)z \\ &= 4\pi\mathcal{D}_{AB}(0.01p/RT)z \\ &= 4\pi(5 \text{ cm}^2/\text{s})(0.01)[(1 \text{ atm})/(82.06 \times 1073 \text{ cm}^3\text{atm/g-mol})](1 \text{ cm}) \\ &= 7.1 \times 10^{-6} \text{ g-mol/s} \end{aligned}$$

(b) Expansion of  $s$  in powers of  $r^2$  at constant  $z$  gives, to second order in  $r$ ,

$$s = \sqrt{z^2 + r^2} = z\sqrt{1 + \frac{r^2}{z^2}} = z \left[ 1 + \frac{1}{2} \frac{r^2}{z^2} - \dots \right]$$

and

$$s - z = z \left[ \frac{1}{2} \frac{r^2}{z^2} - \dots \right]$$

and

$$\frac{z}{s} = \left[ 1 - \frac{1}{2} \frac{r^2}{z^2} + \dots \right]$$

Equation 18C.1-3 then yields the following expansion for constant  $z$ , complete through order  $r^2$ :

$$\begin{aligned} c_A(r, z) &= \frac{W_A}{4\pi\mathcal{D}_{AB}z} \frac{z}{s} \exp[-(v_0/2\mathcal{D}_{AB})(s - z)] \\ &= c_A(0, z) \left[ 1 - \frac{1}{2} \frac{r^2}{z^2} + \dots \right] \left[ 1 - (v_0/2\mathcal{D}_{AB})z \left[ \frac{1}{2} \frac{r^2}{z^2} - \dots \right] + \dots \right] \\ &= c_A(0, z) \left[ 1 - \frac{1}{2} \frac{r^2}{z^2} (1 + (v_0z/2\mathcal{D}_{AB})) + O\left(\frac{r^4}{z^4}\right) \right] \end{aligned}$$

Thus,  $c_A(r, z)$  and  $x_A(r, z)$  will be within 1% of their centerline values as long as the second-order term within the square brackets does not exceed 0.01. The deviation  $r_s$  of the sample collector from the axis, at the given conditions, therefore must satisfy

$$\begin{aligned} r_s^2 &\leq (0.01) \frac{2z^2}{1 + v_0z/2\mathcal{D}_{AB}} \\ &= \frac{(0.02)(1 \text{ cm}^2)}{1 + (50 \text{ cm/s})(1 \text{ cm})/(2 \times 5 \text{ cm}^2/\text{s})} \\ &= 0.00333 \text{ cm}^2 \end{aligned}$$

Hence,

$$r_s \leq \sqrt{0.00333 \text{ cm}^2} = 0.058 \text{ cm}$$

### 18A.6 Determination of diffusivity for ether-air system.

(a) Equation 18.2-17 gives

$$\begin{aligned} D_{AB} &= -\frac{\rho^{(A)} \Delta z_1}{M_A \Delta t} \cdot \frac{(z_2 - z_1)(x_B)_{\ln}}{c(x_{A1} - x_{A2})} \\ &= -\frac{\rho^{(A)} \Delta z_1}{M_A \Delta t} \cdot \frac{RT}{p} \frac{(z_2 - z_1)}{\ln(x_{B2}/x_{B1})} \\ &= -\frac{\rho^{(A)} \Delta z_1}{M_A \Delta t} \cdot \frac{RT}{p} \frac{(z_2 - z_1)}{\ln(p/(p - p_{A,\text{vap}}))} \end{aligned}$$

for each finite increment  $\Delta t$  of time and  $-\Delta z_1$  of decrease in liquid height. Insertion of the given constants gives

$$\begin{aligned} D_{AB}, \text{ cm}^2/\text{s} &= + \frac{(0.712 \text{ g/cm}^3) (0.2 \text{ cm}) 82.06 \times 295.15 \text{ cm}^3 \text{ atm/g-mol}}{(74.12 \text{ g/g-mol}) (\Delta t, \text{s}) (747/760 \text{ atm})} \\ &\quad \cdot \frac{(z_2 - z_1, \text{ cm})}{\ln(747/(747 - 480))} \\ &= \frac{(24642 \text{ cm}^3/\text{g-mol gas}) (0.2 \text{ cm}) (z_2 - z_1, \text{ cm})}{(104.1 \text{ cm}^3/\text{g-mol liquid A}) (\Delta t, \text{s}) \ln(747/267)} \\ &= 46.015 \frac{(z_2 - z_1, \text{ cm})}{(\Delta t, \text{s for 0.2 cm level decrease})} \end{aligned}$$

and the following calculated values for the six time intervals:

$(z_2 - z_1), \text{ av.}, \text{ cm}$	1.0	1.5	2.0	2.5	3.5	4.5
$\Delta t \text{ for } \Delta z_1 = -0.2 \text{ cm}$	590	895	1185	1480	2055	2655
$D_{AB}, \text{ cm}^2/\text{s}$	0.0780	0.0771	0.0779	0.0777	0.0784	0.0780

The average of these values is  $0.07785 \text{ cm}^2/\text{s}$ .

(b) Conversion of the above result to 760 mm Hg and  $0^\circ\text{C}$ , using Eq. 17.2-1 in its nonpolar form, gives

$$D_{AB} = 0.07785 \times (747/760) \times (273.15/295.15)^{1.823} = 0.0664 \text{ cm}^2/\text{s}$$

This result appears preferable to the one reported by Jost.

### 18A.7 Mass flux from a circulating bubble.

(a) With the data provided, Eq. 18.5-20 gives the surface-average mass flux

$$\begin{aligned}(N_A)_{\text{avg}} &= \sqrt{\frac{4D_{AB}v_t}{\pi D}} c_{A0} \\ &= \sqrt{\frac{(4)(1.46 \times 10^{-5} \text{ cm}^2/\text{s})(22 \text{ cm/s})}{(\pi)(0.5 \text{ cm})}} (0.041 \times 10^{-3} \text{ g-mol/cm}^3) \\ &= 1.17 \times 10^{-6} \text{ g-mol/cm}^2 \cdot \text{s}\end{aligned}$$

(b) Equation 18.1-2, with the surface-averaged  $k_c$  obtained by Hamerton and Garner, gives

$$\begin{aligned}(N_A)_{\text{avg}} &= k_c(c_{A0} - c_{A\infty}) \\ &= (117 \text{ cm/hr})(1 \text{ hr}/3600 \text{ s})(0.041 \times 10^{-3} \text{ g-mol/cm}^3) \\ &= 1.14 \times 10^{-6} \text{ g-mol/cm}^2 \cdot \text{s}\end{aligned}$$

### 18B.1 Diffusion through a stagnant film--alternate derivation

From Equation 18.2-1 we get

$$\frac{1}{1-x_A} \frac{dx_A}{dz} = -\frac{N_{Az}}{c\mathcal{D}_{AB}}$$

or

$$-\frac{1}{x_B} \frac{dx_B}{dz} = -\frac{N_{Az}}{c\mathcal{D}_{AB}}$$

Integration gives

$$\int_{x_{B1}}^{x_{B2}} \frac{dx_B}{x_B} = \frac{N_{Az}}{c\mathcal{D}_{AB}} \int_{z_1}^{z_2} dz$$

Hence

$$\ln \frac{x_{B2}}{x_{B1}} = \frac{N_{Az}}{c\mathcal{D}_{AB}} (z_2 - z_1)$$

or

$$N_{Az} = \frac{c\mathcal{D}_{AB}}{z_2 - z_1} \ln \frac{x_{B2}}{x_{B1}}$$

Which is in agreement with Eq. 18.2-14

## 18B.2 Error in neglecting the convection term in evaporation

a. Without the convection term, Eq. 18.2-1 and 4 become

$$N_{Az} = -c_{AB} \frac{dx_A}{dz} \quad \text{and} \quad \frac{d^2 x_A}{dz^2} = 0$$

Integration of the latter equation twice then gives

$$x_A = C_1 z + C_2$$

Then application of the boundary conditions gives two equations:

$$x_{A1} = C_1 z_1 + C_2 \quad \text{and} \quad x_{A2} = C_1 z_2 + C_2$$

These equations may be solved simultaneously to give

$$C_1 = -\frac{x_{A1} - x_{A2}}{z_2 - z_1} \quad \text{and} \quad C_2 = x_{A1} + \frac{x_{A1} - x_{A2}}{z_2 - z_1} z_1$$

Therefore, in the approximation being considered here, the mole-fraction profile in the system is given by

$$\frac{x_{A1} - x_A}{x_{A1} - x_{A2}} = \frac{z - z_1}{z_2 - z_1}$$

b. To get the result in (a) from Eq. 18.2-14, we can expand the latter in a Taylor series, as was done in getting Eq. 18.2-16.

c. To get the solution of Example 18.2-2 by using the result in (a), we make the following calculation

$$N_A RT \quad N_A RT(z_2 - z_1) \quad (7.26 \times 10^{-9})(82.06)(273)(17.1)$$

### 18B.3 Effect of mass transfer rate on the concentration profiles

a. Rewrite Eq. 18.2-14 as

$$N_{Az} = \frac{c\mathcal{D}_{AB}}{z_2 - z_1} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \quad \text{or} \quad \frac{1 - x_{A2}}{1 - x_{A1}} = \exp \frac{N_{Az}(z_2 - z_1)}{c\mathcal{D}_{AB}}$$

When this is substituted into the right side of Eq. 18.2-11, we get

$$\frac{1 - x_A}{1 - x_{A1}} = \left( \exp \frac{N_{Az}(z_2 - z_1)}{c\mathcal{D}_{AB}} \right)^{(z - z_1)/(z_2 - z_1)} = \left( \exp \frac{N_{Az}(z - z_1)}{c\mathcal{D}_{AB}} \right)$$

b. Starting with Eq. 18.2-1 and integrating directly we get

$$\frac{1}{1 - x_A} \frac{d}{dz} = -\frac{N_{Az}}{c\mathcal{D}_{AB}} \quad \text{and} \quad \int_{x_{A1}}^{x_A} \frac{1}{1 - x_A} dx_A = -\frac{N_{Az}}{c\mathcal{D}_{AB}} \int_{z_1}^z dz$$

When the integrals are evaluated we get

$$-\ln \frac{1 - x_A}{1 - x_{A1}} = -\frac{N_{Az}}{c\mathcal{D}_{AB}} (z - z_1)$$

Changing signs and taking the antilogarithm of both sides then gives the result in (a).

c. Expanding the right side of Eq. 18B.3-1 in a Taylor series in the argument of the exponent, we get

$$\frac{1 - x_A}{1 - x_{A1}} = 1 + \frac{N_{Az}}{c\mathcal{D}_{AB}} (z - z_1) + \dots$$

If we retain just two terms in the Taylor series, and bring the "1" on the right side over to the left side, we get

$$x_A = x_{A1} - \frac{N_{Az}(1 - x_{A1})}{c\mathcal{D}_{AB}} (z - z_1)$$

which is of the form  $x_A = mz + b$ , that is, a straight line function.

### 18B.4 Absorption with chemical reaction

a. Equation 18.4-8 remains valid, but now the boundary conditions are: at  $\zeta = 1$ ,  $\Gamma = 1$ ; and at  $\zeta = 0$ ,  $d\Gamma/d\zeta = 0$ . Hence the boundary conditions lead to a pair of simultaneous equations:

$$1 = C_1 \cosh \phi + C_2 \sinh \phi \quad \text{and} \quad 0 = 0 + C_2 \phi$$

from which it follows that  $C_2 = 0$  and  $C_1 = 1/\cosh \phi$ . Then the analog of Eq. 18.4-9 is

$$\Gamma = \cosh \phi \zeta / \cosh \phi$$

The mass flux at the liquid gas interface at  $z = L$  is then:

$$N_{Az}|_{z=L} = +\mathcal{D}_{AB} \left. \frac{dc_A}{dz} \right|_{z=L} = \frac{c_{A0} \mathcal{D}_{AB}}{L} \left. \frac{d\Gamma}{d\zeta} \right|_{\zeta=1} = \frac{c_{A0} \mathcal{D}_{AB}}{L} \frac{\phi \sinh \phi \zeta}{\cosh \phi} \Big|_{\zeta=1}$$

which leads directly to the result in Eq. 18.4-12.

b. We start with Eq. 18.4-7, the solution of which can be written in the form of a superposition of exponentials

$$\Gamma = C_1 e^{\phi \zeta} + C_2 e^{-\phi \zeta}$$

which is to be solved with the boundary conditions given just above Eq. 18.4-8. This leads to the following equations for the constants of integration:

$$1 = C_1 + C_2 \quad \text{and} \quad 0 = C_1 \phi e^{\phi} - C_2 \phi e^{-\phi}$$

These two simultaneous equations can be solved to give

$$C_1 = \frac{1}{1 + e^{2\phi}} = \frac{e^{-\phi}}{e^{\phi} + e^{-\phi}} \quad \text{and} \quad C_2 = \frac{e^{2\phi}}{1 + e^{2\phi}} = \frac{e^{\phi}}{e^{\phi} + e^{-\phi}}$$

Therefore, the dimensionless concentration profile is



$$\Gamma = \frac{e^{-\phi} e^{\phi\zeta}}{e^{\phi} + e^{-\phi}} + \frac{e^{\phi} e^{-\phi\zeta}}{e^{\phi} + e^{-\phi}} = \frac{\frac{1}{2}[e^{\phi(1-\zeta)} + e^{-\phi(1-\zeta)}]}{\frac{1}{2}[e^{\phi} + e^{-\phi}]} = \frac{\cosh[\phi(1-\zeta)]}{\cosh \phi}$$

Thus we are led to the same result that we obtained in Eq. 18.4-9.

c. Equation 18.4-12 can be written thus

$$N_{Az}|_{z=0} = \left( \frac{c_{A0} \mathcal{D}_{AB}}{L} \right) \sqrt{\frac{k_1''' L^2}{\mathcal{D}_{AB}}} \tanh \sqrt{\frac{k_1''' L^2}{\mathcal{D}_{AB}}}$$

Therefore, for very large  $L$  we get (using an expansion appropriate for large values of the argument)

$$N_{Az}|_{z=0} = c_{A0} \sqrt{\mathcal{D}_{AB} k_1'''} \left( 1 - 2 \exp(-2k_1''' L^2 / \mathcal{D}_{AB}) + \dots \right) \xrightarrow{L \rightarrow \infty} c_{A0} \sqrt{\mathcal{D}_{AB} k_1'''}$$

For very small values of  $L$  we get (using an expansion appropriate for very small values of the argument)

$$\begin{aligned} N_{Az}|_{z=0} &= c_{A0} \sqrt{\mathcal{D}_{AB} k_1'''} \sqrt{\frac{k_1''' L^2}{\mathcal{D}_{AB}}} \left( 1 - \frac{1}{3} \frac{k_1''' L^2}{\mathcal{D}_{AB}} + \dots \right) \\ &= c_{A0} k_1''' L \left( 1 - \frac{1}{3} \frac{k_1''' L^2}{\mathcal{D}_{AB}} + \dots \right) \xrightarrow{L \rightarrow 0} 0 \end{aligned}$$

Similarly, Eq. 18.4-10 can be written as

$$\frac{c_A}{c_{A0}} = \cosh \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} z - \tanh \sqrt{\frac{k_1''' L^2}{\mathcal{D}_{AB}}} \sinh \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} z$$

As  $L$  becomes infinite, this becomes

$$\frac{c_A}{c_{A0}} = \cosh \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} z - \sinh \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} z = \exp \left( - \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} z \right)$$

As  $L$  becomes zero, the dimensionless concentration becomes unity.

### 18B.5 Absorption of chlorine by cyclohexene

a. For a second-order reaction, Eq. 18.4-4 has to be replaced by

$$-\mathcal{D}_{AB} \frac{d^2 c_A}{dz^2} + k_2'' c_A^2 = 0$$

with the same boundary conditions as before. Introduce the dimensionless variables  $\Gamma = c_A/c_{A0}$  and  $\zeta = \sqrt{k_2'' c_{A0} / 6\mathcal{D}_{AB}} z$ . Then the differential equation becomes

$$\frac{d^2 \Gamma}{d\zeta^2} - 6\Gamma^2 = 0$$

with boundary conditions  $\Gamma(0) = 1$  and  $\Gamma(\infty) = 0$ . We now let  $d\Gamma/d\zeta = p(\Gamma)$ , so that  $d^2\Gamma/d\zeta^2 = dp/d\zeta = (dp/d\Gamma)(d\Gamma/d\zeta) = p(dp/d\Gamma)$ . Then we obtain a differential equation that is first order and separable

$$p \frac{dp}{d\Gamma} = 6\Gamma^2$$

This may be integrated, and we use the boundary condition that at  $\zeta = \infty$ ,  $\Gamma = 0$  and also that  $d\Gamma/d\zeta = p(\Gamma) = 0$ :

$$\int_0^p p dp = \int_0^\Gamma 6\Gamma^2 d\Gamma$$

from which

$$\frac{1}{2} p^2 = 2\Gamma^3 \quad \text{or} \quad \frac{d\Gamma}{d\zeta} = \pm 2\Gamma^{3/2}$$

Here we must choose the minus sign, since the slope of the concentration vs. distance curve is negative. Then using the first boundary condition, we can integrate this equation to get:

$$\int_1^\Gamma \Gamma^{-3/2} d\Gamma = - \int_0^\zeta d\zeta \quad \text{or} \quad \Gamma^{-1} = (1 + \zeta)^2$$

Hence the final expression for the concentration profile is

$$\frac{c_{A0}}{c_A} = \left( 1 + \sqrt{\frac{k_2'' c_{A0}}{6 \mathcal{D}_{AB}}} z \right)^2$$

b. From the result of (a) we get the absorption rate at the liquid gas interface:

$$N_{Az}|_{z=0} = -\mathcal{D}_{AB} \left. \frac{dc_A}{dz} \right|_{z=0} = \sqrt{\frac{2}{3} k_2'' c_{A0}^3 \mathcal{D}_{AB}}$$

c. The equation to be solved is

$$-\mathcal{D}_{AB} \frac{d^2 c_A}{dz^2} + f(c_A) = 0 \quad \text{or} \quad p \frac{dp}{dc_A} = \frac{f(c_A)}{\mathcal{D}_{AB}}$$

where we have introduced the variable  $p$  as before. The resulting equation is integrated, as before, to give

$$\int_0^p \bar{p} d\bar{p} = \frac{1}{\mathcal{D}_{AB}} \int_0^{c_A} f(\bar{c}_A) d\bar{c}_A \quad \text{or} \quad p = \frac{dc_A}{dz} = -\sqrt{\frac{2}{\mathcal{D}_{AB}} \int_0^{c_A} f(\bar{c}_A) d\bar{c}_A}$$

A second integration yields

$$\int_{c_{A0}}^{c_A} \frac{d\bar{c}_A}{\sqrt{(2/\mathcal{D}_{AB}) \int_0^{\bar{c}_A} f(\bar{c}_A) d\bar{c}_A}} = -\int_0^1 dz = -z$$

Then we differentiate both sides with respect to  $z$  to get

$$\frac{1}{\sqrt{(2/\mathcal{D}_{AB}) \int_0^{c_A} f(\bar{c}_A) d\bar{c}_A}} \frac{dc_A}{dz} = -1 \quad \text{and} \quad \left. \frac{dc_A}{dz} \right|_{z=0} = -\sqrt{(2/\mathcal{D}_{AB}) \int_0^{c_{A0}} f(c_A) dc_A}$$

This together with  $N_{Az}|_{z=0} = -\mathcal{D}_{AB} (dc_A/dz)|_{z=0}$  gives Eq. 18B.5-2.

### 18B.6 Two-bulb experiment for measuring gas diffusivity--quasi-steady-state analysis

a. The molar shell balance on  $\Delta z$  gives for species A

$$SN_{Az}|_z - SN_{Az}|_{z+\Delta z} = 0$$

Division by  $\Delta z$  and taking the limit as  $\Delta z$  goes to zero gives  $dN_{Az}/dz = 0$  or  $N_{Az} = \text{constant}$ .

b. Equation 18.0-1, for this problem, may be simplified thus:

$$N_{Az} = -c\mathcal{D}_{AB}(dx_A/dz) + x_A(N_{Az} + N_{Bz}) = -c\mathcal{D}_{AB}(dx_A/dz)$$

since  $N_{Az} = -N_{Bz}$ ; this is true, because in a system at constant  $c$  for every molecule of A that moves to the right, a molecule of B must move to the left.

c. The equation in (b), with  $N_{Az} = \text{constant}$ , then becomes  $dx_A/dz = -(N_{Az}/c\mathcal{D}_{AB})$ , which when integrated becomes

$$x_A = -\frac{N_{Az}}{c\mathcal{D}_{AB}}z + C_1$$

d. At  $z = L$ ,  $x_A = x_A^+$ , so that

$$x_A^+ = -\frac{N_{Az}}{c\mathcal{D}_{AB}}L + C_1$$

Subtracting the last two equations gives then

$$x_A - x_A^+ = \frac{N_{Az}}{c\mathcal{D}_{AB}}(L - z)$$

e. At  $z = -L$ , we know that  $x_A = x_A^- = 1 - x_A^+$ , so that

$$(1 - x_A^+) - x_A^+ = \frac{N_{Az}}{c\mathcal{D}_{AB}}(L - (-L))$$

from which Eq. 18B.6-2 follows directly.

f. A mass balance over the right bulb states that the time rate of change of moles within  $V$  must exactly equal the rate at which moles enter  $V$  by diffusion at the end of the tube. That is

$$\frac{d}{dt}(Vcx_A^+) = SN_{Az} \quad \text{or} \quad Vc \frac{dx_A^+}{dt} = S\left(\frac{1}{2} - x_A^+\right) \frac{c\mathcal{D}_{AB}}{L}$$

in which  $S$  is the cross-section of the connecting tube.

g. The equation in (f) may be integrated

$$\int \frac{dx_A^+}{\frac{1}{2} - x_A^+} = \int \frac{S\mathcal{D}_{AB}}{LV} dt + C_2 \quad \text{or} \quad -\ln\left(\frac{1}{2} - x_A^+\right) = \frac{S\mathcal{D}_{AB}}{LV} t + C_2$$

The integration constant may be obtained by using the fact that at  $t = 0$ , we know that the mole fraction of  $A$  in the right bulb will be zero, or  $C_2 = -\ln\left(\frac{1}{2} - 0\right)$ . Therefore

$$\ln\left(\frac{1}{2} - x_A^+\right) - \ln\frac{1}{2} = -\frac{S\mathcal{D}_{AB}}{LV} t \quad \text{or} \quad \frac{\frac{1}{2} - x_A^+}{\frac{1}{2}} = \exp\left(-\frac{S\mathcal{D}_{AB}}{LV} t\right)$$

h. If we plot

$$-\frac{LV}{S} \ln\left(\frac{\frac{1}{2} - x_A^+}{\frac{1}{2}}\right) \text{ vs. } t$$

the slope will be the diffusivity,  $\mathcal{D}_{AB}$ .

### 18B.7 Diffusion from a suspended droplet

a. A mass balance on A over a spherical shell of thickness  $\Delta r$  is (in molar units)

$$4\pi r^2 \cdot N_{Ar}|_r - 4\pi(r + \Delta r)^2 \cdot N_{Ar}|_{r+\Delta r} = 0$$

or, equivalently

$$(4\pi r^2 N_{Ar})|_r - (4\pi r^2 N_{Ar})|_{r+\Delta r} = 0$$

Now divide by  $4\pi\Delta r$  and take the limit as  $\Delta r$  goes to zero to get

$$\frac{d}{dr}(r^2 N_{Ar}) = 0$$

This may be integrated to give  $r^2 N_{Ar} = C_1$ . We may use the boundary condition that  $N_{Ar} = N_{Ar1}$  at  $r = r_1$  (the gas liquid interface) to evaluate the constant and obtain  $r^2 N_{Ar} = r_1^2 N_{Ar1}$ .

b. Equation 18.0-1, written for the radial component in spherical coordinates, is

$$N_{Ar} = -c \mathcal{D}_{AB} \frac{dx_A}{dr} + x_A (N_{Ar} + N_{Br})$$

If gas B is not moving, then  $N_{Br}$  may be set equal to zero and the equation may be solved for the molar flux of A:

$$N_{Ar} = -\frac{c \mathcal{D}_{AB}}{1 - x_A} \frac{dx_A}{dr}$$

Multiplying by  $r^2$  and using the result obtained in (a), we get Eq. 19B.7-1:

$$r_1^2 N_{Ar1} = -\frac{c \mathcal{D}_{AB}}{1 - x_A} r^2 \frac{dx_A}{dr}$$

c. Equation 19B.7-1 can be rearranged to give

$$r_1^2 N_{Ar1} \frac{dr}{r^2} = -c \mathcal{D}_{AB} \frac{dx_A}{1-x_A}$$

Integration then gives

$$r_1^2 N_{Ar1} \left( -\frac{1}{r} \right) \Big|_{r_1}^{r_2} = -c \mathcal{D}_{AB} \left[ -\ln(1-x_A) \right] \Big|_{x_{A1}}^{x_{A2}}$$

or

$$r_1^2 N_{Ar1} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = +c \mathcal{D}_{AB} \left[ \ln(1-x_{A2}) - \ln(1-x_{A1}) \right]$$

This may be rearranged to give

$$r_1^2 N_{Ar1} \left( \frac{r_2 - r_1}{r_1 r_2} \right) = c \mathcal{D}_{AB} \ln \frac{x_{B2}}{x_{B1}}$$

or, when solved for the molar flux of A

$$N_{Ar1} = \frac{c \mathcal{D}_{AB}}{r_2 - r_1} \left( \frac{r_2}{r_1} \right) \ln \frac{x_{B2}}{x_{B1}}$$

When  $r_2 \rightarrow \infty$  (and presumably also  $x_{A2} \rightarrow 0$ ), this last result gives

$$N_{Ar1} = \frac{c \mathcal{D}_{AB}}{r_1} \ln \frac{1}{x_{B1}}$$

### 18B.8 Method for separating helium from natural gas

Let  $A$  be helium and  $B$  be pyrex. Then a shell mass balance gives the following equation

$$\frac{d}{dr}(rN_{Ar}) = 0$$

Insertion of Eq. 18.0-1. with  $N_{Br} = 0$  and  $x_A \ll 1$ , gives for constant diffusivity

$$\frac{d}{dr}\left(r \frac{dc_A}{dr}\right) = 0$$

Integrating twice we get

$$c_A = C_1 \ln r + C_2$$

The boundary conditions are: at  $r = R_1$ ,  $c_A = c_{A1}$  and at  $r = R_2$ ,  $c_A = c_{A2}$ . Evaluation of the constants of integration gives for the concentration profile:

$$\frac{c_A - c_{A2}}{c_{A1} - c_{A2}} = \frac{\ln(R_2/r)}{\ln(R_2/R_1)}$$

Then the molar rate of diffusion through the wall is

$$N_{Ar} = -\mathcal{D}_{AB} \frac{dc_A}{dr} = \frac{+\mathcal{D}_{AB}(c_{A1} - c_{A2})}{r \ln(R_2/R_1)}$$

and

$$W_A = 2\pi r L \cdot N_{Ar} = \frac{2\pi L \mathcal{D}_{AB}(c_{A1} - c_{A2})}{\ln(R_2/R_1)}$$

is the molar flow rate of the helium through the pyrex tube.



### 18B.9 Rate of leaching

a. The molar balance for substance A over a thin slab of thickness  $\Delta z$  is

$$N_{Az}|_z S - N_{Az}|_{z+\Delta z} S = 0$$

Division by  $S\Delta z$  and letting the slab thickness  $\Delta z$  go to zero yields

$$\frac{dN_{Az}}{dz} = 0$$

Then inserting an approximate version of Fick's law gives

$$N_{Az} = -\mathcal{D}_{AB} \frac{dc_A}{dz}$$

which is good for a dilute solution of A in B. Thus the diffusion equation becomes

$$\frac{d^2 c_A}{dz^2} = 0$$

b. The above differential equation may be integrated to give

$$c_A = C_1 z + C_2$$

The constants are determined from the boundary conditions that  $c_A = c_{A0}$  at  $z = 0$ , and  $c_A = c_{A\delta}$  at  $z = \delta$ . The final expression is then

$$\frac{c_A - c_{A0}}{c_{A\delta} - c_{A0}} = \frac{z}{\delta} \quad \text{or} \quad \frac{c_A - c_{A\delta}}{c_{A0} - c_{A\delta}} = 1 - \frac{z}{\delta}$$

c. The rate of leaching (per unit area) is then

$$N_{Az}|_{z=0} = -\mathcal{D}_{AB} \left. \frac{dc_A}{dz} \right|_{z=0} = -\mathcal{D}_{AB} (c_{A0} - c_{A\delta}) \left( -\frac{1}{\delta} \right) = \frac{\mathcal{D}_{AB} (c_{A0} - c_{A\delta})}{\delta}$$

### 18B.10 Constant-evaporating mixtures.

(a) For this one-dimensional, steady-state, nonreactive system, the species conservation equations take the form

$$dN_{\alpha z}/dz = 0,$$

and give

$$N_{\alpha z} = \text{const. for each species.}$$

The coefficients  $cD_{\alpha\beta}$  depend only on  $T$  in low-density systems, according to Eq. 17.3-16 and the corresponding formula of Mason and Monchick for polar gas mixtures; thus, each of these coefficients is predicted to be constant over this isothermal system.

Assuming insolubility of nitrogen (3) in the liquid mixture, we obtain  $N_{3z} = 0$ ; then Eq. 17.9-1 gives

$$\frac{dy_3}{dz} = \frac{N_{1z}}{cD_{13}} + \frac{N_{2z}}{cD_{23}}$$

as the Maxwell-Stefan equation for  $y_3$ . Integration and use of the boundary condition at  $z = L$  give

$$\ln y_3 = \left[ \frac{N_{1z}}{cD_{13}} + \frac{N_{2z}}{cD_{23}} \right] (z - L) = A(z - L)$$

whence

$$y_3 = \exp[A(z - L)] \quad (18B.10 - 1)$$

Equation 17.9-1 and the condition  $y_1 + y_2 + y_3 = 1$  then give

$$\begin{aligned} -\frac{dy_1}{dz} &= \frac{y_2 N_{1z} - y_1 N_{2z}}{cD_{12}} + \frac{y_3 N_{1z}}{cD_{13}} \\ &= \frac{(1 - y_1 - y_3)N_{1z} - y_1 N_{2z}}{cD_{12}} + \frac{y_3 N_{1z}}{cD_{13}} \\ &= \frac{N_{1z}}{cD_{12}} - y_1 \frac{N_{1z} + N_{2z}}{cD_{12}} + y_3 \left( \frac{-N_{1z}}{cD_{12}} + \frac{N_{1z}}{cD_{13}} \right) \end{aligned}$$

as the differential equation for the toluene mole fraction profile  $y_1(z)$ . Insertion of the notations  $B$ ,  $C$  and  $D$ , and the solution for  $y_3$ , gives

$$-\frac{dy_1}{dz} = C - y_1 B - D \exp[A(z - L)]$$

Rearrangement of this result gives

$$\frac{dy_1}{dz} - B y_1 = -C + D \exp[A(z - L)]$$

which has the form of Eq. C.1-2, with  $f(z) = -B$  and  $g(z) = -C + D \exp[A(z-L)]$ . Using the solution indicated there, we get

$$\begin{aligned} y_1 &= \exp(Bz) \left[ \int \exp(-Bz) \{-C + D \exp[A(z-L)]\} dz + K \right] \\ &= Ke^{Bz} - Ce^{Bz} \int e^{-Bz} dz + De^{Bz} \int e^{[-Bz+Az-AL]} dz \\ &= Ke^{Bz} - Ce^{Bz} \frac{e^{-Bz}}{-B} + De^{[Bz-AL]} \int e^{(A-B)z} dz \\ &= Ke^{Bz} + \frac{C}{B} + \frac{D}{A-B} e^{[A(z-L)]} \end{aligned}$$

The boundary condition  $y_1 = 0$  at  $z = L$  gives

$$0 = Ke^{BL} + \frac{C}{B} + \frac{D}{A-B}$$

The resulting integration constant is

$$K = \left[ \frac{-C}{B} - \frac{D}{A-B} \right] e^{-BL}$$

Thus, the toluene mole-fraction profile is

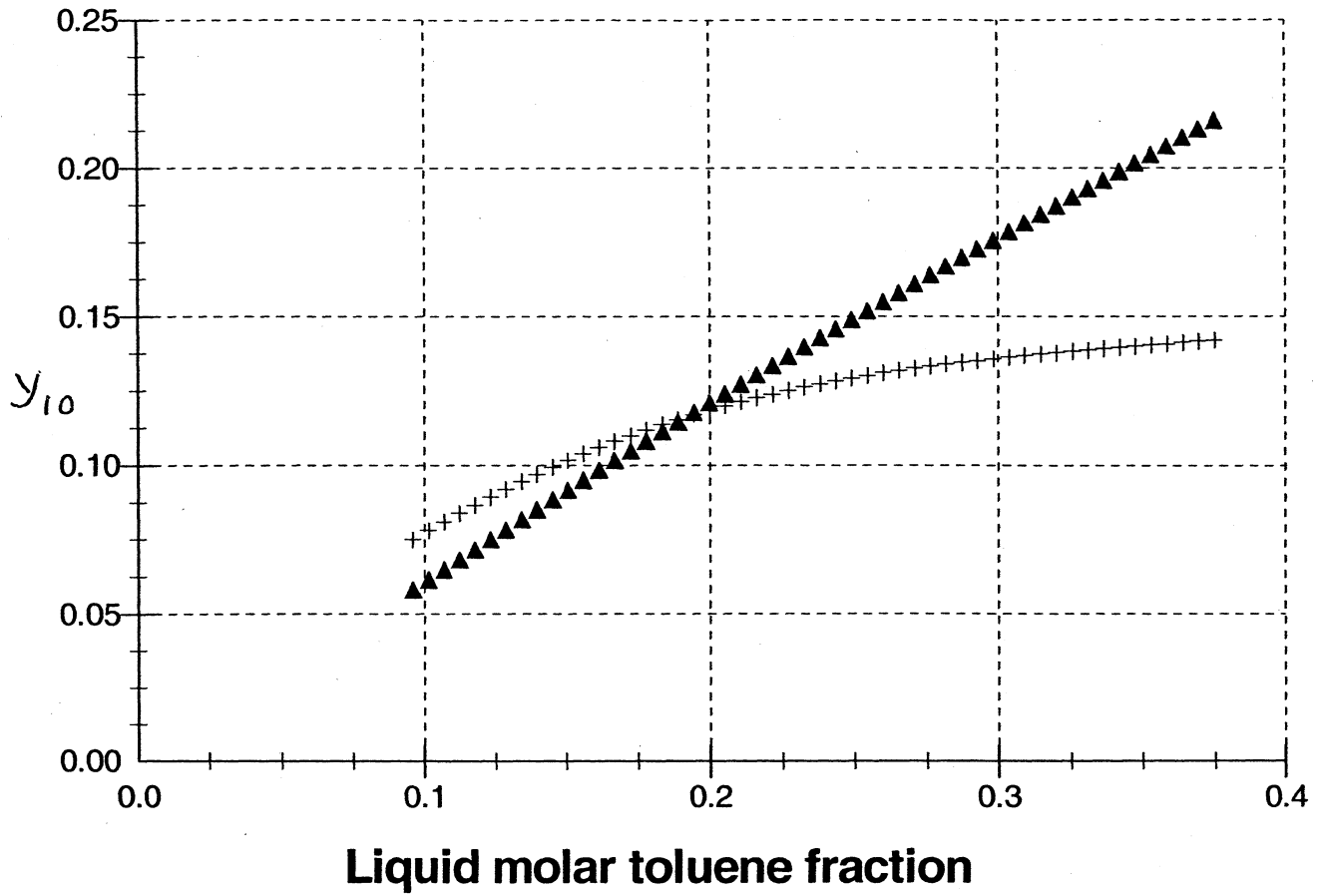
$$y_1(z) = \frac{D}{A-B} e^{[A(z-L)]} - \left[ \frac{C}{B} + \frac{D}{A-B} \right] e^{-BL+Bz} + \frac{C}{B}$$

in agreement with Eq. 18B.10-1.

(b) Numerical results of the suggested calculation procedure are shown in the following graph, prepared by Mike Caracotsios. Cubic spline interpolation was used to get equilibrium vapor compositions over the tabulated range of liquid compositions. The interfacial vapor composition  $y_{10}$  calculated from the equilibrium data becomes equal to that calculated in step (iv) at a liquid composition  $x_{10} = 0.192$ .

Interfacial  
▲ Vapor molar toluene fraction from Diffusion

Interfacial  
+ Vapor molar toluene fraction from Equilibrium



### 18B.11 Diffusion with fast second-order reaction

a. A shell balance on species A plus Fick's first law of diffusion leads to

$$\frac{d^2 x_A}{dz^2} = 0 \quad \text{which has the solution} \quad x_A = C_1 z + C_2$$

When the constants of integration are determined from the boundary conditions that  $x_A(0) = x_{A0}$  and  $x_A(\delta) = 0$ , the mole-fraction profile becomes

$$x_A = x_{A0} \left( 1 - \frac{z}{\delta} \right)$$

Then the rate of dissolution of A at the solid-liquid interface is

$$N_{Az}|_{z=0} = -c \mathcal{D}_{AS} \left. \frac{dx_A}{dz} \right|_{z=0} = \frac{c \mathcal{D}_{AS} x_{A0}}{\delta}$$

b. For the system pictured in Fig. 18B.11, we have the following differential equations

$$\frac{d^2 x_A}{dz^2} = 0 \quad (\text{for } 0 \leq z \leq \kappa\delta) \quad \text{and} \quad \frac{d^2 x_B}{dz^2} = 0 \quad (\text{for } \kappa\delta \leq z \leq \delta)$$

where  $\kappa$  is as yet unknown. These equations have the solutions

$$x_A = C_1 z + C_2 \quad \text{and} \quad x_B = C_3 z + C_4$$

The boundary conditions are now:  $x_A(0) = x_{A0}$ ,  $x_A(\kappa\delta) = 0$ ,  $x_B(\kappa\delta) = 0$ , and  $x_B(\delta) = x_{B\infty}$ . When these are used to get the four constants of integration, we get the following linear profiles:

$$x_A = x_{A0} \left( 1 - \frac{z}{\kappa\delta} \right) \quad \text{and} \quad x_B = x_{B\infty} \left( 1 - \frac{1}{1-\kappa} + \frac{1}{(1-\kappa)\delta} z \right)$$

valid in their respective regions.

Up to this point  $\delta$  is unknown. This quantity can be determined from the statement that the rate of diffusion of A into the reaction plane must be exactly equal to the rate of diffusion of B into the reaction plane at  $z = \delta$ . This is expressed mathematically as:

$$-c \mathcal{D}_{AS} \frac{dx_A}{dz} \Big|_{z=\kappa\delta} = +c \mathcal{D}_{BS} \frac{dx_B}{dz} \Big|_{z=\kappa\delta}$$

When the differentiations are performed, we get

$$-c \mathcal{D}_{AS} \left( -\frac{x_{A0}}{\kappa\delta} \right) = +c \mathcal{D}_{BS} \left( \frac{x_{B\infty}}{(1-\kappa)\delta} \right)$$

or

$$\frac{\kappa}{\mathcal{D}_{AS} x_{A0}} = \frac{1-\kappa}{\mathcal{D}_{BS} x_{B\infty}}$$

From this we get

$$\frac{1}{\kappa} = \left( 1 + \frac{\mathcal{D}_{BS} x_{B\infty}}{\mathcal{D}_{AS} x_{A0}} \right)$$

Then the rate of dissolution of A at the solid-liquid interface is

$$N_{Az} \Big|_{z=0} = -c \mathcal{D}_{AS} \frac{dx_A}{dz} \Big|_{z=0} = \frac{c \mathcal{D}_{AS} x_{A0}}{\kappa\delta} = \frac{c \mathcal{D}_{AS} x_{A0}}{\delta} \left( 1 + \frac{\mathcal{D}_{BS} x_{B\infty}}{\mathcal{D}_{AS} x_{A0}} \right)$$

**18B.12 A sectioned-cell experiment for measuring gas-phase diffusivity**

a. Equation 18.2-1 can be rewritten as

$$N_{Az} = + \frac{c \mathcal{D}_{AB}}{x_B} \frac{dx_B}{dz}$$

Integration from  $z$  to the top of the diffusion tube ( $z_2$ ) gives (since  $N_{Az}$  is constant according to Eq. 18.2-3)

$$\int_{x_B}^{x_{B2}} \frac{dx_B}{x_B} = \frac{N_{Az}}{c \mathcal{D}_{AB}} \int_z^{z_2} dz \quad \text{or} \quad \ln \frac{x_{B2}}{x_B} = \frac{N_{Az}(z_2 - z)}{c \mathcal{D}_{AB}}$$

This may now be rewritten as

$$\ln x_B = \left( \ln x_{B2} - \frac{N_{Az} z_2}{c \mathcal{D}_{AB}} \right) + \left( \frac{N_{Az}}{c \mathcal{D}_{AB}} \right) z$$

This suggests that when  $\ln x_B$  (or  $\log_{10} x_B$ ) is plotted against  $z$ , the slope of the resulting straight line will be  $N_{Az}/c \mathcal{D}_{AB}$  (or  $(N_{Az}/c \mathcal{D}_{AB})$  divided by 2.303).

b. The plot of the experimental data of  $\log_{10} x_B$  vs  $z$  gives a straight line of slope 0.171. The intercept at  $z = z_1 = 0$  is the logarithm of the mole fraction of  $B$  at the interface. The intercept at  $\log_{10} x_B = 0$  is the total length of the diffusion path, where the mole fraction of  $A$  is maintained at zero.

c. We can tabulate, for the four sections of the diffusion tube, the average distance, the average mole fraction of  $B$ , and the logarithm (to the base 10) of the mole fraction of  $B$ , thus:

$z$ (avg)	$x_B$	$\log_{10} x_B$
0.60	0.243	-0.6144
1.60	0.359	-0.4444
2.60	0.531	-0.2749
3.60	0.785	-0.1051

We may now use the equation in (a) to get the diffusivity. We convert all data to c.g.s. units for the numerical calculation. We use the result from (b) that the slope of straight line of  $\log_{10} x_B$  vs  $z$  (from graph) is 0.171. Then

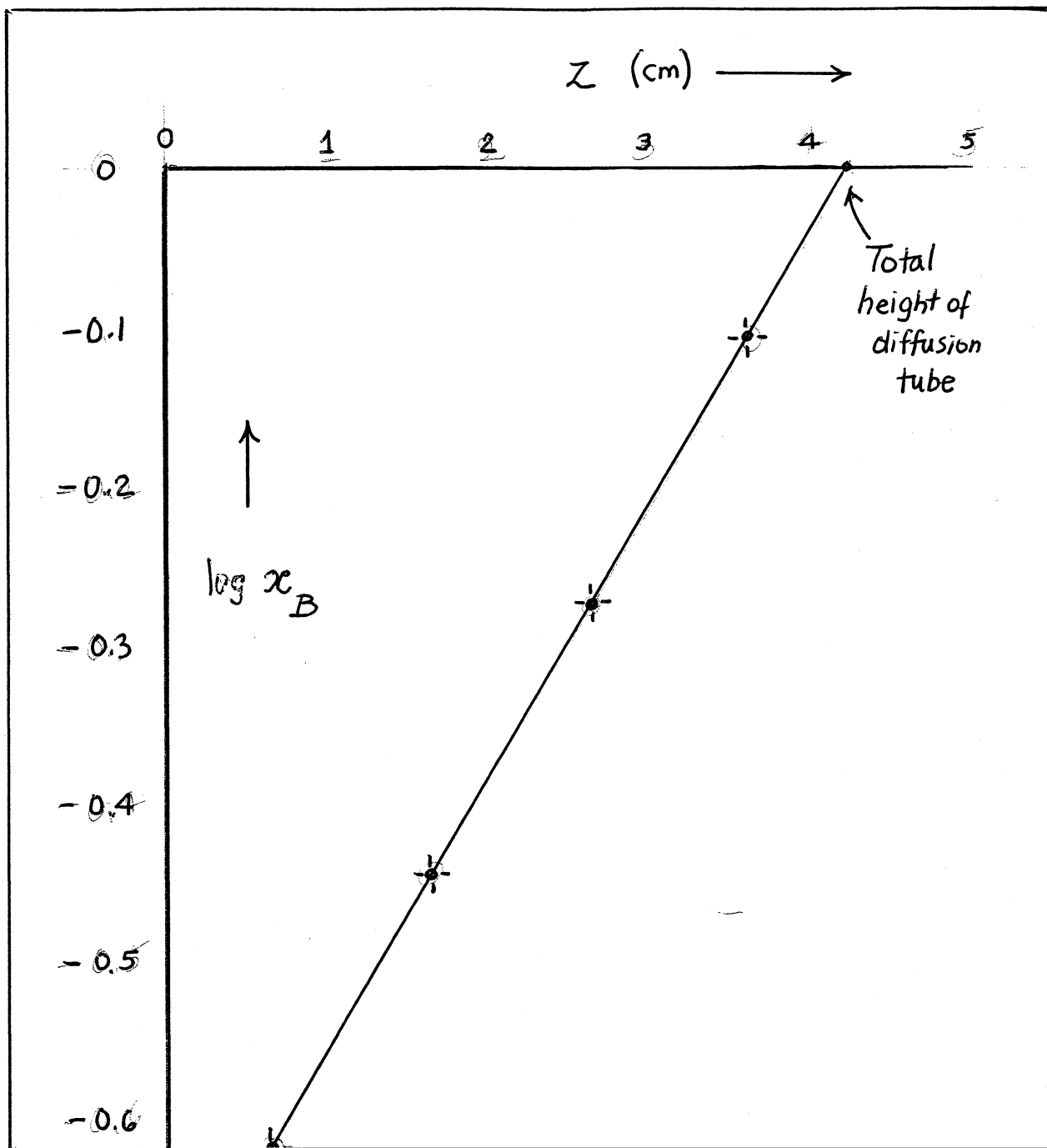
$$0.171 = \frac{N_{Az}}{2.303cD_{AB}}$$

The molar flux of A is obtained from the evaporation rate across a circular region of diameter 2 cm as follows:

The total molar concentration is obtained from the ideal gas law,  
 $p = cRT$ :

$$c = \frac{(741/760 \text{ atm})}{(82.06 \text{ cm}^3 \text{ atm} / \text{g} \cdot \text{mole} \cdot \text{K})(25 + 273.2 \text{ K})}$$
$$= 3.984 \times 10^{-5} \text{ g} \cdot \text{mole} / \text{atm}$$





### 18B.13 Tarnishing of metal surfaces

Fick's first law as applied to the diffusion of oxygen gas through the oxide film is

$$N_{O_2} = -\mathcal{D}_{O_2,MO_x} \frac{dc_{O_2}}{dz}$$

This is the form of Fick's law for a dilute solution of oxygen in virtually stationary metal oxide. This equation may be integrated (for a *quasi-steady-state* situation) with the boundary conditions that  $c_{O_2} = c_0$  at  $z = 0$ , and  $c_{O_2} = 0$  at  $z = z_f(t)$ , where  $z_f(t)$  is the slowly varying oxide film thickness at time  $t$ . The integration gives

$$N_{O_2} = \mathcal{D}_{O_2,MO_x} \frac{c_0}{z_f}$$

Next we write an *unsteady-state* mass balance for the region between  $z_f(t)$  and  $z_f(t + \Delta t)$  to account for the increase in oxygen content between the two planes and the oxygen addition by diffusion

$$(z_f(t + \Delta t) - z_f(t))c_f x = N_{O_2} \Delta t$$

where  $x$  is the stoichiometric coefficient in the oxidation equation, and  $c_f$  is the molar density of the oxide film,  $MO_x$ . Dividing both sides by  $\Delta t$  and letting  $\Delta t$  go to zero then gives the differential equation for the location of the (slowly moving) oxide front

$$\frac{dz_f}{dt} = \frac{N_{O_2}}{c_f x} = \frac{1}{c_f x} \left( \mathcal{D}_{O_2,MO_x} \frac{c_0}{z_f} \right)$$

This equation may be integrated with respect to time, using the initial condition that  $z_f = 0$  at  $t = 0$ . This gives Eq. 18B.13.1 as follows:

$$\frac{1}{2} z_f^2 = \frac{c_0}{c_f x} \mathcal{D}_{O_2,MO_x} t \quad \text{or} \quad z_f = \sqrt{\frac{2c_0}{c_f x} \mathcal{D}_{O_2,MO_x} t}$$

### 18B.14 Effectiveness factors for thin disks

If we make the assumption that the catalyst can be treated as a continuum, then a shell balance on species  $A$  gives:

$$\frac{dN_{Az}}{dz} = R_A$$

Then, inserting the expression for the molar flux analogous to Eq. 18.7-4, we get for an irreversible, first-order chemical reaction

$$\frac{d}{dz} \left( -\mathcal{D}_A \frac{dc_A}{dz} \right) = -k_1'' a c_A \quad \text{or} \quad \mathcal{D}_A \frac{d^2 c_A}{dz^2} - k_1'' a c_A = 0$$

In the second form, it has been assumed that the effective diffusivity is constant. This differential equation may be solved for the boundary conditions that  $c_A(\pm b) = c_{As}$ ; the result is

$$\frac{c_A}{c_{As}} = \frac{\cosh \sqrt{k_1'' a / \mathcal{D}_A} z}{\cosh \sqrt{k_1'' a / \mathcal{D}_A} b} \equiv \frac{\cosh \lambda z}{\cosh \lambda b}$$

The total molar flow (or the effective reaction rate in moles/time) is

$$|W_A| = 2 \cdot \pi R^2 |N_{Az}|_{z=b} = 2 \cdot \pi R^2 \left| -\mathcal{D}_A \frac{dc_A}{dz} \right|_{z=b} = 2 \cdot \pi R^2 \mathcal{D}_A c_{As} \lambda \tanh \lambda b$$

For  $n$  disks of thickness  $b/n$ , this result may be modified thus:

$$|W_A^{(n)}| = n \left( 2\pi R^2 \mathcal{D}_A c_{As} \lambda \tanh(\lambda b/n) \right), \text{ and letting } n \rightarrow \infty$$

$$\begin{aligned} \lim_{n \rightarrow \infty} |W_A^{(n)}| &= \lim_{n \rightarrow \infty} n \left( 2\pi R^2 \mathcal{D}_A c_{As} \lambda \tanh(\lambda b/n) \right) \\ &= \lim_{n \rightarrow \infty} n \left( 2\pi R^2 \mathcal{D}_A c_{As} \lambda [(\lambda b/n) + \dots] \right) = 2\pi R^2 \mathcal{D}_A c_{As} \lambda^2 b = 2\pi R^2 b k_1'' a c_{As} \end{aligned}$$

Then the effectiveness factor is

$$\eta_A = \lim_{n \rightarrow \infty} (W_A / W_A^{(n)}) = \frac{2\pi R^2 \mathcal{D}_A c_{As} \lambda \tanh \lambda b}{2\pi R^2 \mathcal{D}_A c_{As} \lambda^2 b} = \frac{\tanh \lambda b}{\lambda b}$$

### 18B.15 Diffusion and heterogeneous reaction in a slender cylindrical tube with a closed end

a.. The mass balance over a small segment of the tube is

$$n_{Az}|_z S - n_{Az}|_{z+\Delta z} S - P\Delta z f(\omega_{A0}) = 0$$

Division by  $S\Delta z$  and letting the segment thickness go to zero gives

$$-\frac{dn_{Az}}{dz} - \frac{P}{S} f(\omega_{A0}) = 0$$

b. The mass-average velocity is given by

$$v_z = \omega_A v_{Az} + \omega_B v_{Bz}$$

At steady state,  $B$  is not moving so that  $v_{Bz}$  is zero; if substance  $A$  is present only in very small concentrations, then is quite small. Hence  $v_z \approx 0$ .

c. Because of the result in (b), we can write the mass flux as

$$n_{Az} = -\rho \mathcal{D}_{AB} \frac{d\omega_A}{dz}$$

Then the diffusion equation becomes

$$\rho \mathcal{D}_{AB} \frac{d^2 \omega_A}{dz^2} - \frac{P}{S} f(\omega_A) = 0$$

or

$$\frac{d^2 \omega_A}{d\zeta^2} - \frac{PL^2}{S\rho \mathcal{D}_{AB}} k_1'' \omega_A = 0$$

Here we have set the wall mass fraction  $\omega_{A0}$  equal to that in the main stream  $\omega_A$  and we have introduced explicitly the first order reaction kinetics. We have also switched over to a dimensionless coordinate  $\zeta = z/L$ .

The differential equation is to be solved with the boundary conditions:

$$\text{B. C. 1:} \quad \text{at } \zeta = 0, \quad \omega_A = \omega_{Ai}$$

$$\text{B. C. 2:} \quad \text{at } \zeta = 1, \quad d\omega_A/dz = 0$$

The general solution is

$$\omega_A = C_1 \cosh N\zeta + C_2 \sinh N\zeta$$

in which  $N = \sqrt{PL^2k_1''/S\rho\mathcal{D}_{AB}}$ . When the constants are determined from the boundary conditions we get

$$\begin{aligned} \frac{\omega_A}{\omega_{Ai}} &= \cosh N\zeta - \frac{\sinh N}{\cosh N} \sinh N\zeta \\ &= \frac{\cosh N\zeta \cosh N - \sinh N \sinh N\zeta}{\cosh N} \\ &= \frac{\cosh N(1 - \zeta)}{\cosh N} \end{aligned}$$

d. The mass flow rate of A into the capillary is

$$\begin{aligned} w_A|_{z=0} &= -\rho\mathcal{D}_{AB}S \left. \frac{d\omega_A}{dz} \right|_{z=0} \\ &= -\frac{\rho\mathcal{D}_{AB}S}{L} \left. \frac{d\omega_A}{d\zeta} \right|_{\zeta=0} \\ &= -\frac{\rho\mathcal{D}_{AB}S\omega_{Ai}}{L} \left. \frac{(-N)\sinh N(1 - \zeta)}{\cosh N} \right|_{\zeta=0} \\ &= \frac{\rho\mathcal{D}_{AB}S\omega_{Ai}}{L} (N \tanh N) \end{aligned}$$

### 18B.16 Effects of temperature and pressure on evaporation rate

a. For ideal gas behavior,  $x_{A1} = p_{\text{vap},1}/p$ , as pointed out several paragraphs before Eq. 18.2-1. Since the vapor pressure increases with temperature, according to the Clausius-Clapeyron equation,  $x_{A1}$  will also increase. When the total pressure increases,  $x_{A1}$  will decrease.

b. The evaporation rate is given by Eqs 18.2-14 and 15. Since, at constant temperature,  $c \propto p$  and  $\mathcal{D}_{AB} \propto 1/p$ , the evaporation rate should be nearly independent of the imposed pressure.

c. The temperature dependence of the evaporation rate can be estimated as follows:  $c \propto 1/T$  and (for the simple kinetic theory of rigid spheres)  $\mathcal{D}_{AB} \propto T^{3/2}$ . This suggests that

$$(\text{Evaporation rate at } T' : \text{Evaporation rate at } T) = (T'/T)^{1/2}$$

However, it is known that the kinetic theory of rigid spheres underestimates the temperature dependence. If one reads off the slope of the curve in Fig. 17.2-1, we estimate that

$$(\text{Evaporation rate at } T' : \text{Evaporation rate at } T) \approx (T'/T)^{3/4}$$

which is a more believable result.

### 18B.17 Reaction rates in large and small particles

a. Equation 18.7-11 for small  $R$  becomes, on using the expansion of the hyperbolic cotangent for small arguments

$$W_{AR} = 4\pi R \mathcal{D}_A c_{AR} \left[ 1 - \left( 1 + \frac{1}{3} (k_1'' a / \mathcal{D}_A) R^2 + \dots \right) \right] \\ \approx - \left( \frac{4}{3} \pi R^3 \right) (k_1'' a) c_{AR}$$

where we have retained only the leading term.

For large  $R$ , we use the expansion of the hyperbolic cotangent for large arguments (which may be found in mathematics handbooks) to get

$$W_{AR} = 4\pi R \mathcal{D}_A c_{AR} \left[ 1 - (\lambda R + 2\lambda R \exp(-2\lambda R) + \dots) \right] \\ \approx - (4\pi R^2) \sqrt{k_1'' a \mathcal{D}_A} c_{AR}$$

where  $\lambda = \sqrt{k_1'' a / \mathcal{D}_A}$ , and only the leading term has been retained.

Note that for small  $R$  the rate of disappearance of  $A$  is proportional to the volume of the catalyst, whereas for large  $R$  the rate is proportional to the surface area.

b. Equation 18B.14-2 for small  $R$  becomes, using the expansion for the hyperbolic tangent for small arguments

$$|W_A| = 2 \cdot \pi R^2 c_{As} \mathcal{D}_A \lambda \left( \lambda b - \frac{1}{3} \lambda^3 b^3 + \dots \right) \\ \approx (2b\pi R^2) (k_1'' a) c_{As}$$

Here, again, we let  $\lambda = \sqrt{k_1'' a / \mathcal{D}_A}$ , and we have kept only the leading term.

For large  $R$  we use the expansion for the hyperbolic tangent for large arguments to get

$$|W_A| = 2 \cdot \pi R^2 c_{As} \mathcal{D}_A \lambda (1 - 2 \exp(-2\lambda b) + \dots) \\ \approx (2\pi R^2) \sqrt{k_1'' a \mathcal{D}_A} c_{As}$$

Here again,  $|W_A| \propto$  volume for small  $R$ , and  $|W_A| \propto$  surface area for large  $R$ .

**18B.18 Evaporation rate for small mole fraction of the volatile liquid**  
According to Eq. 18.2-13

$$\frac{1}{(x_B)_{\ln}} = \frac{\ln(x_{B2}/x_{B1})}{x_{B2} - x_{B1}} = \frac{1}{x_{A1} - x_{A2}} \ln \frac{1 - x_{A2}}{1 - x_{A1}} = \frac{\ln(1 - x_{A2}) - \ln(1 - x_{A1})}{x_{A1} - x_{A2}}$$

We now wish to expand the logarithms for the situation where the mole fractions are much less than unity. To do this we may use Eq. C.2-3. This gives

$$\begin{aligned} \frac{1}{(x_B)_{\ln}} &= \frac{-(x_{A2} + \frac{1}{2}x_{A2}^2 + \frac{1}{3}x_{A2}^3 + \dots) + (x_{A1} + \frac{1}{2}x_{A1}^2 + \frac{1}{3}x_{A1}^3 + \dots)}{x_{A1} - x_{A2}} \\ &= \frac{(x_{A1} - x_{A2}) + \frac{1}{2}(x_{A1}^2 - x_{A2}^2) + \frac{1}{3}(x_{A1}^3 - x_{A2}^3) + \dots}{x_{A1} - x_{A2}} \\ &= 1 + \frac{1}{2}(x_{A1} + x_{A2}) + \frac{1}{3}(x_{A1}^2 + x_{A1}x_{A2} + x_{A2}^2) + \dots \end{aligned}$$

This is the expression in brackets in Eq. 18.2-16.



### 18B.19 Oxygen uptake by a bacterial aggregate

a. A mass balance over a thin spherical shell gives

$$\left(4\pi r^2 n_{Ar}\right)\Big|_r - \left(4\pi r^2 n_{Ar}\right)\Big|_{r+\Delta r} + (4\pi r^2 \Delta r) r_A = 0$$

in which  $A$  stands for oxygen. Dividing by  $4\pi\Delta r$  and taking the limit as the spherical-shell thickness goes to zero, we get

$$-\frac{d}{dr}\left(r^2 n_{Ar}\right) = -r^2 r_A$$

Then inserting Fick's first law of diffusion and introducing the zero-order chemical reaction rate constant to describe the disappearance of the oxygen, we have

$$\mathfrak{D}_{AB} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\rho_A}{dr} \right) = -r_A = k_0'''$$

The  $B$  in  $\mathfrak{D}_{AB}$  stands for the medium through which the oxygen is diffusing. We then multiply the equation by  $R^2/\rho_0 \mathfrak{D}_{AB}$ , and define the dimensionless quantities:  $\xi = r/R$ ,  $\chi = \rho_A/\rho_0$ , and  $N = R^2 k_0''' / \rho_0 \mathfrak{D}_{AB}$ . Then the diffusion equation becomes, in dimensionless form

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\chi}{d\xi} \right) = N$$

b. If we assume the presence of an anoxic (oxygen-free) core, then we have the following boundary conditions: at  $\xi = 1$ ,  $\chi = 1$ ; at  $\xi = 0$ ,  $\chi = \text{finite}$ ; and at  $\xi = \xi_0$ ,  $\chi = 0$  and  $d\chi/d\xi = 0$ . The physical significance of the last boundary condition is that there must be no diffusion across the boundary between the anoxic core and the outer region of the aggregate. This may occur if all the material that enters across the outer surface of the aggregate is completely used up by the time it reaches the spherical surface at  $\xi = \xi_0$ .

c. Two integrations of the above equation give:

$$\xi^2 \frac{d\chi}{d\xi} = \frac{1}{3}N\xi^3 + C_1 \quad \text{and} \quad \chi = \frac{1}{6}N\xi^2 - C_1\xi^{-1} + C_2$$

The constant  $C_2$  can be found from the boundary condition at  $\xi = 1$ , so that

$$\chi = \frac{1}{6}N(\xi^2 - 1) - C_1(\xi^{-1} - 1) + 1$$

We now have to apply the two boundary conditions at  $\xi = \xi_0$ , in order to determine the two quantities  $C_1$  and  $\xi_0$  (which as yet is unspecified):

$$d\chi/d\xi = 0 \text{ at } \xi = \xi_0: \quad 0 = \frac{1}{3}N\xi_0 + \frac{C_1}{\xi_0^2} \quad \text{or} \quad C_1 = -\frac{1}{3}N\xi_0^3$$

$$\chi = 0 \text{ at } \xi = \xi_0: \quad 0 = \frac{1}{6}N(\xi_0^2 - 1) - C_1(\xi_0^{-1} - 1) + 1$$

Elimination of  $C_1$  between the last results gives, after rearranging

$$\xi_0^3 - \frac{3}{2}\xi_0^2 + \left(\frac{1}{2} - \frac{3}{N}\right) = 0 \quad (***)$$

If  $N$  is very large, the cubic relation has the roots 1, 1, and  $-\frac{1}{2}$ . The last of these is physically impossible, and the other two roots indicate that if the reaction rate is exceedingly large, there the anoxic region will occupy the entire sphere. If we set  $\xi_0$  equal to zero, we find the minimum value of  $N$ , namely  $N = 6$ . Below this value, there will be no anoxic region. Thus the final expression for the concentration profile is:

$$\chi = 1 - \frac{1}{6}N(1 - \xi^2) + \frac{1}{3}N\xi_0^3(\xi^{-1} - 1) \quad \text{for} \quad 1 \geq \xi \geq \xi_0 \geq 0$$

and  $\chi = 0$  for  $0 \leq \xi \leq \xi_0$ . Equation (\*\*\*) above gives the boundary of the anoxic region in terms of  $N$ .

### 18C.1 Diffusion from a point source in a moving stream

a. Make a mass balance (in molar units) over the ring-shaped area element shown in Fig. 18C.1:

$$(2\pi r \Delta r N_{Az})\Big|_z - (2\pi r \Delta r N_{Az})\Big|_{z+\Delta z} + (2\pi \Delta z r N_{Ar})\Big|_r - (2\pi \Delta z r N_{Ar})\Big|_{r+\Delta r} = 0$$

Divide by  $2\pi \Delta z \Delta r$  and take the limit as the dimensions of the ring-shaped element go to zero:

$$\lim_{\Delta z \rightarrow 0} \frac{(rN_{Az})\Big|_{z+\Delta z} - (rN_{Az})\Big|_z}{\Delta z} + \lim_{\Delta r \rightarrow 0} \frac{(rN_{Ar})\Big|_{r+\Delta r} - (rN_{Ar})\Big|_r}{\Delta r} = 0$$

Then using the definition of the partial derivative, we get

$$r \frac{\partial N_{Az}}{\partial z} + \frac{\partial}{\partial r} \left( r \frac{\partial N_{Ar}}{\partial r} \right) = 0 \quad \text{or} \quad \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial N_{Ar}}{\partial r} \right) + \frac{\partial N_{Az}}{\partial z} = 0$$

We now use the expression for the molar flux given in Eq. (D) of Table 17.8-2:

$$N_{Ar} = -c \mathcal{D}_{AB} \frac{\partial x_A}{\partial r} + c_A v_r^* \approx -\mathcal{D}_{AB} \frac{\partial c_A}{\partial r}$$

$$N_{Az} = -c \mathcal{D}_{AB} \frac{\partial x_A}{\partial z} + c_A v_z^* \approx -\mathcal{D}_{AB} \frac{\partial c_A}{\partial z} + c_A v_0$$

In getting the approximate expressions, we have assumed that there is negligible convective diffusion in the  $r$  direction, and that the distinction between molar and mass average velocity is unimportant in this system. These assumptions would be valid if the concentration of  $A$  in the mixture is small. When these expressions are inserted into the equation for the molar flux, we get Eq. 18C.1-1.

b. To make the change of variable, we use  $c_A(r, z) = c_A(s, z)$ , and apply the chain rule of partial differentiation as follows:

$$\left( \frac{\partial c_A}{\partial z} \right)_r = \left( \frac{\partial c_A}{\partial s} \right)_z \left( \frac{\partial s}{\partial z} \right)_r + \left( \frac{\partial c_A}{\partial z} \right)_s = \left( \frac{\partial c_A}{\partial s} \right)_z \frac{z}{s} + \left( \frac{\partial c_A}{\partial z} \right)_s$$

$$\begin{aligned} \left( \frac{\partial^2 c_A}{\partial z^2} \right)_r &= \frac{\partial}{\partial z} \left( \frac{\partial c_A}{\partial z} \right)_r = \left( \frac{\partial}{\partial s} \left( \frac{\partial c_A}{\partial z} \right)_r \right)_z \frac{z}{s} + \left( \frac{\partial}{\partial z} \left( \frac{\partial c_A}{\partial z} \right)_r \right)_s \\ &= \left( \frac{\partial^2 c_A}{\partial s^2} \frac{z}{s} - \frac{\partial c_A}{\partial s} \frac{z}{s^2} + \frac{\partial^2 c_A}{\partial s \partial z} \right) \frac{z}{s} + \left( \frac{\partial^2 c_A}{\partial s \partial z} \frac{z}{s} + \frac{1}{s} \frac{\partial c_A}{\partial s} + \frac{\partial^2 c_A}{\partial z^2} \right) \end{aligned}$$

$$\begin{aligned} \left( \frac{\partial c_A}{\partial r} \right)_z &= \left( \frac{\partial c_A}{\partial s} \right)_z \left( \frac{\partial s}{\partial r} \right)_z = \left( \frac{\partial c_A}{\partial s} \right)_z \frac{r}{s} \\ r \left( \frac{\partial c_A}{\partial r} \right)_z &= \left( \frac{\partial c_A}{\partial s} \right)_z \frac{r^2}{s} = \left( \frac{\partial c_A}{\partial s} \right)_z \frac{s^2 - z^2}{s} \\ \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( \frac{\partial c_A}{\partial r} \right)_z \right] &= \frac{1}{s} \left( \frac{\partial}{\partial s} \left[ r \left( \frac{\partial c_A}{\partial r} \right)_z \right] \right)_z = \left( \frac{\partial^2 c_A}{\partial s^2} \right) \frac{s^2 - z^2}{s^2} + \frac{1}{s} \left( \frac{\partial c_A}{\partial s} \right)_z \frac{s^2 + z^2}{s^2} \end{aligned}$$

When these are substituted into Eq. 18C.1-1, we then get Eq. 18C.1-2.  
c. Let

$$f(s, z) = c_A \cdot \frac{4\pi \mathfrak{D}_{AB}}{W_A} = \frac{1}{s} \exp\left(-\frac{v_0}{2\mathfrak{D}_{AB}}(s-z)\right) \equiv \frac{1}{s} \exp(-\alpha(s-z))$$

Then

$$\left( \frac{\partial f}{\partial z} \right) = \alpha f; \quad \left( \frac{\partial f}{\partial s} \right) = -\frac{f}{s} - \alpha f; \quad \frac{z}{s} \left( \frac{\partial f}{\partial s} \right) = -\frac{zf}{s^2} - \frac{z}{s} \alpha f$$

$$\left( \frac{\partial^2 f}{\partial z^2} \right) = \alpha^2 f; \quad 2 \frac{z}{s} \left( \frac{\partial^2 f}{\partial s \partial z} \right) = \frac{z}{s} \left( -2\alpha \frac{f}{s} - 2\alpha^2 f \right)$$

$$\frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial f}{\partial s} \right) = \alpha^2 f$$

When these expressions are substituted into Eq. 18C.1-2, an identity is obtained.

c. B. C. 1 is clearly satisfied. To examine B. C. 2, we first have to calculate the derivative

$$\frac{\partial c_A}{\partial s} = \frac{W_A}{4\pi\mathcal{D}_{AB}} \left( -\frac{1}{s^2} e^{-\alpha(s-z)} - \frac{\alpha}{s} e^{-\alpha(s-z)} \right)$$

Then

$$-4\pi s^2 \mathcal{D}_{AB} \frac{\partial c_A}{\partial s} = W_A e^{-\alpha(s-z)} (1 - \alpha s)$$

When  $s$  is made to go to zero (which implies that  $z$  goes to zero as well), the right side of the above equation goes to  $W_A$ , and therefore the second boundary condition is satisfied.

To examine B. C. 3 we have to calculate the derivative with respect to  $r$ :

$$\left( \frac{\partial c_A}{\partial r} \right)_z = \left( \frac{\partial c_A}{\partial s} \right)_z \frac{r}{s} = \frac{W_A}{4\pi\mathcal{D}_{AB}} e^{-\alpha(s-z)} (1 - \alpha s) \frac{r}{s}$$

where  $s = \sqrt{r^2 + z^2}$ . When  $r \rightarrow 0$ ,  $s$  goes to  $z$ , and B. C. 3 is satisfied.

The meanings of the three boundary conditions are:

B. C. 1: The concentration of  $A$  on a spherical surface at infinite distance from the injection point must be zero (since  $A$  is diffusing in all directions)

B. C. 2: This is a statement that  $W_A$  is the injection rate of  $A$ .

B. C. 3: This means that the maximum in the concentration must be on the  $z$  axis.

*e.* To determine the diffusivity, one can write Eq. 18C.1-3 as

$$\ln(c_A s) = \ln(W_A / 4\pi\mathcal{D}_{AB}) - (v_0 / 2\mathcal{D}_{AB})(s - z)$$

Hence, if  $c_A s$  is plotted vs.  $(s - z)$  on semi-logarithmic paper, the slope will be  $-(v_0 / 2\mathcal{D}_{AB})$  and the intercept will be  $(W_A / 4\pi\mathcal{D}_{AB})$ .

For more on this subject, see T. K. Sherwood and R. L. Pigford, *Absorption and Extraction*, McGraw-Hill, New York (1952), pp. 42-43; H. S. Carslaw and J. C. Jaeger, *Heat Conduction in Solids*, Oxford University Press, 2d ed. (1959), Eq. 2; H. A. Wilson, *Proc. Camb. Phil. Soc.*, 12, 406 (1904).

### 18C.2 Diffusion and reaction in a partially impregnated catalyst

Use the notation of §18.7 as well as the following dimensionless quantities:  $\xi = r/R$ ,  $\Gamma = c_A/c_{AR}$ , and  $\phi = \sqrt{k_0'' a R^2 / \mathcal{D}_A}$ . Superscripts I and II indicate the two regions.

a. In Region I, the diffusion equation and its solution are

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\Gamma^{(I)}}{d\xi} \right) = 0 \quad \text{and} \quad \Gamma^{(I)} = -\frac{C_1^I}{\xi} + C_2^I$$

In Region II, the diffusion equation and its solution are (cf. Eqs. 18.7-6 and 9)

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\Gamma^{(II)}}{d\xi} \right) = \phi^2 \Gamma^{(II)} \quad \text{and} \quad \Gamma^{(II)} = \frac{C_1^{II}}{\xi} \cosh \phi \xi + \frac{C_2^{II}}{\xi} \sinh \phi \xi$$

The boundary conditions that have to be satisfied are:

B. C. 1: at  $\xi = 0$ ,  $\Gamma^{(I)}$  is finite (whence  $C_1^I = 0$ )

B. C. 2: at  $\xi = \kappa$ ,  $\Gamma^{(I)} = \Gamma^{(II)}$

B. C. 3: at  $\xi = \kappa$ ,  $d\Gamma^{(I)}/d\xi = d\Gamma^{(II)}/d\xi$

B. C. 4: at  $\xi = 1$ ,  $\Gamma^{(II)} = 1$

Boundary conditions 4 and 3 give us the following two equations:

$$1 = C_1^{II} \cosh \phi + C_2^{II} \sinh \phi$$

$$0 = -\frac{C_1^{II}}{\kappa^2} \cosh \phi \kappa + \frac{C_1^{II}}{\kappa} \phi \sinh \phi \kappa - \frac{C_2^{II}}{\kappa^2} \sinh \phi \kappa + \frac{C_2^{II}}{\kappa} \phi \cosh \phi \kappa$$

These two equations may be solved simultaneously to get

$$C_1^{II} = \frac{-\sinh \phi \kappa + \phi \kappa \cosh \phi \kappa}{\sinh \phi (1 - \kappa) - \phi \kappa \cosh \phi (1 + \kappa)}$$

$$C_2^{\text{II}} = \frac{\cosh \phi \kappa - \phi \kappa \sinh \phi \kappa}{\sinh \phi(1 - \kappa) - \phi \kappa \cosh \phi(1 + \kappa)}$$

Therefore the concentration profiles in the two regions are:

$$\Gamma^{\text{(II)}} = \frac{1}{\xi} \left[ \frac{(-\sinh \phi \kappa + \phi \kappa \cosh \phi \kappa) \cosh \phi \xi}{\sinh \phi(1 - \kappa) - \phi \kappa \cosh \phi(1 + \kappa)} + \frac{(\cosh \phi \kappa - \phi \kappa \sinh \phi \kappa) \sinh \phi \xi}{\sinh \phi(1 - \kappa) - \phi \kappa \cosh \phi(1 + \kappa)} \right]$$

$$\Gamma^{\text{(I)}} = \frac{1}{\xi} \frac{\phi \kappa}{\sinh \phi(1 - \kappa) - \cosh \phi(1 + \kappa)}$$

To get the concentration profile for region I, we used B. C. 2.

b. To get the molar flux at the outer surface, we need

$$W_A = -4\pi R^2 \mathcal{D}_A \left. \frac{dc_A^{\text{II}}}{dr} \right|_{r=R} = -4\pi R \mathcal{D}_A c_{AR} \left. \frac{d\Gamma^{\text{(II)}}}{d\xi} \right|_{\xi=1}$$

After evaluating the derivative at the surface, we get finally

$$W_A = 4\pi R \mathcal{D}_A c_{AR} \left[ 1 - \phi \left( \frac{\cosh \phi(1 - \kappa) + \phi \kappa \sinh \phi(1 + \kappa)}{\sinh \phi(1 - \kappa) - \phi \kappa \cosh \phi(1 + \kappa)} \right) \right]$$

In the limit that  $\kappa \rightarrow 0$ , this result simplifies to Eq. 18.7-11.

### 18C.3 Absorption rate in a falling film

a. The total moles of  $A$  transferred per unit time across the gas-liquid interface is  $W_A$ . This has to be equated to the amount of  $A$  that is leaving in the film of finite thickness  $\delta$ :

$$W_A = W \int_0^\delta c_A(x, z) \Big|_{z=L} v_z(x) dx$$

When it is assumed that  $A$  diffuses only a very short distance into the film, then  $v_z(x)$  may be set equal to the fluid velocity at the gas-liquid interface,  $v_{z, \max}$ , and taken outside the integral. Furthermore, since  $c_A(x, z)$  is virtually zero beyond a distance small compared to  $\delta$ , the integration can be extended to infinity. This reasoning leads to Eq. 18C.3-1.

b. Inserting  $c_A(x, z)$  into Eq. 18C.3-1 and changing to the variable  $u$  requires no further explanation.

c. Changing the order of integration requires specifying the region of integration. In this case it is a triangular region extending from  $u = 0$  to  $u = \infty$ , and from the diagonal line  $\xi = u$  across to  $\xi = \infty$ . When the order of integration is reversed, it is necessary to integrate over exactly the same region, but this time from  $\xi = 0$  to  $\xi = \infty$  and from  $u = 0$  up to the diagonal  $u = \xi$ . This leads to Eq. 18C.3-3.

Having done this, the inside integral can be performed analytically to give

$$W_A = W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{z, \max}}{\pi L}} \cdot 2 \int_0^\infty \xi \exp(-\xi^2) d\xi$$

Now the remaining integral can be done also to give

$$= W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{z, \max}}{\pi L}} \left( -\exp(-\xi^2) \right) \Big|_0^\infty = W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{z, \max}}{\pi L}}$$

which is in agreement with Eq. 18.5-18.



### 18C.4 Estimation of the required length of an isothermal reactor

a. The steady state mass balance over a length  $\Delta l$  of the reactor is

$$w\omega_{A0}|_l - w\omega_{A0}|_{l+\Delta l} - (S\Delta l)an_A = 0$$

Dividing by  $w\Delta l$  and letting  $\Delta l$  go to zero gives

$$\frac{d\omega_{A0}}{dl} = -\frac{San_A}{w}$$

or

$$\frac{d\omega_{A0}}{dl} = \frac{SaN_A M_A}{w}$$

b. Next we want to use the result of Eq. 18.3-9 to write

$$\frac{M_A M_B (dx_{A0}/dl)}{(M_A x_{A0} + M_B x_{B0})^2} = \frac{SaM_A}{w} \left( \frac{2c\mathfrak{D}_{AB}}{\delta} \ln \frac{1}{1 - \frac{1}{2}x_{A0}} \right)$$

Then integration gives

$$\left( \frac{M_B w \delta}{2Sac\mathfrak{D}_{AB}} \right) \int_{x_A(0)}^{x_A(L)} \frac{dx_{A0}}{[M_A x_{A0} + M_B (1 - x_{A0})]^2 \ln(1 - \frac{1}{2}x_{A0})} = L$$

### 18C.5 Steady-state evaporation

a, We start with the second form of Eq. 17.9-1, written for diffusion of a 3-component mixture in the  $z$  direction. For convenience, we omit the index  $z$  on the species molar fluxes:

$$\frac{dx_\alpha}{dz} = \sum_{\beta=1}^3 \frac{1}{c\mathcal{D}_{\alpha\beta}} (x_\alpha N_\beta - x_\beta N_\alpha)$$

Consider now the concentration gradient of species 3, taking into account that  $N_1$  and  $N_2$  are constants, and that  $N_3$  is zero:

$$\frac{dx_3}{dz} = \frac{1}{c\mathcal{D}_{13}} (x_3 N_1) + \frac{1}{c\mathcal{D}_{23}} (x_3 N_2) = \left( \frac{N_1}{c\mathcal{D}_{13}} + \frac{N_2}{c\mathcal{D}_{23}} \right) x_3$$

This first-order, separable differential equation is easily integrated to give the result in Eq. 18C.5-1:

$$x_3 = x_{30} \exp(v_{113} + v_{223})\zeta \equiv x_{30} \exp A\zeta$$

in which the notation  $v_{\alpha\beta\gamma}$  is a symbol defined in the textboo.

b. Next we consider the concentration gradient for species 2:

$$\frac{dx_2}{dz} = \frac{1}{c\mathcal{D}_{12}} (x_2 N_1 - x_1 N_2) + \frac{1}{c\mathcal{D}_{23}} (x_2 N_3 - x_3 N_2)$$

or, in dimensionless form,

$$\begin{aligned} \frac{dx_2}{d\zeta} &= (v_{112}x_2 - v_{212}x_1) - v_{223}x_3 = v_{112}x_2 - v_{212}(1 - x_2 - x_3) - v_{223}x_3 \\ &= (v_{112} + v_{212})x_2 + (v_{212} - v_{223})x_3 - v_{212} \end{aligned}$$

When we use the abbreviations given in the text, this equation can be recast in the form

$$\frac{dx_2}{d\zeta} - (v_{112} + v_{212})x_2 = (v_{212} - v_{223})x_{30} \exp(v_{113} + v_{223})\zeta - v_{212} \quad \text{or}$$

$$\frac{dx_2}{d\zeta} - Bx_2 = Cx_{30} \exp A\zeta - v_{212}$$

This is a first-order linear equation, which is readily solved

$$\begin{aligned} x_2 &= e^{B\zeta} \left[ \int_0^\zeta e^{-B\zeta} (Cx_{30} e^{A\zeta} - v_{212}) d\zeta + C_1 \right] \quad (C_1 = x_{20} \text{ from B. C.}) \\ &= e^{B\zeta} \left[ Cx_{30} \frac{e^{(A-B)\zeta} - 1}{(A-B)} - v_{212} \frac{e^{-B\zeta} - 1}{-B} + x_{20} \right] \\ &= \frac{Cx_{30}}{A-B} e^{A\zeta} + \left( x_{20} - \frac{Cx_{30}}{A-B} - \frac{v_{212}}{B} \right) e^{B\zeta} + \frac{v_{212}}{B} \end{aligned}$$

in which

$$\frac{v_{212}}{B} = \frac{N_2}{N_1 + N_2}; \quad e^{B\zeta} = \exp \left[ \frac{(N_1 + N_2)z}{c\mathcal{D}_{12}} \right]; \quad e^{A\zeta} = \exp \left[ \left( \frac{N_1}{c\mathcal{D}_{13}} + \frac{N_2}{c\mathcal{D}_{23}} \right) z \right]$$

$$\frac{C}{A-B} = \frac{N_2 \left( \frac{\mathcal{D}_{23} - \mathcal{D}_{12}}{\mathcal{D}_{23}} \right)}{N_1 \left( \frac{\mathcal{D}_{12} - \mathcal{D}_{13}}{\mathcal{D}_{13}} \right) + N_2 \left( \frac{\mathcal{D}_{12} - \mathcal{D}_{23}}{\mathcal{D}_{23}} \right)}$$

c. The results in (a) and (b) above are in agreement with Eqs. (2) and (3) of the article by Carty and Schrodtt, cited in the text.

d. Figure 3 in the article by Carty and Schrodtt indicates good agreement between the above equations and the experimental data.

### 18D.1 Effectiveness factors for long cylinders

Instead of Eq. 18.7-6 (for spheres) we have now (for cylinders):

$$\mathfrak{D}_A \frac{1}{r} \frac{d}{dr} \left( r \frac{dc_A}{dr} \right) = k_1'' a c_A \quad \text{with } c_A(R) = c_{AR} \text{ and } c_A(0) = \text{finite}$$

The differential equation may also be put into the form

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{dc_A}{dr} \right) - \left( \frac{k_1'' a}{\mathfrak{D}_A} \right) c_A = 0$$

This may be recognized as the equation for a first-order modified Bessel function. Therefore, the solution is

$$c_A = C_1 I_0 \left( \sqrt{\frac{k_1'' a}{\mathfrak{D}_A}} r \right) + C_2 K_0 \left( \sqrt{\frac{k_1'' a}{\mathfrak{D}_A}} r \right)$$

Inasmuch as  $K_0$  cannot satisfy the boundary condition at  $r = 0$ , we must set  $C_2$  equal to zero. The boundary condition at  $r = R$  then gives the constant  $C_1$ . The concentration profile is therefore

$$\frac{c_A}{c_{AR}} = \frac{I_0 \left( \sqrt{k_1'' a / \mathfrak{D}_A} r \right)}{I_0 \left( \sqrt{k_1'' a / \mathfrak{D}_A} R \right)}$$

This is the cylindrical analog of Eq. 18.7-9.

The molar flow of  $A$  at the surface is then

$$\begin{aligned} W_{AR} &= 2\pi RL \left( -\mathfrak{D}_A \frac{dc_A}{dr} \right) \Big|_{r=R} \\ &= -\frac{(2\pi RL) \mathfrak{D}_A c_{AR}}{I_0 \left( \sqrt{k_1'' a / \mathfrak{D}_A} R \right)} I_1 \left( \sqrt{k_1'' a / \mathfrak{D}_A} R \right) \cdot \sqrt{k_1'' a / \mathfrak{D}_A} \end{aligned}$$

which is the cylindrical analog of Eq. 18.7-11. The analog of Eq. 18.7-12 is then

$$W_{AR,0} = (\pi R^2 L)(a)(-k_1'' c_A)$$

Next we evaluate the effectiveness factor

$$\eta_A = \frac{W_{AR}}{W_{AR,0}} = \frac{2I_1(\sqrt{k_1'' a / \mathfrak{D}_A} R)}{(\sqrt{k_1'' a / \mathfrak{D}_A} R) I_0(\sqrt{k_1'' a / \mathfrak{D}_A} R)}$$

The generalized modulus for the cylinder is

$$\Lambda = \sqrt{\frac{k_1'' a}{\mathfrak{D}_A}} \frac{V_P}{S_P} = \sqrt{\frac{k_1'' a}{\mathfrak{D}_A}} \frac{\pi R^2 L}{2\pi R L} = \sqrt{\frac{k_1'' a}{\mathfrak{D}_A}} \frac{R}{2}$$

Therefore the argument of the Bessel functions is

$$\sqrt{k_1'' a / \mathfrak{D}_A} R = 2\Lambda$$

We may now express the effectiveness factor in terms of the generalized modulus thus:

$$\eta_A = \frac{I_1(2\Lambda)}{\Lambda I_0(2\Lambda)}$$

which is the desired result.

## 18D.2 Gas absorption in a falling film with chemical reaction

The problem to be solved is

$$v_{\max} \frac{\partial c_A}{\partial z} = \mathcal{D}_{AB} \frac{\partial^2 c_A}{\partial x^2} - k_1'' c_A$$

with boundary conditions  $c_A(x, 0) = 0$ ,  $c_A(0, z) = c_{A0}$ , and  $c_A(\infty, z) = 0$ , or, in dimensionless notation

$$\frac{\partial c}{\partial \zeta} = \frac{\partial^2 c}{\partial \xi^2} - ac \quad \text{with } c(\xi, 0) = 0, c(0, \zeta) = 1, c(\infty, \zeta) = 0$$

in which  $c = c_A/c_{A0}$ ,  $\zeta = z/L$ ,  $\xi = x\sqrt{v_{\max}/\mathcal{D}_{AB}L}$ , and  $a = k_1''L/v_{\max}$ .

We now take the Laplace transform the partial differential equation and the boundary conditions to get

$$s\bar{c} - c(\xi, 0) = \frac{d^2\bar{c}}{d\xi^2} - a\bar{c} \quad \text{with} \quad \bar{c}(0) = 1/s, \bar{c}(\infty) = 0$$

Because of the boundary condition at  $\zeta = 0$ ,  $c(\xi, 0) = 0$ . The solution of the ordinary differential equation for  $\bar{c}$  with its boundary conditions is

$$\bar{c} = \frac{1}{s} \exp(-\sqrt{(s+a)}\xi)$$

We will not invert this, since all we need is the molar flux at the wall,

$$N_{Ax}(z)|_{x=0} = -\mathcal{D}_{AB} \left. \frac{\partial c_A}{\partial x} \right|_{x=0} = -\mathcal{D}_{AB} c_{A0} \sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}} \left. \frac{dc}{d\xi} \right|_{\xi=0}$$

The Laplace transform of this expression is

$$\overline{N_{Ax}(z)}|_{x=0} = -\mathcal{D}_{AB} c_{A0} \sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}} \left. \frac{d\bar{c}}{d\xi} \right|_{\xi=0} = +\mathcal{D}_{AB} c_{A0} \sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}} \frac{\sqrt{s+a}}{s}$$

Hence the molar flux at the wall is

$$\begin{aligned}
N_{Ax}(z)|_{x=0} &= +\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\mathfrak{L}^{-1}\left\{\frac{\sqrt{s+a}}{s}\right\} \\
&= +\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\mathfrak{L}^{-1}\left\{\frac{s+a}{s\sqrt{s+a}}\right\} \\
&= +\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\left[\mathfrak{L}^{-1}\left\{\frac{1}{\sqrt{s+a}}\right\}+a\mathfrak{L}^{-1}\left\{\frac{1}{s\sqrt{s+a}}\right\}\right] \\
&= +\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\left(\frac{\exp(-a\zeta)}{\sqrt{\pi\zeta}}+\int_0^\zeta\frac{\exp(-a\bar{\zeta})}{\sqrt{\pi\bar{\zeta}}}d\bar{\zeta}\right)
\end{aligned}$$

The first transform was obtained from a table of transforms, and the second by using the convolution theorem.

The total molar flow rate through the interface is then

$$\begin{aligned}
W_A &= W\int_0^L N_{Ax}(z)|_{x=0} dz \\
&= WL\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\int_0^1\left(\frac{\exp(-a\zeta)}{\sqrt{\pi\zeta}}+\int_0^\zeta\frac{\exp(-a\bar{\zeta})}{\sqrt{\pi\bar{\zeta}}}d\bar{\zeta}\right)d\zeta \\
&= WL\mathcal{D}_{AB}C_{A0}\sqrt{\frac{v_{\max}}{\mathcal{D}_{AB}L}}\left[\frac{\operatorname{erf}\sqrt{a}}{\sqrt{a}}+a\left(\frac{\operatorname{erf}\sqrt{a}}{\sqrt{a}}+\frac{\exp(-a)}{\sqrt{\pi a}}-\frac{\operatorname{erf}\sqrt{a}}{2a\sqrt{a}}\right)\right] \\
&= W C_{A0} v_{\max} \sqrt{\mathcal{D}_{AB}/k_1'''}\left[\left(\frac{1}{2}+a\right)\operatorname{erf}\sqrt{a}+\sqrt{a/\pi}\exp(-a)\right]
\end{aligned}$$

The double integral in the second line is evaluated by exchanging the order of integration and then performing the inner integral. In going from the third to the fourth line,  $\sqrt{a}$  was factored out of the denominator.

### 19A.1 Dehumidification of air.

(a) Let A denote H<sub>2</sub>O and B denote air, as in Example 19.4-1. The interfacial mole fraction of A is then estimated as

$$x_{A0} = \frac{p_{\text{H}_2\text{O,vap}}}{p} = \frac{0.178 \text{ psia}}{14.696 \text{ psia}} = 0.0121$$

The "film temperature"  $T_f = \frac{1}{2}(T_0 + T_\delta)$  is 65°F = 291.48 K. The gas-phase properties at  $T_f$  and  $x_B \rightarrow 1.0$  are:

$$\mathcal{D}_{AB} = 0.246 \text{ cm}^2/\text{s} \text{ from Eq. 17.2-1}$$

$$c = p/RT = 4.18 \times 10^{-5} \text{ g-mol/cm}^3$$

$$k = 25.5 \times 10^{-5} \text{ W/cm}\cdot\text{K} \text{ from } \textit{CRC Handbook 2000-2001}, \text{ p. 6-185}$$

The molar heat capacity of the transferred vapor at  $T_f$  is

$$\tilde{C}_{pA} = 8.00 \text{ cal/g}\cdot\text{mol}\cdot\text{K} = 33.47 \text{ J/g}\cdot\text{mol}\cdot\text{K}$$

from O. A. Hougen and K. M. Watson, *CPP Charts*, Wiley, New York (1943), Fig. 26.

Substituting into Eq. 19.4-5 we get:

$$\begin{aligned} \frac{N_{Ay}\tilde{C}_{pA}\delta}{k} &= \left( \frac{N_{Ay}\delta}{c\mathcal{D}_{AB}} \right) \left( \frac{c\mathcal{D}_{AB}\tilde{C}_{pA}}{k} \right) = \left( \ln \frac{1-x_{A\delta}}{1-x_{A0}} \right) \left( \frac{c\mathcal{D}_{AB}\tilde{C}_{pA}}{k} \right) \\ &= \left( \frac{1-0.0180}{1-0.0121} \right) \\ &\quad \cdot \left( \frac{(0.0000418 \times 0.246 \text{ g-mol/cm}\cdot\text{s})(33.47 \text{ J/g}\cdot\text{mol}\cdot\text{K})}{25.5 \times 10^{-5} \text{ W/cm}\cdot\text{K}} \right) \\ &= (-0.00599)(1.350) = -0.0081 \end{aligned}$$

Then the right-hand member of Eq. 19.4-9 takes the value

$$\begin{aligned} \frac{-(N_{Ay}\tilde{C}_{pA}/k)\delta}{1 - \exp(N_{Ay}\tilde{C}_{pA}/k)} &= \frac{0.0081}{1 - \exp(-0.0081)} = \frac{0.0081}{1 - [1 - 0.0081 + \frac{1}{2}(0.0081)^2 + \dots]} \\ &= \frac{1}{1 - \frac{1}{2}(0.0081) + \dots} = 1.004\dots \end{aligned}$$

(b) From Eq. 19.4-9 we see that the quotient just calculated is the ratio of the interfacial conduction fluxes calculated with and without allowance for diffusive energy flux. The diffusive energy flux is evidently unimportant in this problem.



### 19B.1 Steady-state evaporation

a. From Eq. (M) of Table 17.8-1 and the fact that  $B$  is stagnant leads to  $N_{Az} = cv_z^*$ . Equation (D) of Table 17.8-2 states that  $N_{Az} = c_A v_z^* - c \mathcal{D}_{AB} (dx_A/dz)$ . Equating the right sides of these two expressions and dividing by  $c$  gives

$$v_z^* = x_A v_z^* - \mathcal{D}_{AB} \frac{dx_A}{dz} \quad \text{or} \quad v_z^* = -\frac{\mathcal{D}_{AB}}{1-x_A} \frac{dx_A}{dz}$$

b. When this expression for the molar average velocity is combined with Eq. 19.1-17 (when simplified for steady state and unidirectional diffusion with no chemical reactions), we get

$$-\frac{\mathcal{D}_{AB}}{1-x_A} \frac{dx_A}{dz} \cdot \frac{dx_A}{dz} = \mathcal{D}_{AB} \frac{d^2 x_A}{dz^2} \quad \text{or} \quad \frac{d^2 x_A}{dz^2} + \frac{1}{1-x_A} \left( \frac{dx_A}{dz} \right)^2 = 0$$

which is just Eq. 19B.1-1.

c. Equation 19B.1-1 can also be written as (cf. Eq. 18.2-5)

$$(1-x_A) \frac{d}{dz} \left( \frac{1}{1-x_A} \frac{dx_A}{dz} \right) = 0$$

One integration of this equation gives (cf. Eq. 18.2-6)

$$\frac{1}{1-x_A} \frac{dx_A}{dz} = C_1$$

and the second integration gives (cf. Eqs. 18.2-7 and 8)

$$-\ln(1-x_A) = C_1 z + C_2$$

Then one can follow the text in §18.2 until Eq. 18.2-11 is obtained.

## 19B.2 Gas absorption with chemical reaction

Equation 19.1-16 is

$$\rho \left( \frac{\partial \omega_A}{\partial t} + \mathbf{v} \cdot \nabla \omega_A \right) = \rho \mathcal{D}_{AB} \nabla^2 \omega_A + r_A$$

For constant mass density,  $\rho$  can be taken inside the time and space derivatives. This gives:

$$\left( \frac{\partial \rho_A}{\partial t} + \mathbf{v} \cdot \nabla \rho_A \right) = \mathcal{D}_{AB} \nabla^2 \rho_A + r_A$$

We now divide by the molecular weight of species  $A$  to get

$$\left( \frac{\partial c_A}{\partial t} + \mathbf{v} \cdot \nabla c_A \right) = \mathcal{D}_{AB} \nabla^2 c_A + R_A$$

For steady-state diffusion, the time-derivative term can be omitted. Since the bulk motion in the direction of diffusion is presumed to be small, the  $\mathbf{v}$  term can be omitted. Then we further simplify the equation to diffusion in the  $z$  direction. This gives

$$0 = \mathcal{D}_{AB} \frac{d^2 c_A}{dz^2} + R_A$$

where  $R_A$  is the molar rate of production of species  $A$  per unit volume. If  $A$  is disappearing by an irreversible, first-order reaction, then  $R_A = -k_1''' c_A$ , so that we arrive at

$$0 = \mathcal{D}_{AB} \frac{d^2 c_A}{dz^2} - k_1''' c_A$$

which is just Eq. 18.4-4.

### 19B.3 Concentration-dependent diffusivity

a.. For this problem the diffusion equation simplifies to

$$0 = \frac{d}{dz} \left( \mathcal{D}_{AB}(c_A) \frac{dc_A}{dz} \right)$$

b. One integration of this differential equation gives

$$\mathcal{D}_{AB}(c_A) \frac{dc_A}{dz} = C_1$$

and a second integration gives

$$\int_{c_{A0}}^{c_A} \mathcal{D}_{AB}(c'_A) dc'_A = C_1 \int_0^z dz$$

The integration constant may be obtained by applying the boundary condition at  $z = b$ :

$$\int_{c_{A0}}^{c_{Ab}} \mathcal{D}_{AB}(c'_A) dc'_A = C_1 \int_0^b dz$$

Taking the quotient of these two equations gives

$$\frac{\int_{c_{A0}}^{c_A} \mathcal{D}_{AB}(c'_A) dc'_A}{\int_{c_{A0}}^{c_{Ab}} \mathcal{D}_{AB}(c'_A) dc'_A} = \frac{z}{b}$$

which is equivalent to Eq. 19B.3-1.

c. The molar flux at the solid-liquid interface is then

$$N_{Az}|_{z=0} = -\mathcal{D}_{AB} \frac{dc_A}{dz} \Big|_{z=0} = -\mathcal{D}_{AB} \left( \frac{1}{b \mathcal{D}_{AB}} \int_{c_{A0}}^{c_{Ab}} \mathcal{D}_{AB}(c'_A) dc'_A \right)$$

which is equivalent to Eq. 19B.3-2. The quantity in parentheses is the concentration gradient, obtained by differentiating the result in (b) with respect to  $z$  using the Leibniz formula.

d. When Eq. 19B.3-3 is inserted into Eq. 19B.3-2, we get

$$\begin{aligned}
N_{Az}|_{z=0} &= \frac{\overline{D}_{AB}}{b} \int_{c_{Ab}}^{c_{A0}} \left[ 1 + \beta_1(c_A - \bar{c}_A) + \beta_2(c_A - \bar{c}_A)^2 + \dots \right] dc_A \\
&= \frac{\overline{D}_{AB}}{b} \left[ (c_{A0} - c_{Ab}) + \frac{1}{2}\beta_1(c_A - \bar{c}_A)^2 \Big|_{c_{Ab}}^{c_{A0}} + \frac{1}{3}\beta_2(c_A - \bar{c}_A)^3 \Big|_{c_{Ab}}^{c_{A0}} + \dots \right]
\end{aligned}$$

In the second term on the right side we have

$$\begin{aligned}
(c_A - \bar{c}_A)^2 \Big|_{c_{Ab}}^{c_{A0}} &= (c_{A0}^2 - 2c_{A0}\bar{c}_A + \bar{c}_A^2) - (c_{Ab}^2 - 2c_{Ab}\bar{c}_A + \bar{c}_A^2) \\
&= (c_{A0}^2 - c_{Ab}^2) - 2(c_{A0} - c_{Ab})\bar{c}_A \\
&= (c_{A0}^2 - c_{Ab}^2) - 2(c_{A0} - c_{Ab})\frac{1}{2}(c_{A0} + c_{Ab}) = 0
\end{aligned}$$

In the third term on the right side we have

$$\begin{aligned}
(c_A - \bar{c}_A)^3 \Big|_{c_{Ab}}^{c_{A0}} &= (c_{A0}^3 - 3c_{A0}^2\bar{c}_A + 3c_{A0}\bar{c}_A^2 - \bar{c}_A^3) \\
&\quad - (c_{Ab}^3 - 3c_{Ab}^2\bar{c}_A + 3c_{Ab}\bar{c}_A^2 - \bar{c}_A^3) \\
&= (c_{A0}^3 - c_{Ab}^3) + 3(c_{A0}^2 - c_{Ab}^2)\bar{c}_A + 3(c_{A0} - c_{Ab})\bar{c}_A^2 \\
&= (c_{A0} - c_{Ab}) \left[ (c_{A0}^2 + c_{A0}c_{Ab} + c_{Ab}^2) - 3(c_{A0} + c_{Ab})\frac{1}{2}(c_{A0} + c_{Ab}) \right. \\
&\quad \left. + 3\left(\frac{1}{2}\right)^2(c_{A0} + c_{Ab})^2 \right] \\
&= (c_{A0} - c_{Ab}) \left[ \frac{1}{4}c_{A0}^2 - \frac{1}{2}c_{A0}c_{Ab} + \frac{1}{4}c_{Ab}^2 \right] \\
&= \frac{1}{4}(c_{A0} - c_{Ab})(c_{A0} - c_{Ab})^2
\end{aligned}$$

When this is substituted into the molar-flux expression above, we get the result in Eq. 19B.3-4.

*e.* If the diffusivity is linear in the concentration, so that the terms in Eq. 19B.3-3 containing terms higher than the quadratic term may be omitted, then the result in Eq. 19.3-4 is valid, but the expression in brackets is just unity. This means that one gets a valid expression for the mass flux by using the formula for constant diffusivity, but using the diffusivity at the average concentration.

#### 19B.4 Oxidation of silicon

a. Solution of Fick's second law (Eq. 19.1-18) for unidirectional diffusion with the quasi-steady-state assumption gives  $c_A(z) = C_1z + C_2$ . The integration constants are determined from the boundary conditions that  $c_A(0) = c_{A0}$  and  $c_A(\delta) = c_{A\delta}$ . This gives Eq. 19B.4-1.

b. The unsteady molar balance on oxygen gives

$$\frac{d}{dt} \int_{V(t)} c_A(z,t) dV = S \left( -\mathcal{D}_{AB} \left. \frac{dc_A}{dz} \right|_{z=0} - k_1'' c_{A\delta} \right)$$

The left side is the time rate of change of total number of moles of oxygen within the region. The first term on the right side is the rate at which oxygen enters an area  $S$  of the gas-solid interface, and the second term is the rate at which oxygen leaves the system through an area of the silicon-silicon-dioxide interface, by virtue of surface reaction. The left side can be rewritten (using the Leibniz formula) as

$$\int_{V(t)} \frac{\partial c_A}{\partial t} dV + \int_{S(t)} (\mathbf{n} \cdot \mathbf{v}_S) c_A dS \approx c_{A\delta} S \frac{d\delta}{dt}$$

The first term on the left can be neglected, because of the quasi-steady-state assumption. When the right side of this expression and the right side of the previous equation are equated (and divided through by  $S$ ) we get Eq. 19B.4-2.

c. The unsteady molar balance on the silicon dioxide gives

$$\frac{d}{dt} \int_{V(t)} c_B(z,t) dV = S(k_1'' c_{A\delta})$$

This states that the mass of silicon oxide increases because of the

where  $\tilde{V}_B$  is the molar volume of the silicon dioxide. Equating the right sides of the last two equations gives Eq. 19B.4-3.

d. Following the directions given in the text we get

$$\tilde{V}_B k_1'' c_{A\delta}^2 = -\mathfrak{D}_{AB} \left( -\frac{c_{A0} - c_{A\delta}}{\delta} \right) - k_1'' c_{A\delta}$$

and this may be rearranged to give Eq. 19B.4-4.

e. The differential equation for the movement of the boundary is

$$k_1'' \left[ \frac{c_{A0}}{1 + (k_1'' \delta / \mathfrak{D}_{AB})} \right] = \frac{1}{\tilde{V}_B} \frac{d\delta}{dt}$$

or

$$\tilde{V}_B c_{A0} k_1'' = \left( 1 + \frac{k_1'' \delta}{\mathfrak{D}_{AB}} \right) \frac{d\delta}{dt}$$

This is a separable first-order differential equation, which may be solved with the initial condition that  $\delta(0) = 0$ :

$$\tilde{V}_B c_{A0} k_1'' \int_0^t dt = \int_0^\delta \left( 1 + \frac{k_1'' \delta}{\mathfrak{D}_{AB}} \right) d\delta$$

and this yields

$$\tilde{V}_B c_{A0} k_1'' t = \delta + \frac{k_1'' \delta^2}{2\mathfrak{D}_{AB}}$$

which may be rearranged to give Eq. 19B.4-5.

### 19B.5 The Maxwell-Stefan equations for multicomponent gas mixtures

a. If we start with the first form of the Maxwell-Stefan equations, we have

$$\nabla x_A = -\frac{x_A x_B}{\mathcal{D}_{AB}} (\mathbf{v}_A - \mathbf{v}_B)$$

From this, we get, by rearranging

$$c(\mathbf{v}_A - \mathbf{v}_B) = -\frac{c\mathcal{D}_{AB}}{x_A x_B} \nabla x_A$$

which is just Eq. (F) of Table 17.8-2.

b. If we start with the second form of the Maxwell-Stefan equation we have

$$\nabla x_A = -\frac{1}{c\mathcal{D}_{AB}} (x_B \mathbf{N}_A - x_A \mathbf{N}_B) \quad \text{or} \quad x_B \mathbf{N}_A - x_A \mathbf{N}_B = -c\mathcal{D}_{AB} \nabla x_A$$

If now we add and subtract  $x_A \mathbf{N}_A$  on the left side, we get

$$(x_A + x_B) \mathbf{N}_A - x_A (\mathbf{N}_A + \mathbf{N}_B) = -c\mathcal{D}_{AB} \nabla x_A$$

or

$$\mathbf{N}_A = x_A (\mathbf{N}_A + \mathbf{N}_B) - c\mathcal{D}_{AB} \nabla x_A$$

which is just Eq. (D) of Table 17.8-2.

### 19B.6 Diffusion and chemical reaction in a liquid

a. The differential equation for the steady-state diffusion from a sphere is

$$\mathcal{D}_{AB} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc_A}{dr} \right) - k_1''' c_A = 0 \quad \text{or} \quad \frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\Gamma}{d\xi} \right) - b^2 \Gamma = 0$$

According to Eq. C.1-6b, the solution to this equation is

$$\Gamma = \frac{C_1}{\xi} e^{-b\xi} + \frac{C_2}{\xi} e^{b\xi}$$

Application of the boundary conditions that  $\Gamma(1) = 1$  and  $\Gamma(\infty) = 0$  determines the constants, and the final result is (cf. Eq. 19B.6-1)

$$\Gamma = \frac{1}{\xi} \frac{e^{-b\xi}}{e^{-b}}$$

The mass flux at the sphere surface is then

$$N_{Ar}|_{r=R} = -\mathcal{D}_{AB} \frac{dc_A}{dr} \Big|_{r=R} = -\frac{\mathcal{D}_{AB} c_{A0}}{R} \frac{d\Gamma}{d\xi} \Big|_{\xi=1} = +\frac{\mathcal{D}_{AB} c_{A0}}{R} (1+b)$$

and the total loss of A from the sphere in moles per unit time is

$$W_A = 4\pi R^2 \left( \frac{\mathcal{D}_{AB} c_{A0}}{R} \right) \left( 1 + \sqrt{\frac{k_1''' R^2}{\mathcal{D}_{AB}}} \right)$$

b. The unsteady-state mass balance on the dissolving sphere of species A is

$$-\frac{d}{dt} \left( \frac{4}{3} \pi R^3 \rho_{\text{sph}} \right) = 4\pi R^2 \left( \frac{\mathcal{D}_{AB} c_{A0} M_A}{R} \right) \left( 1 + \sqrt{\frac{k_1''' R^2}{\mathcal{D}_{AB}}} \right)$$



Since we have used here the steady-state expression for the molar flux at the surface of the sphere, this is a quasi-steady-state treatment.

The integration of this equation can be accomplished as follows: First we divide through by  $4\pi\rho_{\text{sph}}$  to get

$$-R^2 \frac{dR}{dt} = \frac{\mathcal{D}_{AB}c_{A0}M_A}{\rho_{\text{sph}}} R \left( 1 + \sqrt{\frac{k_1'''R^2}{\mathcal{D}_{AB}}} \right)$$

Next, put all the factors containing  $R$  on the left side

$$-\frac{R}{1 + (k_1'''R^2/\mathcal{D}_{AB})} \frac{dR}{dt} = \frac{\mathcal{D}_{AB}c_{A0}M_A}{\rho_{\text{sph}}}$$

Next we introduce a new dimensionless variable  $Y = R\sqrt{k_1'''/\mathcal{D}_{AB}}$  and write

$$-\frac{Y}{1+Y} \frac{dY}{dt} = \frac{k_1''c_{A0}M_A}{\rho_{\text{sph}}}$$

Then we integrate

$$-\int_{Y_0}^Y \frac{Y}{1+Y} dY = \frac{k_1''c_{A0}M_A}{\rho_{\text{sph}}} \int_{t_0}^t dt$$

and finally

$$(Y - Y_0) - \ln \frac{1+Y}{1+Y_0} = -\frac{k_1''c_{A0}M_A}{\rho_{\text{sph}}} (t - t_0) \quad \text{or}$$

$$\sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} (R - R_0) - \ln \frac{1 + \sqrt{k_1'''/\mathcal{D}_{AB}} R}{1 + \sqrt{k_1'''/\mathcal{D}_{AB}} R_0} = -\frac{k_1''c_{A0}M_A}{\rho_{\text{sph}}} (t - t_0)$$

From this one can get the dependence of the sphere radius on the time.

### 19B.7 Various forms of the species continuity equation

a. To get Eq. (A) of Table 19.2-1 from Eq. 19.1-7, use Eq. (C) of Table 17.7-1, in the form  $\rho_\alpha = \rho\omega_\alpha$  on the left side of Eq. 19.1-7, and Eq. (S) of Table 17.8-1 on the right side.

To get Eq. (b) of Table 19.2-3 from Eq. 19.1-7, move the term  $-(\nabla \cdot \rho_\alpha \mathbf{v}^*)$  to the left side of the equation, and then use Eq. 3.5-4 (with  $f$  identified as  $\omega_\alpha$ ).

b. Rearrange Eq. 19.1-11 to get

$$\frac{\partial c_\alpha}{\partial t} + (\nabla \cdot c_\alpha \mathbf{v}^*) = -(\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha$$

Then rewrite the divergence term on the left side by differentiating the product

$$\frac{\partial c_\alpha}{\partial t} + c_\alpha (\nabla \cdot \mathbf{v}^*) + (\mathbf{v}^* \cdot \nabla c_\alpha) = -(\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha$$

Then write  $c_\alpha = cx_\alpha$  and once again differentiate the products, thus:

$$c \frac{\partial x_\alpha}{\partial t} + x_\alpha \frac{\partial c}{\partial t} + x_\alpha c (\nabla \cdot \mathbf{v}^*) + c (\mathbf{v}^* \cdot \nabla x_\alpha) + x_\alpha (\mathbf{v}^* \cdot \nabla c) = -(\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha$$

or, on rearranging

$$c \left( \frac{\partial x_\alpha}{\partial t} + (\mathbf{v}^* \cdot \nabla x_\alpha) \right) + x_\alpha \left( \frac{\partial c}{\partial t} + (\nabla \cdot c \mathbf{v}^*) \right) = -(\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha$$

Next we may make use of the overall equation of continuity in Eq. 19.1-12 to modify the second term on the left (with the prefactor  $x_\alpha$ )

$$c \left( \frac{\partial x_\alpha}{\partial t} + (\mathbf{v}^* \cdot \nabla x_\alpha) \right) + x_\alpha \sum_{\beta=1}^N R_\beta = -(\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha$$

This equation can be put into the form given in Eq. 19.1-15. No assumptions have been made in getting to this result from Eq. 19.1-11.

### 19C.1 Alternate form of the binary diffusion equation

Equation 19.1-17, in the absence of chemical reactions, is

$$\frac{\partial x_A}{\partial t} + (\mathbf{v}^* \cdot \nabla x_A) = \mathfrak{D}_{AB} \nabla^2 x_A$$

Equation 19C.1-1 can be written as

$$\begin{aligned} \frac{1}{M} \frac{\partial M}{\partial t} + \frac{1}{M} (\mathbf{v} \cdot \nabla M) &= \mathfrak{D}_{AB} \left( \nabla \cdot \frac{1}{M} \nabla M \right) \\ &= \mathfrak{D}_{AB} \left[ \frac{1}{M} \nabla^2 M - \frac{1}{M^2} (\nabla M \cdot \nabla M) \right] \end{aligned}$$

To compare this with Eq. 19.1-17, we multiply through by  $M$  and then replace  $M$  by its definition:  $M = x_A M_A + x_B M_B = x_A M_A + (1 - x_A) M_B = x_A (M_A - M_B) + M_B$ . This leads to

$$\frac{\partial x_A}{\partial t} + (\mathbf{v} \cdot \nabla x_A) = \mathfrak{D}_{AB} \nabla^2 x_A + \mathfrak{D}_{AB} \frac{(M_A - M_B)(\nabla x_A \cdot \nabla x_A)}{M}$$

To get this result, we have also divided through by the factor  $M_A - M_B$  (which is never exactly equal to zero).

When this last equation is compared to the first equation above, we see that the two results are the same, if

$$\mathbf{v}^* = \mathbf{v} + (1/M)(M_A - M_B) \mathfrak{D}_{AB} \nabla x_A$$

To show this we introduce the definitions of  $\mathbf{v}$  and  $\mathbf{v}^*$ , and also Fick's first law in the form of Eq. (F) of Table 17.8-2. This yields

$$\begin{aligned} x_A \mathbf{v}_A + x_B \mathbf{v}_B &= \frac{1}{M} (M_A x_A \mathbf{v}_A + M_B x_B \mathbf{v}_B) - \frac{M_A - M_B}{M} x_A x_B (\mathbf{v}_A - \mathbf{v}_B) \\ &= \frac{1}{M} [(M_A - M_A x_B + M_B x_B) x_A \mathbf{v}_A + (M_B - M_B x_A + M_A x_A) x_B \mathbf{v}_B] \\ &= (1/M) [(M_A x_A + M_B x_B) x_A \mathbf{v}_A + (M_B x_B + M_A x_A) x_B \mathbf{v}_B] \end{aligned}$$

Since this is an identity, the proof is completed.

### 19D.1 Derivation of the equation of continuity

a. The equation of continuity for species  $A$  states that for an arbitrary fixed volume  $V$  the time rate of change of the total mass of species  $A$  must equal the net rate of addition of  $A$  over the bounding surface  $S$  (by convection and diffusion) plus the rate of production of species  $A$  by chemical reactions. This statement in integral form is given by Eq. 19D.1-1. The surface integral may be transformed into a volume integral by using the Gauss divergence theorem to give

$$\int_V \frac{\partial}{\partial t} \rho_A dV = - \int_V (\nabla \cdot \mathbf{n}_A) dV + \int_V r_A dV$$

Here we have also moved the time-derivative operator inside the integral, inasmuch as the volume is not changing with time. Since the volume is completely arbitrary, we may remove the integral signs to get the equation of motion in the form of Eq. 19.1-6:

$$\frac{\partial \rho_A}{\partial t} = -(\nabla \cdot \mathbf{n}_A) + r_A$$

b. For an arbitrarily chosen "blob" of fluid, contained within the volume  $V(t)$ , whose boundaries are moving with the mass-average velocity, we may write the mass conservation statement as follows: the time rate of change of  $A$  within the volume equals the rate of addition of  $A$  by diffusion across the surface  $S(t)$ , plus the rate of production of  $A$  by chemical reaction within  $V(t)$  :

$$\frac{d}{dt} \int_{V(t)} \rho_A dV = - \int_{S(t)} (\mathbf{n} \cdot \mathbf{j}_A) dS + \int_{V(t)} r_A dV$$

Next we apply the Leibniz formula to the left side to get

$$\int_{V(t)} \frac{\partial}{\partial t} \rho_A dV + \int_{S(t)} \rho_A (\mathbf{n} \cdot \mathbf{v}_S) dS = - \int_{S(t)} (\mathbf{n} \cdot \mathbf{j}_A) dS + \int_{V(t)} r_A dV$$

This may be rearranged to give

$$\int_{V(t)} \frac{\partial}{\partial t} \rho_A dV = - \int_{S(t)} (\mathbf{n} \cdot (\mathbf{j}_A + \rho_A \mathbf{v})) dS + \int_{V(t)} r_A dV$$

where use has been made of the fact that the surface of the blob is everywhere moving with the mass-average velocity, i.e.,  $\mathbf{v}_s = \mathbf{v}$ . Then, we make use of the Gauss divergence theorem for the surface integral, to obtain

$$\int_{V(t)} \frac{\partial}{\partial t} \rho_A dV = - \int_{V(t)} (\nabla \cdot (\mathbf{j}_A + \rho_A \mathbf{v})) dV + \int_{V(t)} r_A dV$$

Since the volume element  $V(t)$  was chosen arbitrarily, we may remove the integrals to get the species equation of continuity for  $A$  in the form of Eq. 19.1-7:

$$\frac{\partial \rho_A}{\partial t} = -(\nabla \cdot (\mathbf{j}_A + \rho_A \mathbf{v})) + r_A$$

## 19D.2 Derivation of the equation of change for temperature for a multicomponent system

a. Applying the chain rule for the functions related in Eq. 19D.2-1, we get

$$\begin{aligned} \left( \frac{\partial H}{\partial m_\alpha} \right)_{m_\gamma} &= \sum_{\beta=1}^{N-1} \left( \frac{\partial(m\hat{H})}{\partial \omega_\beta} \right)_{\omega_\gamma, m} \left( \frac{\partial \omega_\beta}{\partial m_\alpha} \right)_{m_\gamma} + \left( \frac{\partial(m\hat{H})}{\partial m} \right)_{\omega_\gamma} \left( \frac{\partial m}{\partial m_\alpha} \right)_{m_\gamma} \\ &= m \sum_{\beta=1}^{N-1} \left( \frac{\partial \hat{H}}{\partial \omega_\beta} \right)_{\omega_\gamma} \left( \frac{\delta_{\alpha\beta}}{\sum_\gamma m_\gamma} - \frac{m_\beta}{(\sum_\gamma m_\gamma)^2} \right) + \hat{H} \\ &= \sum_{\beta=1}^{N-1} \left( \frac{\partial \hat{H}}{\partial \omega_\beta} \right)_{\omega_\gamma} \left( \delta_{\alpha\beta} - \frac{m_\beta}{m} \right) + \hat{H} \quad (\text{for } \alpha \neq N) \end{aligned}$$

$$\begin{aligned} \left( \frac{\partial H}{\partial m_N} \right)_{m_\gamma} &= \sum_{\beta=1}^{N-1} \left( \frac{\partial(m\hat{H})}{\partial \omega_\beta} \right)_{\omega_\gamma, m} \left( \frac{\partial \omega_\beta}{\partial m_N} \right)_{m_\gamma} + \left( \frac{\partial(m\hat{H})}{\partial m} \right)_{\omega_\gamma} \left( \frac{\partial m}{\partial m_N} \right)_{m_\gamma} \\ &= m \sum_{\beta=1}^{N-1} \left( \frac{\partial \hat{H}}{\partial \omega_\beta} \right)_{\omega_\gamma} \left( -\frac{m_\beta}{m^2} \right) + \hat{H} = \sum_{\beta=1}^{N-1} \left( \frac{\partial \hat{H}}{\partial \omega_\beta} \right)_{\omega_\gamma} \left( -\frac{m_\beta}{m} \right) + \hat{H} \quad (\text{for } \alpha = N) \end{aligned}$$

Subtraction of these two results gives Eq. 19D.2-4.

b. Regard  $H$  as a function of  $p$ ,  $T$ , and the first  $(N - 1)$  mass fractions, so that

$$d\hat{H} = \left( \frac{\partial \hat{H}}{\partial p} \right)_{T, \omega_\gamma} dp + \left( \frac{\partial \hat{H}}{\partial T} \right)_{p, \omega_\gamma} dT + \sum_{\alpha=1}^{N-1} \left( \frac{\partial \hat{H}}{\partial \omega_\alpha} \right)_{p, T, \omega_\gamma} d\omega_\alpha$$

When this is applied to a fluid element moving with the fluid, Eq. 19D.2-5 results. Equations 19D.2-6 and 7 are standard thermodynamic results.

c. Because of the relation  $m_\alpha = n_\alpha M_\alpha$ , the differential quotients in the last term in the last equation can be rewritten, with the help of Eq. 19D.2-4, in terms of partial molar quantities:

$$\begin{aligned} \left( \frac{\partial \hat{H}}{\partial \omega_\alpha} \right)_{\omega_\gamma} &= \left( \frac{\partial H}{\partial m_\alpha} \right)_{m_\gamma} - \left( \frac{\partial H}{\partial m_N} \right)_{m_\gamma} \\ &= \frac{1}{M_\alpha} \left( \frac{\partial H}{\partial n_\alpha} \right)_{m_\gamma} - \frac{1}{M_N} \left( \frac{\partial H}{\partial n_N} \right)_{m_\gamma} = \frac{\bar{H}_\alpha}{M_\alpha} - \frac{\bar{H}_N}{M_N} \end{aligned}$$

In Eq. 19D.2-5, we use Eq. (E) of Table 19.2-4 for the substantial derivative of the enthalpy, and we use Eq. 19.1-14 for the substantial derivative of the mole fractions. We also use Eqs. 19D.2-6 and 7 for the other differential quotients. Then Eq. 19D.2-5 becomes

$$\begin{aligned} -(\nabla \cdot \mathbf{q}) - (\boldsymbol{\tau} : \nabla \mathbf{v}) + \frac{Dp}{Dt} &= \left[ 1 - \left( \frac{\partial \ln \hat{V}}{\partial \ln T} \right)_{p, \omega_\gamma} \right] \frac{Dp}{Dt} + \rho \hat{C}_p \frac{DT}{Dt} \\ &\quad + \sum_{\alpha=1}^{N-1} \left( \frac{\bar{H}_\alpha}{M_\alpha} - \frac{\bar{H}_N}{M_N} \right) (-(\nabla \cdot \mathbf{j}_\alpha) + r_\alpha) \end{aligned}$$

d. Rearranging we get

$$\begin{aligned} \rho \hat{C}_p \frac{DT}{Dt} &= -(\nabla \cdot \mathbf{q}) - (\boldsymbol{\tau} : \nabla \mathbf{v}) + \left( \frac{\partial \ln \hat{V}}{\partial \ln T} \right)_{p, \omega_\gamma} \frac{Dp}{Dt} \\ &\quad + \sum_{\alpha=1}^{N-1} \left( \frac{\bar{H}_\alpha}{M_\alpha} - \frac{\bar{H}_N}{M_N} \right) ((\nabla \cdot \mathbf{j}_\alpha) - r_\alpha) \end{aligned}$$

The last term in this equation can be simplified as follows:

$$\begin{aligned} &+ \sum_{\alpha=1}^{N-1} \frac{\bar{H}_\alpha}{M_\alpha} ((\nabla \cdot \mathbf{j}_\alpha) - r_\alpha) - \left( \sum_{\alpha=1}^{N-1} ((\nabla \cdot \mathbf{j}_\alpha) - r_\alpha) \right) \frac{\bar{H}_N}{M_N} \\ &= \sum_{\alpha=1}^{N-1} \bar{H}_\alpha ((\nabla \cdot \mathbf{J}_\alpha) - R_\alpha) + \bar{H}_N ((\nabla \cdot \mathbf{J}_N) - R_N) \\ &= \sum_{\alpha=1}^N \bar{H}_\alpha ((\nabla \cdot \mathbf{J}_\alpha) - R_\alpha) \end{aligned}$$

This, then, leads to Eq. (F) of Table 19.2-4.

### 19D.3 Gas separation by atmolysis or "sweep diffusion"

a. The Maxwell-Stefan equation for a three-component mixture are

$$\frac{dx_A}{dz} = \frac{1}{c\mathcal{D}_{AB}}(x_A N_{Bz} - x_B N_{Az}) + \frac{1}{c\mathcal{D}_{AC}}(x_A N_{Cz} - x_C N_{Az})$$

$$\frac{dx_B}{dz} = \frac{1}{c\mathcal{D}_{AB}}(x_B N_{Az} - x_A N_{Bz}) + \frac{1}{c\mathcal{D}_{BC}}(x_B N_{Cz} - x_C N_{Bz})$$

We now make the substitution  $x_C = 1 - x_A - x_B$  in order to have just two independent variables. Then by introducing the indicated dimensionless variables, we get Eqs. 19D.3-1 and 2.

b. Next we take the Laplace transform of Eqs. 19D.3-1 and 2:

$$p\bar{x}_A - x_{A1} = Y_{AA}\bar{x}_A + Y_{AB}\bar{x}_B + p^{-1}Y_A$$

$$p\bar{x}_B - x_{B1} = Y_{BA}\bar{x}_A + Y_{BB}\bar{x}_B + p^{-1}Y_B$$

This set of equations can be solved simultaneously to give for  $\bar{x}_A$

$$\bar{x}_A = \frac{X_A(x_{A1}, x_{B1}; p)}{p(p - p_+)(p - p_-)}$$

in which  $p_+$  and  $p_-$  are given by Eq. 19D.3-4, and  $X_A(x_{A1}, x_{B1}; p)$  by Eq. 19D.3-5. Similar equations can be given for  $\bar{x}_B$  by interchanging the subscripts A and B.

The transformed expression  $\bar{x}_A$  can be inverted by using the Heaviside partial fractions expansion theorem if we exclude the relatively unimportant cases  $p_+ = p_-$  and  $p_+$  (or  $p_-$ ) = 0. Thus we get

$$x_A(\zeta) = \frac{X(x_{A1}, x_{B1}; 0)}{p_+ p_-} + \frac{X(x_{A1}, x_{B1}; p_+) e^{p_+ \zeta}}{p_+ (p_+ - p_-)} + \frac{X(x_{A1}, x_{B1}; p_-) e^{p_- \zeta}}{p_- (p_- - p_+)}$$

The expression for  $x_B$  is obtained by interchanging all indices A and B.



c. Finally, at  $\zeta = 1$ ,  $x_A = x_{A2}$ , so that

$$x_{A2} = \frac{X(x_{A1}, x_{B1}; 0)}{p_+ p_-} + \frac{X(x_{A1}, x_{B1}; p_+) e^{p_+ \zeta}}{p_+ (p_+ - p_-)} + \frac{X(x_{A1}, x_{B1}; p_-) e^{p_- \zeta}}{p_- (p_- - p_+)}$$

and a similar expression for  $x_B$ . We hence have a pair of equations giving the relations among  $x_{A1}$ ,  $x_{A2}$ ,  $x_{B1}$ , and  $x_{B2}$ , the dimensionless fluxes  $v_\alpha$ , and the dimensionless diffusivity ratios. Keys and Pigford go further and give a plot of the separation factor

$$\alpha = \frac{x_{A2}/x_{B2}}{x_{A1}/x_{B1}}$$

for the special case of very small mole fractions.

Note that the choice of notation in this problem has the advantage that there is symmetry between  $A$  and  $B$ , which makes it easy to give the results for both species after the result for one species has been worked out.

### 19D.4 Steady-state diffusion from a rotating disk

a. Equation 19.1-16 for steady-state diffusion in the absence of chemical reactions is

$$(\mathbf{v} \cdot \nabla \rho_A) = \mathfrak{D}_{AB} \nabla^2 \rho_A(z)$$

For the special case that  $\rho_A$  depends on  $z$  alone, the diffusion equation simplifies further to

$$v_z \frac{d\rho_A}{dz} = \mathfrak{D}_{AB} \frac{d^2 \rho_A}{dz^2} \quad \text{or} \quad H(\zeta) \frac{d\rho_A}{d\zeta} = \frac{1}{Sc} \frac{d^2 \rho_A}{d\zeta^2}$$

in which the dimensionless coordinate  $\zeta = z\sqrt{\Omega/\nu}$  has been introduced.

b. The differential equation is solved by setting  $d\rho_A/d\zeta = p$ , so that we get the first-order separable equation  $dp/d\zeta = ScH(\zeta)p$ , which has the solution

$$\ln p = Sc \int_0^\zeta H(\zeta) d\zeta + \ln C_1 \quad \text{or} \quad \frac{d\rho_A}{d\zeta} = p = C_1 \exp\left(Sc \int_0^\zeta H(\bar{\zeta}) d\bar{\zeta}\right)$$

A further integration gives

$$\rho_A = C_1 \int_0^\zeta \exp\left(Sc \int_0^{\bar{\zeta}} H(\bar{\zeta}) d\bar{\zeta}\right) d\bar{\zeta} + C_2$$

The boundary conditions that  $\rho_A(0) = \rho_{A0}$  and  $\rho_A(\infty) = 0$  then give

$$\frac{\rho_A}{\rho_{A0}} = 1 - \frac{\int_0^\zeta \exp\left(Sc \int_0^{\bar{\zeta}} H(\bar{\zeta}) d\bar{\zeta}\right) d\bar{\zeta}}{\int_0^\infty \exp\left(Sc \int_0^{\bar{\zeta}} H(\bar{\zeta}) d\bar{\zeta}\right) d\bar{\zeta}} \rightarrow 1 - \frac{\int_0^\zeta \exp\left(\frac{1}{3} Sca \bar{\zeta}^3\right) d\bar{\zeta}}{\int_0^\infty \exp\left(\frac{1}{3} Sca \bar{\zeta}^3\right) d\bar{\zeta}}$$

the second expression being the high Schmidt number limit, i.e., taking only the first term in the expansion for  $H$ . The integral in the denominator can be evaluated analytically

$$\int_0^{\infty} \exp\left(\frac{1}{3} Sca \bar{\zeta}^3\right) d\bar{\zeta} = \frac{\int_0^{\infty} \exp(-u^3) du}{\sqrt[3]{\frac{1}{3} Sca}} = \frac{\frac{1}{3} \Gamma\left(\frac{1}{3}\right)}{\sqrt[3]{\frac{1}{3} Sca}}$$

Hence the final expression for the concentration profile is

$$\frac{\rho_A}{\rho_{A0}} = 1 - \frac{\sqrt[3]{\frac{1}{3} Sca}}{\Gamma\left(\frac{4}{3}\right)} \int_0^{\zeta} \exp\left(-\frac{1}{3} Sca \bar{\zeta}^3\right) d\bar{\zeta}$$

c. The mass flux in the  $z$  direction is then

$$j_{Az} = -\mathcal{D}_{AB} \frac{d\rho_A}{dz} = +\rho_{A0} \mathcal{D}_{AB} \frac{\sqrt[3]{\frac{1}{3} Sca}}{\Gamma\left(\frac{4}{3}\right)} \exp\left(-\frac{1}{3} Sca \zeta^3\right) \frac{d\zeta}{dz}$$

in which  $d\zeta/dz = \sqrt{\Omega/\nu}$ . At the surface of the disk the mass flux is

$$\begin{aligned} j_{Az}|_{z=0} &= \rho_{A0} \mathcal{D}_{AB} \frac{\sqrt[3]{\frac{1}{3} Sca}}{\Gamma\left(\frac{4}{3}\right)} \sqrt{\frac{\Omega}{\nu}} = \frac{\sqrt[3]{\frac{1}{3} (0.510)}}{\Gamma\left(\frac{4}{3}\right)} \rho_{A0} \mathcal{D}_{AB} Sc^{1/3} \Omega^{1/2} \nu^{-1/2} \\ &= 0.620 \rho_{A0} \mathcal{D}_{AB} (\nu/\mathcal{D}_{AB})^{1/3} \Omega^{1/2} \nu^{-1/2} \end{aligned}$$

which is the result in Eq. 19D.4-7.

### 20A.1 Measurement of diffusivity by unsteady-state evaporation.

Assuming ideal gas behavior, and insolubility of species "B" in the liquid, we estimate the mole fraction of ethyl propionate in the interfacial vapor as

$$x_{A0} = \frac{p_{A,\text{vap}}}{p} = \frac{41.5}{761.2} = 0.0545$$

Eq. 20.1-1-22 gives

$$\Delta V(t) = Sx_{A0}\psi\sqrt{\frac{4D_{AB}}{\pi}}[\sqrt{t} - \sqrt{240}]$$

Linear interpolation to  $x_{A0} = 0.0545$  in Table 20.1-1 gives  $\psi = 1.0235$ , whence

$$\begin{aligned} D_{AB} \text{ cm}^2/\text{s} &= \frac{\pi}{4(Sx_{A0}\psi)^2} \left[ \frac{\Delta V(t)}{\sqrt{t} - \sqrt{240}} \right]^2 \\ &= 16.48 \left[ \frac{\Delta V(t)}{\sqrt{t} - \sqrt{240}} \right]^2 \end{aligned}$$

with  $\Delta V$  in  $\text{cm}^3$  and  $t$  in s. Application of this formula to the tabulated data gives the following results:

$\sqrt{t}$	15.5	19.4	23.4	26.9	30.5	34.0	37.5	41.5
$D_{AB}$	1.2	0.0281	0.0278	0.0272	0.0273	0.0270	0.0273	0.0269

The average of the last seven determinations of  $D_{AB}$  is  $0.0274 \text{ cm}^2/\text{s}$ .

## 20A.2 Absorption of oxygen from a growing bubble.

The interfacial molar flux of oxygen into the liquid is given by Eq. 20.1-75 as

$$N_{A0}(t) = c_{A0} \sqrt{\frac{(2n+1)\mathcal{D}_{AB}}{\pi t}}$$

for a bubble with interfacial area  $S(t) = at^n$  and interfacial liquid concentration  $c_{A0}$ , when  $a$ ,  $n$  and  $c_{A0}$  are constants. The solubility  $\omega_{A0}$  corresponds to a molar concentration

$$\begin{aligned} c_{A0} &= \rho\omega_{A0}/M_A \\ &= (1.0 \text{ g soln/cm}^3)(7.78 \times 10^{-4} \text{ g O}_2/\text{g soln})/(32 \text{ g O}_2/\text{g-mol O}_2) \\ &= 2.43 \times 10^{-5} \text{ g-mol O}_2/\text{cm}^3 \end{aligned}$$

which is used here as the interfacial concentration of dissolved  $\text{O}_2$ .

(a) For constant growth rate of the bubble volume,  $r_s^3 \propto t$ , so that  $r_s \propto t^{1/3}$  and  $S(t) \propto r_s^2 \propto t^{2/3}$ , giving  $n = 2/3$  in Eq. 20.1-75. Then at  $t = 2$  s, the interfacial molar flux of  $\text{O}_2$  into the liquid is

$$\begin{aligned} N_{A0}(t) &= c_{A0} \sqrt{\frac{(\frac{4}{3} + 1)\mathcal{D}_{AB}}{\pi t}} \\ &= (2.43 \times 10^{-5} \text{ g-mol/cm}^3) \sqrt{\frac{(7/3)(2.60 \times 10^{-5} \text{ cm}^2/\text{s})}{(3.1416)(2 \text{ s})}} \\ &= 7.55 \times 10^{-8} \text{ g-mol/cm}^2 \cdot \text{s} \end{aligned}$$

The total absorption rate in g/s is then

$$\begin{aligned} w_A(t) &= 4\pi r_s^2(t)N_{A0}(t)M_A \\ &= 4\pi(0.1/2 \text{ cm})^2(7.55 \times 10^{-8} \text{ g-mol/cm}^2 \cdot \text{s})(32 \text{ g/g-mol}) \\ &= 7.6 \times 10^{-8} \text{ g/s} \end{aligned}$$

(b) For constant radial growth rate,  $r_s \propto t$  and  $S(t) \propto t^2$ , giving  $n = 2$  in Eq. 20.1-75. Then the interfacial flux at time  $t = 2$  s is

$$\begin{aligned} N_{A0} &= c_{A0} \sqrt{\frac{(4+1)\mathcal{D}_{AB}}{\pi t}} \\ &= (2.43 \times 10^{-5} \text{ g-mol/cm}^3) \sqrt{\frac{(5)(2.60 \times 10^{-5} \text{ cm}^2/\text{s})}{\pi(2 \text{ s})}} \\ &= 1.11 \times 10^{-7} \text{ g-mol/cm}^2 \cdot \text{s} \end{aligned}$$

and the total absorption rate in g/s is

$$\begin{aligned} w_A &= 4\pi r_s^2(t)N_{A0}(t)M_A \\ &= 4\pi(0.1/2 \text{ cm})^2(1.11 \times 10^{-7} \text{ g-mol/cm}^2 \cdot \text{s})(32 \text{ g/g-mol}) \\ &= 1.11 \times 10^{-7} \text{ g/s} \end{aligned}$$

### 20A.3 Rate of evaporation of *n*-octane.

Table E-1 gives the following Lennard-Jones parameters:

Species	M	$\sigma$ , Å	$\epsilon$ , K
A: <i>n</i> -C <sub>8</sub> H <sub>18</sub>	114.23	7.035	361.
B: N <sub>2</sub>	28.013	3.667	99.8

Eqs. 17.3-14,15 then give the interaction parameters  $\sigma_{AB} = 5.351$  Å and  $\epsilon_{AB} = 189.8$  K, and Eq. 17.3-10 gives

$$\begin{aligned} \mathcal{D}_{AB}, \text{ cm}^2/\text{s} &= 0.0018583 \sqrt{(293.15)^3 \left( \frac{1}{114.23} + \frac{1}{28.013} \right) \frac{1}{(p, \text{ atm})(5.351)^2(1.185)}} \\ &= 0.0580/(p, \text{ atm}) \end{aligned}$$

(a) If  $p = 1$  atm, then  $\mathcal{D}_{AB} = 0.0580$  cm<sup>2</sup>/s and  $x_{A0} = 10.45/760 = 0.01375$ . Interpolation in Table 20.1-1 gives  $\varphi = 0.00859$ , and Eq. 20.1-20 gives the volume of vapor produced in 24.5 hr as

$$\begin{aligned} V_A &= S\varphi\sqrt{4\mathcal{D}_{AB}t} \\ &= (1.29 \text{ cm}^2)(0.00859)\sqrt{4(0.0580 \text{ cm}^2/\text{s})(24.5 \times 3600 \text{ s})} \\ &= 1.585 \text{ cm}^3 \end{aligned}$$

The mass of vapor produced in 24.5 hr is

$$\begin{aligned} m_A &= \frac{pV_A M_A}{RT} \\ &= \frac{(1 \text{ atm})(1.585 \text{ cm}^3)(114.23 \text{ g/g-mol})}{82.0578 \times 293.15 \text{ cm}^3 \text{ atm/g-mol}} \\ &= 0.0075 \text{ g} \end{aligned}$$

(b) If  $p = 2$  atm, then  $\mathcal{D}_{AB} = 0.0290$  cm<sup>2</sup>/s and  $x_{A0} = 0.01375/2 = 0.0688$ . Table 20.1-1 then gives  $\varphi = 0.00430$ , whence

$$\begin{aligned} V_A &= S\varphi\sqrt{4\mathcal{D}_{AB}t} \\ &= (1.29 \text{ cm}^2)(0.00430)\sqrt{4(0.0290 \text{ cm}^2/\text{s})(24.5 \times 3600 \text{ s})} \\ &= 0.561 \text{ cm}^3 \end{aligned}$$

and the mass of vapor produced in 24.5 hr is

$$\begin{aligned} m_A &= \frac{pV_A M_A}{RT} \\ &= \frac{(2 \text{ atm})(0.561 \text{ cm}^3)(114.23 \text{ g/g-mol})}{82.0578 \times 293.15 \text{ cm}^3 \text{ atm/g-mol}} \\ &= 0.0053 \text{ g} \end{aligned}$$

#### 20A.4 Effect of bubble size on interfacial composition.

Equations 20A.4-1 and 2 give

$$\omega_A = H \left[ p_\infty + \frac{2\sigma}{r_s} \right]$$

Assuming  $H$  to be independent of  $r_s$ , the ratio of  $\omega_A$  to its value for a very large bubble is

$$\frac{\omega_{A0}(r)}{\omega_{A0}(\infty)} = \frac{p_\infty + 2\sigma/r_s}{p_\infty} = 1 + \frac{2\sigma}{p_\infty r_s}$$

Thus, the bubble radius corresponding to a 10% increase of  $\omega_{A0}$  over its value for a very large bubble is given by

$$\frac{2\sigma}{p_\infty r_s} = 0.1 \quad \text{or} \quad r_s = \frac{2\sigma}{p_\infty}$$

For a gas bubble in water at 25°C, with  $p_\infty = 1$  atm, this gives the required bubble radius as

$$\begin{aligned} r_s &= \frac{(2)(72 \text{ dynes/cm})}{(0.1)(1.0133 \times 10^6 \text{ dyne/cm}^2)} \\ &= 0.00142 \text{ cm} = 14 \text{ microns} \end{aligned}$$

The (normally minor) dependence of liquid-phase free energy on total pressure has been neglected here. To include this effect, one would need partial molar volume data for the particular system.

### 20A.5 Absorption with rapid second-order reaction

a. The first thing one has to do is to determine the parameter  $\gamma$  from Eq. 20.1-37, using the concentrations and diffusivities given in Fig. 20.1-2. By a trial-and-error procedure we have found that  $\gamma = 4.9 \times 10^{-5} \text{ mm}^2/\text{s}$ . We now verify this by substituting into Eq. 20.1-37. We first have to convert the diffusivities in  $\text{ft}^2/\text{hr}$  into units of  $\text{mm}^2/\text{s}$ :

$$\mathcal{D}_{AS} = (3.9 \times 10^{-5} \text{ ft}^2/\text{hr}) \frac{(12 \cdot 2.54 \cdot 10 \text{ mm}/\text{ft})^2}{3600 \text{ s/hr}} = 1.006 \times 10^{-3} \text{ mm}^2/\text{s}$$

$$\mathcal{D}_{BS} = 1.95 \times 10^{-5} \text{ ft}^2/\text{hr} = 0.503 \times 10^{-3} \text{ mm}^2/\text{s}$$

Substituting into Eq. 20.1-37 now gives:

$$1 - \text{erf} \sqrt{\frac{4.9 \times 10^{-5}}{0.503 \times 10^{-3}}}$$

$$= \left(\frac{4}{1}\right) \sqrt{\frac{0.503 \times 10^{-3}}{1.006 \times 10^{-3}}} \text{erf} \sqrt{\frac{4.9 \times 10^{-5}}{1.006 \times 10^{-3}}} \exp\left(\frac{4.9 \times 10^{-5}}{1.006 \times 10^{-3}} - \frac{4.9 \times 10^{-5}}{0.503 \times 10^{-3}}\right)$$

or

$$1 - \text{erf} 0.3121 = (2.828)(\text{erf} 0.2207)(0.9525)$$

When the error functions are evaluated, using a table, we get

$$1 - 0.341 = (2.828)(0.245)(0.9525)$$

This gives  $0.66 = 0.66$ . Therefore,  $z_R(t) = \sqrt{4\gamma t}$  gives the location of the reaction zone as a function of  $t$ . Thus we get the following table of results that can be compared with Fig. 19.1-2:

$t$	$z_R(t) = \sqrt{4\gamma t}$
0.625 s	0.011 mm
2.5	0.022
10.0	0.044



This is not in very good agreement with the graph in Fig. 19.1-2. The reason for this may be that Eq. 415 on p. 336 of *Absorption and Extraction* by Sherwood and Pigford (which corresponds to our Eq. 20.1-37), contains two errors: the  $r$  on the left side should be  $\sqrt{r}$  and the  $D_A$  in the argument of the second error function should be  $D_B$ .

b. To get  $N_{A0}$  at 2.5 seconds, we use Eq. 20.1-38, as follows:

$$\begin{aligned}
 N_{A0} &= \frac{c_{A0}}{\operatorname{erf} \sqrt{\gamma / \mathcal{D}_{AS}}} \sqrt{\frac{\mathcal{D}_{AS}}{\pi t}} \\
 &= \frac{(1 \text{ gmol/dm}^3)(10 \text{ cm/dm})^3}{\operatorname{erf} \sqrt{(4.9 \times 10^{-5}) / (1.006 \times 10^{-3})}} \sqrt{\frac{1.006 \times 10^{-3} \text{ mm}^2/\text{s}}{(3.14159)(2.5 \text{ s})(100 \text{ mm}^2/\text{cm}^2)}} \\
 &= \frac{1000}{0.245} (1.13 \times 10^{-3}) = 4.61 \text{ gmol/cm}^2\text{s}
 \end{aligned}$$

## 20A.6 Rapid forced-convection mass transfer into a laminar boundary layer.

Equation (20.2-51) gives, for the conditions of this problem,

$$\begin{aligned} R_\omega &= \frac{(\omega_0 - \omega_\infty)}{n_{A0}/(n_{A0} + n_{B0}) - \omega_{A0}} \\ &= \frac{(0.9 - 0.1)}{1 - 0.9} = 8.0 \end{aligned}$$

Fig. 22.8-5 gives a dimensionless mass flux  $\phi$  of 1.55 for mass transfer at  $R_\omega = 8.0$  and  $Sc = 2.0$ . With this result, Eq. 22.8-21 and Table 20.2-1 give

$$1.55 = \frac{K\Lambda}{\Pi'(0, \Lambda, 0)} = \frac{K \times 2.0}{0.5972}$$

so that

$$K = 1.55 \times 0.5972/2 = 0.463$$

The definition of  $K$  in Eq. 20.2-48 then gives the total interfacial mass flux

$$\begin{aligned} n_{A0}(x) + n_{B0}(x) &= \rho_0 v_0(x) = K \rho v_\infty \sqrt{\frac{\nu}{2v_\infty x}} \\ &= 0.33 \sqrt{\rho v_\infty \mu / x} \end{aligned}$$

In this problem  $n_{B0}(x)$  is stated to be zero, so the previous result reduces to

$$n_{A0}(x) = 0.33 \sqrt{\rho v_\infty \mu / x}$$

**20A.7 Slow forced-convection mass transfer into a laminar boundary layer.**

(a) Equation (20.2-51) gives, for the conditions of this problem, the binary mass flux ratio

$$\begin{aligned} R_\omega &= \frac{(\omega_0 - \omega_\infty)}{n_{A0}/(n_{A0} + n_{B0}) - \omega_{A0}} \\ &= \frac{(0.05 - 0.01)}{1 - 0.05} = 0.0421 \end{aligned}$$

Eq. (20.2-55) and Table 20.2-2, with  $Sc = 0.6$ , then give

$$\begin{aligned} K &= a\Lambda^{-2/3} \frac{R_\omega}{1 + bR_\omega} \\ &= 0.4642 \times (0.6^{-2/3}) \frac{0.0421}{1 + 0.768 \times 0.0421} = 0.0266 \end{aligned}$$

Equation 20.2-48, with the specification  $n_{B0}(x) = 0$ , then gives the evaporative mass flux

$$\begin{aligned} n_{A0}(x) = \rho_0 v_0(x) &= K \rho v_\infty \sqrt{\frac{\nu}{2v_\infty x}} \\ &= 0.0266 \sqrt{\rho v_\infty \mu / 2x} \\ &= 0.0188 \sqrt{\rho v_\infty \mu / x} \end{aligned}$$

(b) Eq. 20.2-57 gives

$$\frac{n_{A0} - \omega_{A0}(n_{A0} + n_{B0})}{\rho v_\infty} (\omega_{A0} - \omega_{A\infty}) Sc^{2/3} = 0.332 \sqrt{\frac{\nu}{v_\infty x}}$$

which gives, since  $n_{B0} = 0$ ,

$$\begin{aligned} n_{A0} &= 0.332 Sc^{-2/3} \frac{\omega_{A0} - \omega_{A\infty}}{1 - \omega_{A0}} \rho v_\infty \sqrt{\frac{\nu}{v_\infty x}} \\ &= 0.332 (0.6)^{-2/3} \frac{0.05 - 0.01}{1 - 0.05} \sqrt{\rho v_\infty \mu / x} \\ &= 0.0196 \sqrt{\rho v_\infty \mu / x} \end{aligned}$$

(c) At the value  $K = 0.0266$  found in (a), Table 20.2-1 gives the interpolated interfacial gradient  $\Pi'(0, Sc, K) = 0.3797$ . Then Eq. 20.2-47, with  $n_{B0} = 0$ , gives the reference solution

$$\begin{aligned} n_{A0} &= \frac{\omega_0 - \omega_\infty}{1 - \omega_0} \frac{\Pi'(0, Sc, K)}{Sc} \rho v_\infty \sqrt{\frac{\nu}{2v_\infty x}} \\ &= \frac{0.05 - 0.01}{1 - 0.05} \frac{0.3797}{0.6} \sqrt{\rho v_\infty \mu / 2x} \\ &= 0.0188 \sqrt{\rho v_\infty \mu / x} \end{aligned}$$

in excellent agreement with the truncated expansion used in part (a).

## 20B.1 Extension of the Arnold problem to account for interphase transfer of both species

Equations 20.1-1, 2, and 3 are still valid if both species are crossing the interface. In Eq. 20.1-3 we now eliminate  $c$  by using Eq. (D) of Table 17.8-2 (evaluated at the interface) to get

$$v_z^* = -\frac{(N_{Az0} + N_{Bz0})}{N_{Az0} - x_{A0}(N_{Az0} + N_{Bz0})} \frac{\partial x_A}{\partial z} \Big|_{z=0} = -\frac{(1+r)}{1-x_{A0}(1+r)} \frac{\partial x_A}{\partial z} \Big|_{z=0}$$

When  $N_{Bz0} = 0$  (or the ratio  $r = N_{Bz0}/N_{Az0}$  goes to zero), this equation simplifies to Eq. 20.1-4.

Equation 20.1-5 is then replaced by

$$\frac{\partial x_A}{\partial t} - \left( \frac{(1+r)}{1-x_{A0}(1+r)} \frac{\partial x_A}{\partial z} \Big|_{z=0} \right) \frac{\partial x_A}{\partial z} = \mathfrak{D}_{AB} \frac{\partial^2 x_A}{\partial z^2}$$

We now introduce the dimensionless variables  $\Pi$  (defined in Eq. 20.1-23) and  $Z$  (defined just below Eq. 20.1-8); note that when  $x_{A\infty} = 0$ ,  $\Pi$  is the same as  $-(X-1)$ . Then the combination of variables method gives (cf. 20.1-9) the ordinary differential equation

$$\frac{d^2 \Pi}{dZ^2} + 2(Z - \varphi) \frac{d\Pi}{dZ} = 0$$

along with

$$\varphi(x_{A0}, r) = +\frac{1}{2} \frac{(x_{A0} - x_{A\infty})(1+r)}{1-x_{A0}(1+r)} \frac{d\Pi}{dZ} \Big|_{Z=0}$$

This is Eq. 20.1-24. If  $r = 0$  and  $x_{A\infty} = 0$ , it reduces to Eq. 20.1-10. The sign discrepancy comes about because (in the limit that  $x_{A\infty}$  is zero,  $\Pi$  is the same as  $-(X-1)$ ). The solution of the ordinary differential equation for  $\Pi$  proceeds exactly as that for  $X$  in the text, and the final result is

$$\Pi = \frac{\text{erf}(Z - \varphi) + \text{erf} \varphi}{1 + \text{erf} \varphi}$$

for the concentration profile. If  $r=0$  and  $x_{A\infty}=0$ , this reduces exactly to Eq. 20.1-16. When this concentration profile is used to evaluate  $d\Pi/dZ$  at  $Z=0$ , then we get an expression for  $\varphi(x_{A0}, r)$ :

$$\varphi(x_{A0}, r) = + \frac{1}{2} \frac{(x_{A0} - x_{A\infty})(1+r)}{1 - x_{A0}(1+r)} \left( \frac{2}{\sqrt{\pi}} \frac{\exp(-\varphi^2)}{1 + \operatorname{erf}\varphi} \right)$$

This may be rearranged to give

$$\frac{(x_{A0} - x_{A\infty})(1+r)}{1 - x_{A0}(1+r)} = \sqrt{\pi}(1 + \operatorname{erf}\varphi)\varphi \exp(+\varphi^2)$$

in agreement with Eq. 20.1-25.

## 20B.2 Extension of the Arnold problem to nonisothermal diffusion

a. Equation (M) of Table 19.2-4 without the last two terms is:

$$\frac{\partial}{\partial t} \sum_{\alpha=1}^N c_{\alpha} \bar{H}_{\alpha} + \left( \nabla \cdot \sum_{\alpha=1}^N \mathbf{N}_{\alpha} \bar{H}_{\alpha} \right) = (\nabla \cdot k \nabla T)$$

Replacing the partial molar quantities by quantities per mole (see comment after Eq. 19.3-6), and assuming that  $k$  is constant then gives

$$\frac{\partial}{\partial t} \sum_{\alpha=1}^N c_{\alpha} \tilde{H}_{\alpha} + \left( \nabla \cdot \sum_{\alpha=1}^N \mathbf{N}_{\alpha} \tilde{H}_{\alpha} \right) = k \nabla^2 T$$

Differentiating the products in the first and second terms allows us to rewrite this as

$$\sum_{\alpha=1}^N c_{\alpha} \frac{\partial \tilde{H}_{\alpha}}{\partial t} + \sum_{\alpha=1}^N \frac{\partial c_{\alpha}}{\partial t} \tilde{H}_{\alpha} + \sum_{\alpha=1}^N (\nabla \cdot \mathbf{N}_{\alpha}) \tilde{H}_{\alpha} + \sum_{\alpha=1}^N (\mathbf{N}_{\alpha} \cdot \nabla \tilde{H}_{\alpha}) = k \nabla^2 T$$

In the second term of this equation, we replace the derivative of the concentration by using Eq. 19.1-10 (omitting the reaction-rate term), and then we see that the second and third terms just exactly cancel. Next, we replace the enthalpy by the heat capacity multiplied by a temperature difference in accordance with Eq. 9.8-8, to get

$$\sum_{\alpha=1}^N c_{\alpha} \frac{\partial \tilde{C}_{p\alpha}}{\partial t} (T - T^{\circ}) + \sum_{\alpha=1}^N (\mathbf{N}_{\alpha} \cdot \nabla \tilde{C}_{p\alpha} (T - T^{\circ})) = k \nabla^2 T$$

For constant heat capacities this then becomes:

$$\sum_{\alpha=1}^N c_{\alpha} \tilde{C}_{p\alpha} \frac{\partial T}{\partial t} + \sum_{\alpha=1}^N \tilde{C}_{p\alpha} (\mathbf{N}_{\alpha} \cdot \nabla T) = k \nabla^2 T$$

If all the heat capacities are alike, then they can be taken outside the

Next we make use of  $c\tilde{C}_p = \rho\hat{C}_p$ , and then divide the entire equation by  $\rho\hat{C}_p$ ; this gives, with the help of Eq. (M) of Table 17.8-1

$$\frac{\partial T}{\partial t} + \left( \left( \frac{1}{c} \sum_{\alpha=1}^N \mathbf{N}_\alpha \right) \cdot \nabla T \right) = \alpha \nabla^2 T \quad \text{or} \quad \frac{\partial T}{\partial t} + (\mathbf{v}^* \cdot \nabla T) = \alpha \nabla^2 T$$

which is just the 3-dimensional version of Eq. 20B.2-1.

b. When Eq. 20B.2-1 is rewritten in terms of the dimensionless temperature, we get

$$\frac{\partial \Pi_T}{\partial t} + v_z^* \frac{\partial \Pi_T}{\partial z} = \alpha \frac{\partial^2 \Pi_T}{\partial z^2}$$

We now postulate that the dimensionless temperature is a function only of the variable  $Z_T = z/\sqrt{4\alpha t}$ . This leads us to the following ordinary differential equation:

$$\frac{d^2 \Pi_T}{dZ_T^2} + 2(Z_T - \varphi_T) \frac{d\Pi_T}{dZ_T} = 0 \quad \text{where} \quad \varphi_T = v_z^* \sqrt{\frac{t}{\alpha}} = \varphi \sqrt{\frac{\mathcal{D}_{AB}}{\alpha}}$$

It was shown in Eq. 21.1-24 that  $\varphi$  is a function of the terminal mole fractions and the interfacial molar-fluxes, but not of time. Therefore, since  $\varphi_T$  is just  $\varphi$  multiplied by the square root of the Lewis number, it may be treated as a constant in the above ordinary differential equation. This equation may be solved by the same technique used in §20.1 to give

$$\Pi_T = 1 - \frac{1 - \operatorname{erf}(Z_T - \varphi_T)}{1 + \operatorname{erf}\varphi_T} = \frac{\operatorname{erf}(Z_T - \varphi_T) + \operatorname{erf}\varphi_T}{1 + \operatorname{erf}\varphi_T}$$

c. To get the interfacial heat flux, we use Fourier's law:

$$q_0 = -k \left. \frac{\partial T}{\partial z} \right|_{z=0} = -\frac{k(T_\infty - T_0)}{1 + \operatorname{erf}\varphi_T} \left. \frac{d}{dz} \operatorname{erf}(Z_T - \varphi_T) \right|_{z=0}$$

$$\begin{aligned}
&= -\frac{k(T_\infty - T_0)}{1 + \operatorname{erf}\phi_T} \frac{2}{\sqrt{\pi}} \exp\left[-(Z_T - \phi_T)^2\right] \Big|_{z=0} \frac{d}{dz}(Z_T - \phi_T) \\
&= -\frac{k(T_\infty - T_0)}{1 + \operatorname{erf}\phi_T} \frac{2}{\sqrt{\pi}} \exp(-\phi_T^2) \frac{1}{\sqrt{4\alpha t}} \\
&= \frac{k(T_0 - T_\infty)}{\sqrt{\pi}(1 + \operatorname{erf}\phi_T) \exp(+\phi_T^2) \sqrt{\alpha t}}
\end{aligned}$$

Next we calculate the ratio in Eq. 20B.2-4:

$$\frac{N_{A0} + N_{B0}}{c v_z^*} = \frac{c \phi_T \sqrt{\alpha/t}}{k}$$

$$\begin{aligned}
&= \frac{c \tilde{C}_p \phi_T \sqrt{\alpha/t}}{k} \left[ \sqrt{\pi}(1 + \operatorname{erf}\phi_T) \exp(+\phi_T^2) \sqrt{\alpha t} \right] \\
&= \frac{\alpha \phi_T}{k/\rho \hat{C}_p} \left[ \sqrt{\pi}(1 + \operatorname{erf}\phi_T) \exp(+\phi_T^2) \right] \\
&= \sqrt{\pi}(1 + \operatorname{erf}\phi_T) \phi_T \exp(+\phi_T^2)
\end{aligned}$$

In the first step, we used Eq. (M) of Table 17.8-1, and later we used the relation  $c \tilde{C}_p = \rho \hat{C}_p$ .



### 20B.3 Stoichiometric boundary condition for rapid irreversible reaction

We begin by rewriting Eq. 20B.3-1 as

$$\frac{1}{a}c_A[(v_{Az} - v_z^*) + (v_z^* - v_R)] = -\frac{1}{b}c_A[(v_{Bz} - v_z^*) + (v_z^* - v_R)]$$

Then, using Fick's first law in the form of Eq. (B) of Table 17.8-2 (along with Eq. (I) of Table 17.8-1, we get

$$-\frac{1}{a}c_A \mathcal{D}_{AS} \frac{\partial x_A}{\partial z} + \frac{1}{a}c_A(v_z^* - v_R) = +\frac{1}{b}c_A \mathcal{D}_{BS} \frac{\partial x_B}{\partial z} - \frac{1}{b}c_A(v_z^* - v_R)$$

We now make use of the fact that the system has constant  $c$  so that

$$-\frac{1}{a} \mathcal{D}_{AS} \frac{\partial c_A}{\partial z} = +\frac{1}{b} \mathcal{D}_{BS} \frac{\partial c_B}{\partial z} - (v_z^* - v_R) \left( \frac{1}{a}c_A + \frac{1}{b}c_B \right)$$

At the plane  $z = z_R$ , there is no  $A$  or  $B$  present, so that the last term on the right side is zero. Therefore, we get

$$-\frac{1}{a} \mathcal{D}_{AS} \frac{\partial c_A}{\partial z} = +\frac{1}{b} \mathcal{D}_{BS} \frac{\partial c_B}{\partial z}$$

for one of the boundary conditions at  $z = z_R$  (cf. 20.1-31).

## 20B.4 Taylor dispersion in slit flow

This problem can be solved by paralleling the treatment in §20.5 for circular tubes. We give here the intermediate results along with the corresponding equation numbers in the text. Some results from Problem 2B.3 are needed here.

$$\frac{\partial \omega_A}{\partial t} + v_{z,\max} \left[ 1 - \left( \frac{x}{B} \right)^2 \right] \frac{\partial \omega_A}{\partial z} = \mathfrak{D}_{AB} \frac{\partial^2 \omega_A}{\partial x^2} \quad (20.5-1)$$

$$\langle \omega_A \rangle = \frac{1}{B} \int_0^B \omega_A dx \quad (20.5-3)$$

$$\frac{\partial^2 \omega_A}{\partial \xi^2} = \frac{v_{z,\max} B^2}{\mathfrak{D}_{AB}} \left( \frac{1}{3} - \xi^2 \right) \frac{\partial \omega_A}{\partial \bar{z}} \quad \text{where } \xi = \frac{x}{B} \quad (20.5-7)$$

$$\omega_A = \frac{v_{z,\max} B^2}{6\mathfrak{D}_{AB}} \left( \xi^2 - \frac{1}{2} \xi^4 \right) \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} + \omega_A(0, \bar{z}) \quad (20.5-10)$$

$$\langle \omega_A \rangle = \frac{v_{z,\max} B^2}{6\mathfrak{D}_{AB}} \left( \frac{7}{30} \right) \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} + \omega_A(0, \bar{z}) \quad (20.5-11)$$

$$\omega_A - \langle \omega_A \rangle = \frac{\frac{3}{2} \langle v_z \rangle B^2}{6\mathfrak{D}_{AB}} \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} \left( -\frac{7}{30} + \xi^2 - \frac{1}{2} \xi^4 \right) \quad (20.5-12)$$

$$\begin{aligned} 2BW\rho \langle \omega_A (v_z - \langle v_z \rangle) \rangle &= 2BW\rho \langle v_z \rangle \left\langle \omega_A \left( \frac{v_z}{\langle v_z \rangle} - 1 \right) \right\rangle \\ &= 2BW\rho \langle v_z \rangle \left[ \frac{\frac{3}{2} \langle v_z \rangle B^2}{6\mathfrak{D}_{AB}} \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} \right] \int_0^1 \left( -\frac{7}{30} + \xi^2 - \frac{1}{2} \xi^4 \right) \frac{3}{2} \left( \frac{1}{3} - \xi^2 \right) d\xi \\ &= 2BW\rho \langle v_z \rangle \left[ \frac{\frac{3}{2} \langle v_z \rangle B^2}{6\mathfrak{D}_{AB}} \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} \right] \left( -\frac{8}{105} \right) \\ &= -2BW\rho \frac{\partial \langle \omega_A \rangle}{\partial \bar{z}} \left[ \frac{2B^2 \langle v_z \rangle^2}{105\mathfrak{D}_{AB}} \right] \quad (20.5-13) \end{aligned}$$

The quantity in brackets is the Taylor dispersion coefficient.

## 20B.5 Diffusion from an instantaneous point source

a. The relevant diffusion equation is

$$\frac{\partial \rho_A}{\partial t} = \mathcal{D}_{AB} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \rho_A}{\partial r} \right)$$

The time derivative of Eq. 20B.5-1 is

$$\frac{\partial \rho_A}{\partial t} = \rho_A \left( -\frac{3}{2t} + \frac{r^2}{4\mathcal{D}_{AB}t^2} \right)$$

Next we build up the quantity on the right side of the diffusion equation by differentiating Eq. 20B.5-1, thus:

$$\frac{\partial \rho_A}{\partial r} = \rho_A \left( -\frac{r}{2\mathcal{D}_{AB}t} \right) \quad \text{and} \quad r^2 \frac{\partial \rho_A}{\partial r} = \rho_A \left( -\frac{r^3}{2\mathcal{D}_{AB}t} \right)$$

$$\frac{\partial}{\partial r} \left( r^2 \frac{\partial \rho_A}{\partial r} \right) = \rho_A \left[ \left( -\frac{r}{2\mathcal{D}_{AB}t} \right) \left( -\frac{r^3}{2\mathcal{D}_{AB}t} \right) - \frac{3r^2}{2\mathcal{D}_{AB}t} \right]$$

$$\mathcal{D}_{AB} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \rho_A}{\partial r} \right) = \rho_A \left( \frac{r^2}{4\mathcal{D}_{AB}t} - \frac{3}{2t} \right)$$

b. As  $r \rightarrow \infty$ , we find that  $\rho_A \rightarrow 0$ , as it should.

c. Integrating over all space in spherical coordinates, we get

$$\begin{aligned} & \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{m_A}{(4\pi\mathcal{D}_{AB}t)^{3/2}} \exp(-r^2/4\mathcal{D}_{AB}t) r^2 dr \sin\theta d\theta d\phi \\ &= 4\pi \frac{m_A}{(4\pi\mathcal{D}_{AB}t)^{3/2}} \int_0^\infty \exp(-u^2) u^2 du \cdot (4\mathcal{D}_{AB}t)^{3/2} \\ &= 4\pi \frac{m_A}{(4\pi\mathcal{D}_{AB}t)^{3/2}} \cdot \frac{\sqrt{\pi}}{4} \cdot (4\mathcal{D}_{AB}t)^{3/2} = m_A \end{aligned}$$

In going from the first to the second line, we have made a change of variable:  $r/\sqrt{4\mathcal{D}_{AB}t} = u$ .

d. Let  $n = (1/4)\mathcal{D}_{AB}t$ . Then Eq. 20B.5-1 becomes

$$\rho_A = m_A (n/\pi)^{3/2} \exp(-nr^2)$$

The limit of this function as  $n \rightarrow \infty$  is  $\rho_A = m_A \delta(x)\delta(y)\delta(z)$ . That is we get a delta function in the three spatial variables. In other words, all the material is "piled up" at the origin. [For more on this, see R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 2, *Kinetic Theory*, Wiley-Interscience, New York (1987), §E.4, p. 405.]

## 20B.6 Unsteady diffusion with first-order chemical reaction

(a) the thin disk catalyst particle

The reference problem is

$$\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial \eta^2}; \Theta(0, \eta) = 1; \Theta(\pm 1) = 0$$

The problem of interest here is

$$\frac{\partial \omega}{\partial \tau} = \frac{\partial^2 \omega}{\partial \eta^2} - \kappa \omega; \omega(0, \eta) = 1; \omega(\pm 1) = 0$$

Attempt a solution of the form

$$\omega = \Theta \exp(-\kappa \tau)$$

Putting this trial solution into the differential equation for  $\omega$  gives the original equation for  $\Theta$ , and the new equation also satisfies the initial and boundary conditions. It is our desired solution.

(b) diffusion and reaction from a point source

Again we may write the solution by inspection as

$$p = g e^{kt}$$

Here  $g$  is the normalized probability of finding a diffusing particle, originally at the coordinate origin, at any point and time.

**20B.7 Simultaneous momentum, heat, and mass transfer:  
alternate boundary conditions.**

(a) With  $n_{B0} = 0$ , Eq. 20.2-51 gives the mass flux ratio

$$R_w = \frac{\omega_{A0} - \omega_{A\infty}}{1 - \omega_{A0}}$$

Then with  $\Lambda = Sc$  for binary diffusion, Eq. 20.2-52 gives the following implicit equation for the dimensionless mass flux,

$$K = \frac{1}{Sc} \frac{\omega_{A0} - \omega_{A\infty}}{1 - \omega_{A0}} \Pi'(0, Sc, K)$$

which can be solved conveniently with Fig. 22.8-5, Eq. 22.8-21, and Table 20.2-1, in the manner of the solution given for Problem 20A.6.

(b) With  $\omega_{A0} = 0$  and  $n_{A0} = 2n_{B0}$ , Eq. 20.2-51 gives the mass flux ratio

Then with  $\Lambda = Sc$  for diffusion in the binary gas phase, Eq. 20.2-52 gives the following implicit equation for the dimensionless mass flux,

$$K = \frac{1}{Sc} \omega_{A\infty} \Pi'(0, Sc, K)$$

which can be solved directly with the aid of Fig. 22.8-5, as noted in (a).

(c) A steady-state energy balance from the inner to the outer boundary of the wall gives, for the region of laminar boundary layer,

$$\rho_0 v_0 \hat{C}_p T_a = \rho v_0 \hat{C}_p T_0 + q_0$$

whence

### 20B.8 Absorption from a pulsating bubble

a. The essential point here is the calculation of the integral in Eq. 20.1-72. Let the surface of the bubble oscillate between  $S_1 = 4\pi R_1^2$  and  $S_2 = 4\pi R_2^2$ , with  $S_2/S_1 \geq 1$ , so that

$$\begin{aligned} S(t) &= S_1 & 2n \leq \omega t \leq 2n+1 & \quad \text{for } n = 0, 1, 2, \dots \\ S(t) &= S_2 & 2n+1 \leq \omega t \leq 2n+2 & \quad \text{for } n = 0, 1, 2, \dots \end{aligned}$$

We further let  $(S_2/S_1)^2 = r \geq 1$ . Then in each time region, we can calculate the value of  $1/t$  times the integral in Eq. 20.1-72 as follows:

$$0 \leq \omega t \leq 1: \quad \frac{1}{t} \int_0^t \left( \frac{S_1}{S_1} \right)^2 d\bar{t} = 1$$

$$1 \leq \omega t \leq 2: \quad \frac{1}{t} \int_0^{1/\omega} \left( \frac{S_1}{S_2} \right)^2 d\bar{t} + \frac{1}{t} \int_{1/\omega}^t \left( \frac{S_2}{S_2} \right)^2 d\bar{t} = \frac{1}{\omega t} \left( \frac{1}{r} - 1 \right) + 1$$

$$\begin{aligned} 2 \leq \omega t \leq 3: \quad & \frac{1}{t} \int_0^{1/\omega} \left( \frac{S_1}{S_1} \right)^2 d\bar{t} + \frac{1}{t} \int_{1/\omega}^{2/\omega} \left( \frac{S_2}{S_1} \right)^2 d\bar{t} + \frac{1}{t} \int_{2/\omega}^t \left( \frac{S_1}{S_1} \right)^2 d\bar{t} \\ & = \frac{1}{\omega t} (r - 1) + 1 \end{aligned}$$

$$\begin{aligned} 3 \leq \omega t \leq 4: \quad & \frac{1}{t} \int_0^{1/\omega} \left( \frac{S_1}{S_2} \right)^2 d\bar{t} + \frac{1}{t} \int_{1/\omega}^{2/\omega} \left( \frac{S_2}{S_2} \right)^2 d\bar{t} + \frac{1}{t} \int_{2/\omega}^{3/\omega} \left( \frac{S_1}{S_2} \right)^2 d\bar{t} \\ & + \frac{1}{t} \int_{3/\omega}^t \left( \frac{S_1}{S_2} \right)^2 d\bar{t} = \frac{2}{\omega t} \left( \frac{1}{r} - 1 \right) + 1 \end{aligned}$$

$$4 \leq \omega t \leq 5: \quad \frac{2}{\omega t} (r - 1) + 1$$

$$5 \leq \omega t \leq 6: \quad \frac{3}{\omega t} \left( \frac{1}{r} - 1 \right) + 1$$

We have now gone sufficiently far to be able to see what the pattern is, and we can summarize the results as follows:

$$\begin{array}{ccc}
 & j \text{ even} & j \text{ odd} \\
 j \leq \omega t \leq j+1 & \frac{j}{2\omega t}(r-1)+1 & \frac{(j+1)}{2\omega t}\left(\frac{1}{r}-1\right)+1 \\
 (j = 0,1,2,\dots) & & 
 \end{array}$$

In for large values of the time, these expressions become very nearly

$$\begin{array}{ccc}
 j \leq \omega t \leq j+1 & \frac{1}{2}(1+r) & \frac{1}{2}\left(1+\frac{1}{r}\right) \\
 (j = 0,1,2,\dots) & & 
 \end{array}$$

Thus, the dimensionless molar transfer rate at the interface becomes (according to Eq. 20.1-72) at large values of the time:

$$\begin{array}{ccc}
 j \leq \omega t \leq j+1 & \frac{N_{A0}(t)}{c_{A0}\sqrt{\mathcal{D}_{AB}/\pi t}} = & \sqrt{\frac{2}{1+r}} \quad \sqrt{\frac{2}{1+(1/r)}} \\
 (j = 0,1,2,\dots) & & 
 \end{array}$$

If  $r = 1$ , then there is no droplet oscillation and the dimensionless molar transfer rate is 1. For  $r = 2$ , say, the dimensionless molar transfer rate has a square-wave form, oscillating between  $\sqrt{\frac{2}{3}}$  and  $\sqrt{\frac{4}{3}}$ .

b. A more interesting problem might be to get the total moles of A transferred at time  $t$ , using Eq. 20.1-73; for large values of the time, we get:

$$\begin{array}{ccc}
 j \leq \omega t \leq j+1 & \frac{M_A(t)/S(t)}{c_{A0}\sqrt{4\mathcal{D}_{AB}t/\pi}} = & \sqrt{\frac{1}{2}(1+r)} \quad \sqrt{\frac{1}{2}\left(1+\frac{1}{r}\right)} \\
 (j = 0,1,2,\dots) & & 
 \end{array}$$

Now, if  $S(t) = \frac{1}{2}(S_1 + S_2)$  (a constant),

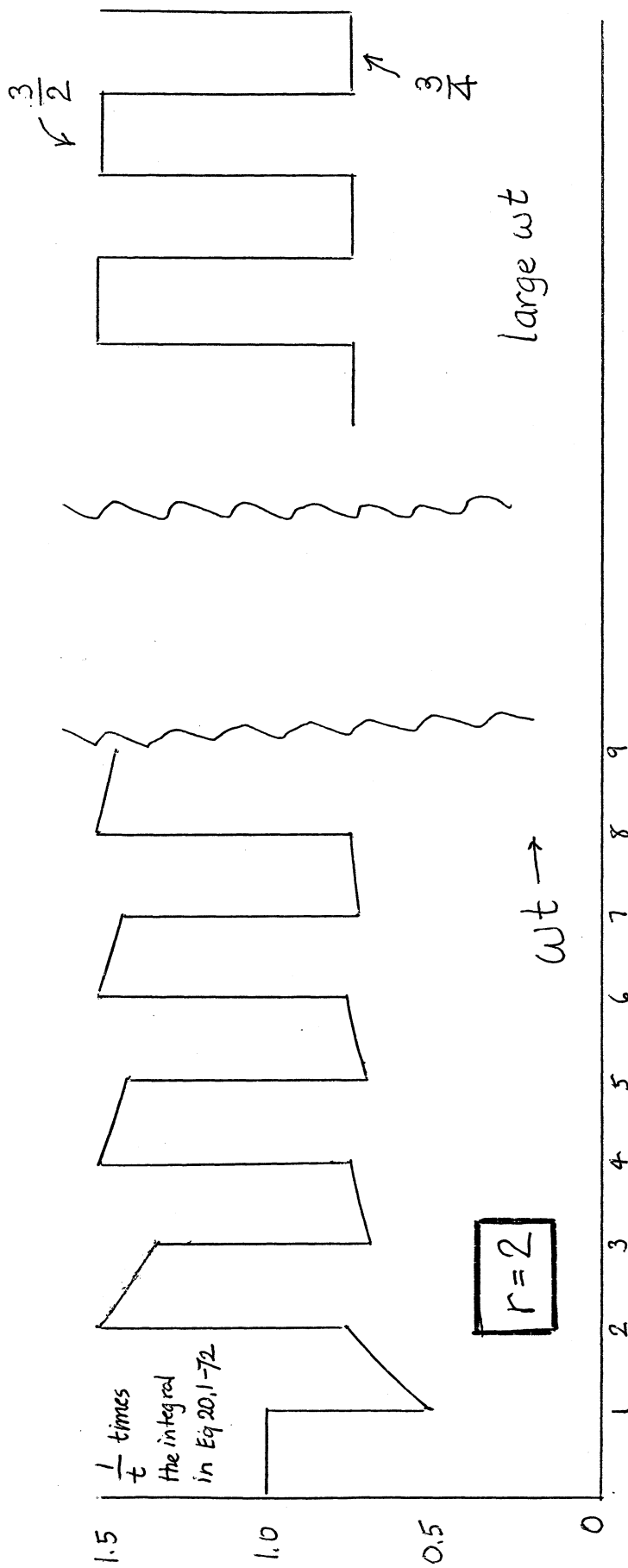
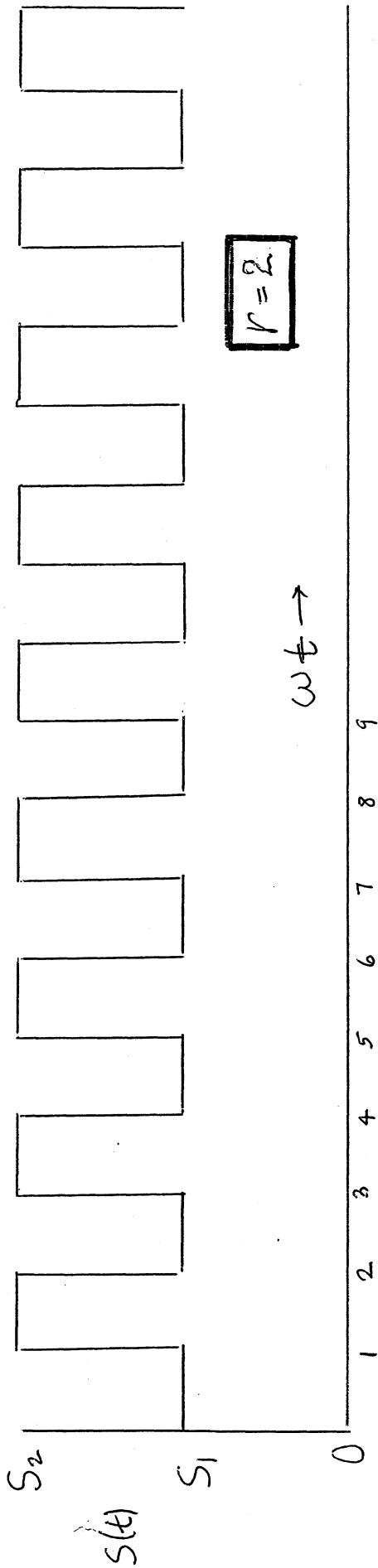
$$M_A(t) = \frac{1}{2}S_1(1+r)c_{A0}\sqrt{4\mathcal{D}_{AB}t/\pi}$$



If, on the other hand,  $S(t)$  is oscillating between  $S_1$  and  $S_2$ ,

$$\begin{aligned}M_A(t) &= \left[ \frac{1}{2} S_1 \sqrt{\frac{1}{2}(1+r)} + \frac{1}{2} S_2 \sqrt{\frac{1}{2} \left(1 + \frac{1}{r}\right)} \right] c_{A0} \sqrt{4 \mathcal{D}_{AB} t / \pi} \\ &= \frac{1}{2\sqrt{2}} S_1 \left[ \sqrt{(1+r)} + r \sqrt{\left(1 + \frac{1}{r}\right)} \right] c_{A0} \sqrt{4 \mathcal{D}_{AB} t / \pi}\end{aligned}$$

For  $r=2$ , the first expression (constant surface area) gives a numerical constant of 1.50, whereas the second (oscillating area) gives 1.47. Keep in mind that the second expression is approximate (for large  $t$  and that this may account for the discrepancy between the two values.



20B.9 Verification of the solution of the Taylor-dispersion equation

(a) Begin by writing

$$u \equiv z - \langle v \rangle t$$

$$dq = \left( \frac{\partial q}{\partial t} \right)_z dt + \left( \frac{\partial q}{\partial z} \right)_t dz$$

$$\begin{aligned} \left( \frac{\partial q}{\partial t} \right)_u &= \left( \frac{\partial q}{\partial t} \right)_z \cdot 1 + \left( \frac{\partial q}{\partial z} \right)_t \left( \frac{\partial z}{\partial t} \right)_u \\ &= \left( \frac{\partial q}{\partial t} \right)_z + \left( \frac{\partial q}{\partial z} \right)_t (\langle v \rangle) \end{aligned}$$

$$\left( \frac{\partial q}{\partial u} \right)_t = \left( \frac{\partial q}{\partial z} \right)_t; \quad \left( \frac{\partial^2 q}{\partial u^2} \right)_t = \left( \frac{\partial^2 q}{\partial z^2} \right)_t$$

where  $q$  is any scalar, here  $\langle \rho \rangle$ . Putting these results into Eq. 20.5-17 gives

$$\left( \frac{\partial \langle \rho \rangle}{\partial t} \right)_u = K \left( \frac{\partial^2 \langle \rho \rangle}{\partial u^2} \right)_t$$

which is the desired result.

(b) Our differential equation is of the form  $\frac{\partial q}{\partial t} = K \frac{\partial^2 q}{\partial z^2}$

where  $q$  is  $\langle \rho \rangle$  and the proposed solution can be written as

$$q = \frac{A}{\sqrt{t}} \exp\left(-\frac{u^2}{4Kt}\right)$$

Now

$$\frac{\partial q}{\partial t} = -\frac{q}{2t} + \frac{u^2}{4Kt^2} q$$

$$\frac{\partial q}{\partial u} = -\frac{u}{2Kt} q$$

$$\frac{\partial^2 q}{\partial u^2} = -\frac{q}{2Kt} + \frac{u^2 q}{4K^2 t^2}$$

$$K \frac{\partial^2 q}{\partial u^2} = -\frac{q}{2t} + \frac{u^2 q}{4Kt^2}$$

The differential equation is satisfied.

(c) Simple inspection shows that these conditions are met.

< end >

20C.1 Order-of-magnitude analysis of gas absorption from a growing bubble

(a) The volumetric flow rate for this system is constant at a value

$$Q = \frac{d}{dt} \frac{4}{3} \pi r_s^3 = 4\pi r_s^2 \frac{dr_s}{dt}$$

$$v_r|_{r=r_s} = (Q / 4\pi) \frac{1}{r_s^2}$$

The same volumetric flow must occur at any distance, and this constraint requires the suggested result.

(b) This is obtained simply by putting the above result into the spherically symmetric continuity equation.

(c) The expression

$$\frac{r_s^2}{(y - r_s)} = \frac{1}{(1 - y / r_s)^2}$$

The desired expression can be obtained simply by division, and it is also available in many standard tables, for example, H. B. Dwight, Tables of Integrals and Other Mathematical Data, Macmillan, #9.06.

(d) Terms (5), (6) and (7) are second, third and fourth order respectively.

< end >

### 20C.3 Absorption with chemical reaction in a semi-infinite medium

a. First, introduce the following dimensionless variables:

$\Gamma = c_A/c_{A0}$ ,  $\xi = \sqrt{k_1''/\mathcal{D}_{AB}}x$ , and  $\tau = k_1''t$ ; also, define the combinations  $m = \left[ \left( \xi/2\sqrt{\tau} \right) - \sqrt{\tau} \right]$  and  $p = \left[ \left( \xi/2\sqrt{\tau} \right) + \sqrt{\tau} \right]$ . Then Eqs. 20C.3-1 and 2 are

$$\frac{\partial \Gamma}{\partial \tau} = \frac{\partial^2 \Gamma}{\partial \xi^2} - \Gamma \quad \text{and} \quad 2\Gamma = e^{-\xi} \operatorname{erfc} m + e^{\xi} \operatorname{erfc} p$$

Then we calculate the derivatives as follows:

$$2 \frac{\partial \Gamma}{\partial \tau} = \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi}} \left( \frac{\xi}{2\tau^{3/2}} + \frac{1}{\sqrt{\tau}} \right) + \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi}} \left( \frac{\xi}{2\tau^{3/2}} - \frac{1}{\sqrt{\tau}} \right)$$

$$2 \frac{\partial \Gamma}{\partial \xi} = -e^{-\xi} \operatorname{erfc} m - \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi\tau}} + e^{\xi} \operatorname{erfc} p - \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi\tau}}$$

$$2 \frac{\partial^2 \Gamma}{\partial \xi^2} = e^{-\xi} \operatorname{erfc} m + \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi\tau}} + \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi\tau}} + \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi\tau}} \left( \frac{\xi}{2\sqrt{\tau}} - \sqrt{\tau} \right) \\ + e^{\xi} \operatorname{erfc} p - \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi\tau}} - \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi\tau}} + \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi\tau}} \left( \frac{\xi}{2\sqrt{\tau}} + \sqrt{\tau} \right)$$

When these contributions are substituted into the diffusion equation, it may be seen that the equation is satisfied.

At  $t = 0$ , we find that  $m = \infty$  and  $p = \infty$ , so that  $\operatorname{erfc} m$  and  $\operatorname{erfc} p$  are both equal to zero, and hence the initial condition is satisfied.

At  $x = 0$ ,  $\Gamma = \frac{1}{2} [\operatorname{erfc}(-k_1''t) + \operatorname{erfc}(+k_1''t)]$  which may also be written as  $\frac{1}{2} [1 - \operatorname{erf}(-k_1''t) + 1 - \operatorname{erf}(+k_1''t)]$ ; however  $\operatorname{erf}(-u) = -\operatorname{erf}(u)$ , so that we are left with  $\frac{1}{2} \cdot 2 = 1$ , which indicates that the boundary condition at  $x = 0$  is satisfied.

At  $x = \infty$ ,  $\operatorname{erfc} m$  and  $\operatorname{erfc} p$  both go to zero, and  $e^{-\xi}$  also. Hence we have to prove that  $e^{\xi} \operatorname{erfc} p$  goes to zero:

$$\lim_{\xi \rightarrow \infty} \frac{\operatorname{erfc}(\xi/2\sqrt{t})}{e^{-\xi}} = \lim_{\xi \rightarrow \infty} \frac{(2/\sqrt{\pi})(\exp(-\xi^2/4t))(1/2\sqrt{t})}{-e^{-\xi}} = 0$$

which shows that the boundary condition at  $x = \infty$  is satisfied.

b. To get the molar flux at the wall, we once again make use of dimensionless variables:

$$\begin{aligned} N_{Ax}|_{x=0} &= -\mathcal{D}_{AB}c_{A0} \left. \frac{\partial \Gamma}{\partial x} \right|_{x=0} = -\mathcal{D}_{AB}c_{A0} \sqrt{\frac{k_1'''}{\mathcal{D}_{AB}}} \left. \frac{\partial \Gamma}{\partial \xi} \right|_{\xi=0} \\ &= -\frac{1}{2}c_{A0} \sqrt{\mathcal{D}_{AB}k_1'''} \left[ -e^{-\xi} \operatorname{erfc} m - \frac{e^{-\xi} e^{-m^2}}{\sqrt{\pi\tau}} + e^{\xi} \operatorname{erfc} p - \frac{e^{\xi} e^{-p^2}}{\sqrt{\pi\tau}} \right]_{\xi=0} \\ &= -\frac{1}{2}c_{A0} \sqrt{\mathcal{D}_{AB}k_1'''} \left[ -\operatorname{erfc}(-\sqrt{\tau}) - \frac{e^{-\tau}}{\sqrt{\pi\tau}} + \operatorname{erfc}(\sqrt{\tau}) - \frac{e^{-\tau}}{\sqrt{\pi\tau}} \right] \\ &= -\frac{1}{2}c_{A0} \sqrt{\mathcal{D}_{AB}k_1'''} \left[ -2\operatorname{erf}\sqrt{\tau} - \frac{2e^{-\tau}}{\sqrt{\pi\tau}} \right] \end{aligned}$$

which is equivalent to Eq. 20C.3-3. Actually a neater form of the result is:

$$N_{Ax}|_{x=0} = c_{A0} \sqrt{\frac{\mathcal{D}_{AB}}{\pi t}} \left[ \sqrt{\pi k_1''' t} \operatorname{erf} \sqrt{k_1''' t} + e^{-k_1''' t} \right]$$

In this form, the quantity in the brackets is the correction factor for the absorption rate because of the chemical reaction that is occurring.

c. The total moles absorbed through an area  $A$  is

$$\begin{aligned} M_A &= A \int_0^{k_1''' t} N_{Ax}|_{x=0} dt = \frac{A}{k_1'''} \int_0^{k_1''' t} N_{Ax}|_{x=0} d\tau \\ &= \frac{A}{k_1'''} c_{A0} \sqrt{\mathcal{D}_{AB}k_1'''} \int_0^{k_1''' t} \left[ \operatorname{erf}\sqrt{\tau} + \frac{e^{-\tau}}{\sqrt{\pi\tau}} \right] d\tau \end{aligned}$$

We now perform the two integrations; in both of them we make the change of variable  $\sqrt{\tau} = y$ :

$$\int_0^{k_1''t} \frac{e^{-\tau}}{\sqrt{\pi\tau}} d\tau = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k_1''t}} e^{-y^2} dy = \text{erf} \sqrt{k_1''t}$$

$$\begin{aligned} \int_0^{k_1''t} \text{erf} \sqrt{\tau} d\tau &= \int_0^{\sqrt{k_1''t}} (\text{erf} y) 2y dy = \int_0^{\sqrt{k_1''t}} \left( \frac{2}{\sqrt{\pi}} \int_0^y e^{-s^2} ds \right) 2y dy \\ &= \frac{4}{\sqrt{\pi}} \int_0^{\sqrt{k_1''t}} \left( \int_s^{\sqrt{k_1''t}} y dy \right) e^{-s^2} ds = \frac{4}{\sqrt{\pi}} \int_0^{\sqrt{k_1''t}} \left[ \frac{1}{2} (k_1''t - s^2) \right] e^{-s^2} ds \\ &= k_1''t \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k_1''t}} e^{-s^2} ds - \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k_1''t}} s^2 e^{-s^2} ds \\ &= k_1''t \text{erf} \sqrt{k_1''t} - \frac{2}{\sqrt{\pi}} \left[ -\frac{1}{2} s e^{-s^2} \Big|_0^{\sqrt{k_1''t}} + \frac{1}{2} \int_0^{\sqrt{k_1''t}} e^{-s^2} ds \right] \\ &= k_1''t \text{erf} \sqrt{k_1''t} + \frac{1}{\sqrt{\pi}} \sqrt{k_1''t} e^{-k_1''t} - \frac{1}{2} \text{erf} \sqrt{k_1''t} \end{aligned}$$

When these integrals are substituted into the expression for  $M_A$ , we end up with Eq. 20C.3-4.

*d.* For large values of  $k_1''t$ , the exponential in the last term goes to zero, the error function goes to unity, and the only remaining terms are those in the large parentheses in Eq. 20C.3-4. In this way, Eq. 20C.3-5 is obtained.

## 20C.4 Design of fluid control circuits

The response to a pulse input to a “long” tube can be expressed as

$$\rho_i(L, t) = \frac{m_i / A}{\sqrt{4\pi Et}} \exp \left[ -\frac{(t - L/v)^2}{4(Et/v^2)} \right]$$

Here  $m_i$  is the mass of solute “i” fed to a tube of length  $L$  and cross-sectional area  $A$ . This is just 20.5-18, modified to be explicit in time, and using a generalized dispersion coefficient  $E$ .

For a short pulse most of the solute leaves near the mean residence time

$$\bar{t} \equiv L/v$$

where  $v$  is the flow average velocity,  $\langle v \rangle$ . The term “ $E$ ” is the sum of Taylor dispersion and molecular diffusivity:

$$E = K + \mathcal{D}_{im}$$

If we then approximate  $t$  as  $\bar{t}$  the exit composition has the form of a normal probability distribution with variance

$$\sigma^2 = 2E\bar{t} / v^2$$

and  $\sigma$  is the standard deviation of the distribution.

A reasonable set of design criteria is then that

$$\sqrt{2E\bar{t}} / v \leq 0.05t_0$$

$$L \gg 2vR^2 / (3.8)^2 \mathcal{D}_{im} \quad (\text{Eq. 20.5-4})$$

In practice the “ $\gg$ ” requirement need not be very large. It is really only necessary that there not be much tailing. A discussion of this point is beyond the scope of the present discussion.

In any event for most “long” ducts we may approximate “ $E$ ” as the “ $K$ ” of Eq. 20.5-15:

$$K = R^2 v^2 / 48 \mathcal{D}_{im}; \quad 2Rv/v < 2,100$$

For higher  $Re$  turbulence results in much smaller dispersion coefficients

$$K \approx 10Rv^*$$



We will not explore this turbulent region here.

We thus find

$$\frac{R^2 v^2}{48 \mathcal{D}_{im}} < 0.05^2 t_0^2 \frac{v^3}{L}$$
$$t_0^2 > 8.333 \frac{LR^2}{v \mathcal{D}_{im}}; t_0 > 2.89 \sqrt{\frac{LR^2}{v \mathcal{D}_{im}}}$$

with the constraint on length introduced above. This in turn means that

$$t_0 \gg \frac{2.89 \cdot \sqrt{2}}{3.8} \sqrt{\frac{R^2}{\mathcal{D}_{im}}} = 1.07 R^2 / \mathcal{D}_{im}$$
$$= 2.7 \cdot 10^{-3} \text{ cm}^2 / \mathcal{D}_{im}$$

Then for typical liquids, with diffusivities on the order of  $10^{-5} \text{ cm}^2/\text{s}$ ,

$$t_0 \gg 2.7 \cdot 10^2 \text{ s} = 4.5 \text{ min}$$

whereas for gases with diffusivities of, let us say 0.27,

$$t_0 \gg 0.01 \text{ s}$$

< end >

### 20C.5 Dissociation of a gas caused by a temperature gradient

[The small Roman numerals after the equations correspond to the equations given by Dirac in his paper.]

#### a. The equation of state

It is assumed that the diffusing mixture is at constant temperature and that the *ideal gas law* is applicable, then we have

$$p = (n_1 + n_2)kT \quad \text{or} \quad (n_1 + n_2)T = p/k = \text{constant}$$

Here  $n_1$  and  $n_2$  are the number densities of the single and double species at any point in the tube. Then if  $n_1^0$  and  $n_2^0$  are the values of  $n_1$  and  $n_2$  at the same pressure and temperature in a system with no temperature gradient, then we have also

$$(n_1^0 + n_2^0)T = p/k = \text{constant}$$

Then Dirac defines a quantity  $\sigma$  by the following:

$$n_1 - n_1^0 = \sigma \quad \text{and} \quad n_2 - n_2^0 = -\sigma \quad (\text{i})$$

Thus  $\sigma$  gives the deviation from the equilibrium state, resulting from the temperature gradient.

#### b. The equation of continuity for the mixture

Equation 3.1-4 (or Eq. (D) of Table 19.2-1) gives, for steady state,

$$\frac{d}{dz} \rho v_z = 0 \quad \text{or} \quad \rho v_z = \text{constant}$$

where  $v_z$  is the mass-average velocity. Therefore, if we make use of Eq. (B) of Table 17.7-2, and if we make use of the fact that there is no net movement of mass across any plane  $z = \text{constant}$ , then we have

$$\rho_1 v_1 + \rho_2 v_2 = 0 \quad \text{or} \quad n_1 m_1 v_1 + n_2 m_2 v_2 = 0$$

where  $m_1$  and  $m_2$  are the masses of single and double molecules, respectively. Then

$$n_1 m_1 v_1 + n_2 (2m_1) v_2 = 0 \quad \text{or} \quad n_1 v_1 + 2n_2 v_2 = 0 \quad (\text{ii})$$

c. *The energy equation for the mixture*

For a steady-state system with all species subject to the same external force, the one-dimensional energy equation of Eq. (C) gives  $e_z = E$ , a constant. Then we use the approximate expression for the energy flux (also used by Dirac) given in Eq. 19.3-6

$$-k \frac{dT}{dz} + (N_1 \bar{H}_1 + N_2 \bar{H}_2) = E \quad \text{or} \quad -k \frac{dT}{dz} + c_1 v_1 \tilde{H}_1 + c_2 v_2 \tilde{H}_2 = E$$

where the partial molar enthalpies have been replaced by the enthalpies per mole, as is normally done for ideal-gas systems. Then switching to quantities per molecule, we may write

$$-k \frac{dT}{dz} + n_1 v_1 h_1 + n_2 v_2 h_2 = E \quad \text{or} \quad -k \frac{dT}{dz} + \frac{1}{2} n_1 v_1 (2h_1 - h_2) = E$$

Then if we define the heat of dissociation by  $\Delta h_{\text{dissoc}} = 2h_1 - h_2$ , the energy equation becomes

$$-k \frac{dT}{dz} + \frac{1}{2} n_1 v_1 \Delta h_{\text{dissoc}} = E \quad (\text{iii})$$

d. *The expression for the molar flux*

If we write Eq. 24.2-8 for species "1" in a 2-component mixture, it becomes:

$$\frac{x_1 x_2}{\mathcal{D}_{12}} (v_1 - v_2) = -\frac{dx_1}{dz} - \frac{x_1 x_2}{\mathcal{D}_{12}} \left( \frac{D_1^T}{\rho_1} - \frac{D_2^T}{\rho_2} \right) \frac{d \ln T}{dz}$$

This equation is a generalization of Eq. (F) of Table 17.8-2, which takes into account the extra term needed to describe thermal diffusion. Since  $D_1^T + D_2^T = 0$  (see paragraph just above Eq. 24.2-3), the above equation may be written as

$$n_1 - n_2 = -\frac{\mathcal{D}_{12}}{D_1^T} \frac{dx_1}{dz} - \frac{D_1^T}{D_1^T} \frac{d \ln T}{dz} \quad (\text{iv})$$

This is exactly Dirac's equation (iv) if  $-D_1^T/\rho$  is relabeled as  $D'$ .

*e. The equation of continuity for species "1"*

Equation 19.1-10 at steady state is

$$0 = -\frac{d}{dz}c_1v_1 + R_1 \quad \text{or} \quad 0 = -\frac{d}{dz}n_1v_1 + R_1\tilde{N}$$

the second form being in molecular, rather than molar, quantities. Dirac then postulates that, for systems not too far removed from equilibrium, first order kinetics can be assumed so that

$$\frac{d}{dz}n_1v_1 = -k_1'''\sigma \quad (\text{v})$$

The above set of equations (i to v) are the equations that Dirac derived, and these have to be solved simultaneously for  $n_1$ ,  $n_2$ ,  $v_1$ ,  $v_2$ , and  $T$ . for temperature dependent thermal conductivity, diffusivity, and thermal diffusion coefficient.

First he shows how to reduce the set of five equations to a set of two equations. Then he resorts to numerical methods to complete the calculation for some sample values of the constants in the system.

## 20D.1 Two-bulb experiment for measuring gas diffusivities--analytical solution

The diffusion equation to be solved is

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 c_A}{\partial z^2}$$

with the initial conditions that  $c_A(z,0) = c_A^+$  for  $0 < z < L$  and that  $c_A(z,0) = c_A^-$  for  $-L < z < 0$ , and the following boundary conditions:

$$\text{At } z = 0, \quad c_A = \frac{1}{2}(c_A^+ + c_A^-)$$

$$\text{At } z = \pm L, \quad \mp \mathcal{D}_{AB} \frac{\partial c_A}{\partial z} = V \frac{\partial c_A}{\partial t}$$

Next, we introduce dimensionless quantities as follows:  $\zeta = z/L$ ,  $\tau = \mathcal{D}_{AB}t/L^2$ ,  $\Gamma = [c_A - \frac{1}{2}(c_A^+ + c_A^-)] / [\frac{1}{2}(c_A^+ - c_A^-)]$ , and  $N = SL/V$ . Then the problem may be restated as

$$\frac{\partial \Gamma}{\partial \tau} = \frac{\partial^2 \Gamma}{\partial \zeta^2}$$

with initial condition that  $\Gamma(\zeta,0) = 1$  for  $0 < \zeta < 1$  and the boundary conditions

$$\text{At } \zeta = 0, \quad \Gamma = 0; \quad \text{and at } \zeta = 1, \quad -\frac{\partial \Gamma}{\partial \zeta} = \frac{1}{N} \frac{\partial \Gamma}{\partial \tau}$$

That is, we solve only the right half of the problem, with the understanding that the left side can be obtained from symmetry conditions.

We assume a product solution  $\Gamma(\zeta, \tau) = Z(\zeta)T(\tau)$ . Then when this is substituted into the partial differential equation, we get the following two ordinary differential equations

$$\frac{dT}{d\tau} = -\gamma^2 T \quad \text{and} \quad \frac{d^2 Z}{d\zeta^2} + \gamma^2 Z = 0$$

in which  $\gamma^2$  is the separation constant. These equations have the solutions

$$T = A_0 \exp(-\gamma^2 \tau) \quad \text{and} \quad Z = A_1 \sin \gamma \zeta + A_2 \cos \gamma \zeta$$

The first boundary condition gives  $A_2 = 0$ . The second boundary condition gives  $\gamma \tan \gamma = N$  which has an infinite number of

$$\int_0^1 \sin \gamma_m \zeta \sin \gamma_n \zeta d\zeta = -N(-1)^{m+n} \frac{1}{\sqrt{\gamma_n^2 + N^2}} \frac{1}{\sqrt{\gamma_m^2 + N^2}} \neq 0 \quad (m \neq n)$$

Although the sine functions are not orthogonal, the cosines are:

$$\int_0^1 \cos \gamma_m \zeta \cos \gamma_n \zeta d\zeta = \frac{1}{2} \left( \frac{\gamma_n^2 + N^2 + N}{\gamma_n^2 + N^2} \right) \delta_{mn}$$

Next we use this last bit of information to get the  $D_n$ . The late Professor R. J. Buehler (Department of Statistics, University of Minnesota) suggested the following procedure: We first rewrite the initial condition (#) as

$$\lim_{B \rightarrow 0} (1 - e^{-\zeta/B}) = \sum_{n=1}^{\infty} D_n \sin \gamma_n \zeta$$

Then we consider the same condition, but without taking the limit:

$$(1 - e^{-\zeta/B}) = \sum_{n=1}^{\infty} D_n(B) \sin \gamma_n \zeta$$

This may be differentiated to give

Now take the limit as  $B$  goes to zero, so that the left side becomes unity, and

$$D_m = \frac{2}{\gamma_m} \left( \frac{\gamma_m^2 + N^2}{\gamma_m^2 + N^2 + N} \right)$$

Hence the final solution for the concentration in the two-bulb system is

$$\Gamma(\zeta, \tau) = \sum_{n=1}^{\infty} \frac{2}{\gamma_n} \left( \frac{\gamma_n^2 + N^2}{\gamma_n^2 + N^2 + N} \right) \exp(-\gamma_n^2 \tau) \sin \gamma_n \zeta$$

The concentration in the reservoir at  $\zeta = 1$  is then

$$\begin{aligned} \Gamma(1, \tau) &= \sum_{n=1}^{\infty} \frac{2}{\gamma_n} \left( \frac{\gamma_n^2 + N^2}{\gamma_n^2 + N^2 + N} \right) \exp(-\gamma_n^2 \tau) \sin \gamma_n \\ &= \sum_{n=1}^{\infty} \frac{2}{\gamma_n} \left( \frac{\gamma_n^2 + N^2}{\gamma_n^2 + N^2 + N} \right) \exp(-\gamma_n^2 \tau) \frac{(-1)^{n+1} N}{\sqrt{\gamma_n^2 + N^2}} \\ &= \sum_{n=1}^{\infty} \frac{2N(-1)^{n+1}}{\gamma_n} \left( \frac{\sqrt{\gamma_n^2 + N^2}}{\gamma_n^2 + N^2 + N} \right) \exp(-\gamma_n^2 \tau) \end{aligned}$$



## 20D.2 Unsteady-state interphase diffusion

a. Take the Laplace transform of Eq. 20C.2-1 and 2:

$$p\bar{c}_I - c_I(0) = \mathcal{D}_I \frac{d^2\bar{c}_I}{dz^2} \quad \text{and} \quad p\bar{c}_{II} - c_{II}(0) = \mathcal{D}_{II} \frac{d^2\bar{c}_{II}}{dz^2}$$

Then using the initial conditions and rearranging, we get

$$\mathcal{D}_I \frac{d^2\bar{c}_I}{dz^2} - p\bar{c}_I = -c_I^\circ \quad \text{and} \quad \mathcal{D}_{II} \frac{d^2\bar{c}_{II}}{dz^2} - p\bar{c}_{II} = -c_{II}^\circ$$

These ordinary differential equations can be solved to give

$$\bar{c}_I = C_1 \exp(\sqrt{p/\mathcal{D}_I}z) + C_2 \exp(-\sqrt{p/\mathcal{D}_I}z) + \frac{c_I^\circ}{p}$$

$$\bar{c}_{II} = C_3 \exp(\sqrt{p/\mathcal{D}_{II}}z) + C_4 \exp(-\sqrt{p/\mathcal{D}_{II}}z) + \frac{c_{II}^\circ}{p}$$

The boundary conditions at plus and minus infinity require that  $C_2$  and  $C_3$  be zero. The boundary conditions at the interface ( $z = 0$ ) yield:

$$\left( C_1 + \frac{c_I^\circ}{p} \right) m = \left( C_4 + \frac{c_{II}^\circ}{p} \right) \quad \text{and} \quad C_4 = -\sqrt{\frac{\mathcal{D}_I}{\mathcal{D}_{II}}} C_1$$

From these two equations we get the integration constants

$$C_1 = \frac{1}{p} \frac{c_{II}^\circ - mc_I^\circ}{m + \sqrt{\mathcal{D}_I/\mathcal{D}_{II}}} \quad \text{and} \quad C_4 = -\sqrt{\frac{\mathcal{D}_I}{\mathcal{D}_{II}}} C_1 = -\frac{1}{p} \frac{c_{II}^\circ - mc_I^\circ}{m\sqrt{\mathcal{D}_{II}/\mathcal{D}_I}}$$

Then the expressions for the transformed concentrations are

$$\bar{c}_I = \frac{1}{p} \frac{c_{II}^\circ - mc_I^\circ}{m + \sqrt{\mathcal{D}_I/\mathcal{D}_{II}}} \exp(\sqrt{p/\mathcal{D}_I}z) + \frac{c_I^\circ}{p}$$

$$\bar{c}_{II} = -\frac{1}{p} \frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m\sqrt{\mathcal{D}_{II}/\mathcal{D}_{I}}} \exp\left(-\sqrt{p/\mathcal{D}_{II}}z\right) + \frac{c_{II}^{\circ}}{p}$$

Then, taking the inverse transform (using a table of transforms), we get

$$c_{I} = \left( \frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m + \sqrt{\mathcal{D}_{I}/\mathcal{D}_{II}}} \right) \operatorname{erfc}\left( -\frac{z}{\sqrt{4\mathcal{D}_{I}t}} \right) + c_{I}^{\circ}$$

$$c_{II} = -\frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m\sqrt{\mathcal{D}_{II}/\mathcal{D}_{I}}} \operatorname{erfc}\left( \frac{z}{\sqrt{4\mathcal{D}_{II}t}} \right) + c_{II}^{\circ}$$

Then using the fact that  $\operatorname{erfc} x = 1 - \operatorname{erf} x$ , and that  $-\operatorname{erf}(-x) = \operatorname{erf} x$ , we finally get

$$c_{II} = -\frac{1}{p} \frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m\sqrt{\mathcal{D}_{II}/\mathcal{D}_{I}} + 1} \operatorname{erfc}\left( \frac{z}{\sqrt{4\mathcal{D}_{II}t}} \right) + c_{II}^{\circ}$$

$$\frac{c_{II} - c_{II}^{\circ}}{c_{I}^{\circ} - (1/m)c_{II}^{\circ}} = \frac{1 - \operatorname{erf}\left(z/\sqrt{4\mathcal{D}_{II}t}\right)}{(1/m) + \sqrt{\mathcal{D}_{II}/\mathcal{D}_{I}}}$$

b. To get the flux at the interface, we can differentiate the concentration profiles:

$$\begin{aligned} N_{Az}|_{z=0} &= -\mathcal{D}_{I} \frac{\partial c_{I}}{\partial z} \Big|_{z=0} \\ &= -\mathcal{D}_{I} \left( \frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m + \sqrt{\mathcal{D}_{I}/\mathcal{D}_{II}}} \right) \frac{2}{\sqrt{\pi}} \exp\left(-z^2/4\mathcal{D}_{I}t\right) \left( \frac{1}{\sqrt{4\mathcal{D}_{I}t}} \right) \Big|_{z=0} \\ &= -\left( \frac{c_{II}^{\circ} - mc_{I}^{\circ}}{m + \sqrt{\mathcal{D}_{I}/\mathcal{D}_{II}}} \right) \sqrt{\frac{\mathcal{D}_{I}}{\pi t}} \end{aligned}$$

Alternatively one can take the transform of the molar flux expression, differentiate  $\bar{c}_{I}$  with respect to  $z$ , then take the inverse transform to get the molar flux expression just found.

### 20D.3 Critical size of an autocatalytic system

(a) The general non-reactive transient solution for cylinders is

$$c_i = \sum_1^{\infty} A_n J_0(\alpha_n r) \exp(-\alpha_n^2 \mathcal{D} t / R^2)$$

and the reactive solution is just

$$c_{i,reactive} = \sum_1^{\infty} A_n J_0(\alpha_n r) \exp(k_1''' t - \alpha_n^2 \mathcal{D} t / R^2)$$

(b) Initial concentrations will decrease whenever all exponentials are negative, and the first term will be the most likely to be positive. Critical mass is then reached when

$$R = \alpha_1 \sqrt{\mathcal{D} / k_1'''}$$

(c) This answer is given in the problem statement.

20D.4 Dispersion of a broad pulse in steady laminar axial flow in a tube

(a) The approach here is to take advantage of the problem linearity and to add weighted pulse response solutions, or transfer functions, which are called here  $h(z,t)$ . For our situation the transfer function is

$$h(L,t) = \frac{1}{\sqrt{4\pi Kt}} \exp\left[-\frac{(L - \langle v \rangle t)^2}{4Kt}\right]$$

It only remains now to weight individual differential pulses, by  $f(t')$ , each introduced at a time  $t'$ , and add them up by integration from time zero to observer time  $t$ .

The response to an input of mass  $m_i$  added over a cross-sectional area of column  $A$ , in a short time period is just

$$(m_i / A)h(L,t)$$

The mass of solute per unit area can in turn be written as

$$dm_i / A = \rho_A|_{0,t'} \langle v \rangle dt' = f dt'$$

for uniform concentration over the inlet cross-section. Summing, or more specifically integrating over the time interval of interest then leads directly to the solution suggested

$$\langle \rho_A \rangle|_{L,t} = \frac{1}{\sqrt{4\pi K}} \int_{-\infty}^t f(t') \frac{\exp\left[-\frac{(l - \langle v \rangle t')^2}{4Kt'}\right]}{\sqrt{t'}} dt'$$

(b) For the square pulse one need only replace  $f$  by  $f_0 = \rho_{A0} \langle v \rangle$  and change the lower limit of integration to "0".

< end >

## 20D.5 Velocity divergence in interfacially embedded coordinates.

(a) Integration of Eq. 20.4-7 over the boundary  $S_D$  of any closed domain  $D(u, w, y)$  in the boundary layer gives

$$\int_{S_D} (\mathbf{V} \cdot d\mathbf{S}_D) = \int_{S_D} (\mathbf{v} \cdot d\mathbf{S}_D) + \int_{S_D} \left( \frac{\partial \mathbf{r}(u, w, y, t)}{\partial t} \cdot d\mathbf{S}_D \right) \quad (20D.5 - 1)$$

(b) Since the third dot product is the outward normal component of the velocity of the boundary element  $d\mathbf{S}_D$  relative to stationary coordinates, its integral is the rate of change of the volume  $V_D$  of the domain  $D(u, w, y)$ . With the aid of Eq. 20.4-3, we can rewrite this term as follows,

$$\begin{aligned} \int_{S_D} \left( \frac{\partial \mathbf{r}(u, w, y, t)}{\partial t} \cdot d\mathbf{S}_D \right) &= \frac{d}{dt} \int_D \sqrt{g(u, w, y, t)} du dw dy \\ &= \int_D \frac{\partial \sqrt{g(u, w, y, t)}}{\partial t} du dw dy \quad (20D.5 - 2) \end{aligned}$$

using Leibniz' rule to differentiate the second integral.

(c) Application of Eq. A.5-1 (in which  $\mathbf{v}$  is any differentiable vector function) to Eq. 20D.5-1, after use of Eq. 20D.5-2, gives the following equation in terms of volume integrals:

$$\int_{V_D} (\nabla \cdot \mathbf{V}) dV_D = \int_{V_D} (\nabla \cdot \mathbf{v}) dV_D + \int_D \frac{\partial \sqrt{g(u, w, y, t)}}{\partial t} du dw dy$$

Expressing each integral in the coordinates of Eq. 20.4-3, we then obtain

$$\int_D \left[ (\nabla \cdot \mathbf{V}) - \nabla \cdot \mathbf{v} - \frac{1}{\sqrt{g(u, w, y, t)}} \frac{d\sqrt{g(u, w, y, t)}}{dt} \right] \sqrt{g(u, w, y, t)} du dw dy = 0$$

In order that this equation hold for every domain  $D$  of nonzero  $g(u, w, y, t)$ , the quantity in square brackets must vanish identically in such regions, giving

$$(\nabla \cdot \mathbf{V}) = (\nabla \cdot \mathbf{v}) + \frac{\partial \ln \sqrt{g(u, w, y, t)}}{\partial t}$$

there in accordance with Eq. 20.4-8.

21A.1 Determination of eddy diffusivity

$$\ln(sc_A) = \ln(W_A / 4\pi D_{AB}) - (v_0 / 2D_{AB})(s - z)$$

Assume that

$$W_{CO_2} = 0.001 \cdot W_{Air}$$

(a) Begin by examining the behavior at  $r = 0$ , and note that

$$W_{air} = c_{tot} v \left( \frac{\pi D^2}{4} \right)$$

so that the volume fraction (equal to the mole fraction) of carbon dioxide

$$\phi_{CO_2} = \frac{1}{16} \cdot \frac{v_0 D^2}{z K_{ACO_2}} \cdot 0.001$$

where  $K_{ACO_2}$  is the effective diffusivity of carbon dioxide in air. Here we have assumed the ideal gas law to hold. We must now estimate the volume fractions, and here they will be taken as 0.0105 and 0.007 for distances of 112.5 and 152.7 cm respectively. Solving the above equation for the effective diffusivity then gives:

$$K_{A-CO_2} = 18.6, 21.9 \text{ cm}^2 / \text{s}$$

respectively.

## 21A.2 Heat and mass transfer analogy

Begin by defining the parameters

$$\Theta_{AB} = \frac{c_A - c_{A1}}{j_{A0} R / D_{AB}} \quad \xi = \frac{z}{v_{\max} R^2 / D_{AB}}$$

The desired solution then follows directly

$$\frac{D_{AB}(c_0 - c_b)}{j_{A0} D} = 2 \left( \frac{v_{\max}}{\langle v_z \rangle} \right)^2 \int_0^1 \frac{[I(\xi)]^2}{\xi [1 + (v^{(t)} / v)(Sc / Sc^{(t)})]} d\xi$$

**21B.1 Wall mass flux for turbulent flow with no chemical reactions.**

a. The Blasius formula for turbulent flow in a tube may be found in Eq. 6.2-12:

$$f = \frac{0.0791}{\text{Re}^{1/4}}$$

The mass-transfer analog of Eq. 13.3-7 is

$$\text{Sh} = \frac{1}{17.5} \sqrt{\frac{f}{2}} \text{Re} \text{Sc}^{1/3}$$

When these are combined, we get

$$\text{Sh} = 0.0114 \text{Re}^{7/8} \text{Sc}^{1/3}$$

b. If on the other hand, we use the mass-transfer analog of Eq. 13.4-20,

$$\text{Sh} = \frac{1}{12.48} \sqrt{\frac{f}{2}} \text{Re} \text{Sc}^{1/3} \quad (\text{large } \text{Sc})$$

then we get

$$\text{Sh} = 0.0160 \text{Re}^{7/8} \text{Sc}^{1/3}$$

which is in better agreement with experimental data.



21B.2 Alternate expressions for the turbulent mass flux.

Seek an asymptotic expression for the turbulent mass flux for long circular tubes and a boundary condition of constant wall mass flux. Assume net mass transfer across the wall is negligible.

- a) Parallel the approach to laminar flow heat transfer in §10.8 to write

$$\Pi(\xi, \zeta) = C_1 \zeta + \Pi_\infty(\xi) + C_2$$

and show that

$$C_1 = 4$$

Here  $\Pi = -(\omega_A - \omega_{A0}) / (j_{A0} D / \rho D_{AW})$ ;  $\xi = r / D$ ;  $\zeta = (z / D) / \text{Re} Sc$  and the subscript "0" indicates conditions at the wall. This is given in Section 10.8

- b) Put these results into the species continuity equation to obtain

$$-4 \frac{v_z}{\langle v_z \rangle} = \frac{1}{\xi} \frac{d}{d\xi} \left[ \left( 1 + \frac{Sc}{Sc^{(t)}} \frac{\mu^{(t)}}{\mu} \right) \xi \frac{d\Pi_\infty}{d\xi} \right]$$

This equation is to be integrated with the boundary conditions

At  $\xi = 1/2$   $\Pi_\infty = 0$  and  $d\Pi_\infty/d\xi = -1$

- c) Integrate once with respect to  $\xi$  to obtain:

$$-\frac{d\Pi_\infty}{d\xi} = \frac{\frac{1}{2} - 4 \int_{\xi}^{1/2} \frac{v_z}{\langle v_z \rangle} \xi d\xi}{\xi \left[ 1 + \frac{Sc}{Sc^{(t)}} \frac{\mu^{(t)}}{\mu} \right]}$$

Here  $Sc^{(t)} = \mu^{(t)} / \rho D_{AW}^{(t)}$ .

21B.3 An asymptotic expression for the turbulent mass flux.

Start with Eq. 21B.3-1 in the form

$$-\frac{1}{D} \frac{d\Pi_\infty}{d\xi} = + \frac{d\Pi}{dy} = \frac{1}{D} \frac{1}{[1 + Sc(yv^*/14.5v)^3]}$$

Making the suggested substitution yields

$$\frac{d\Pi}{dy} = \frac{d\Pi}{d\eta} \frac{Sc^{1/3} v^*}{14.5v}$$

so that

$$\frac{d\Pi}{d\eta} = \frac{14.5v}{Dv_* Sc^{1/3}} \frac{1}{1 + \eta^3}$$

and

$$\Pi(\infty) - \Pi(0) = \frac{14.5v}{Dv_* Sc^{1/3}} \int_0^\infty \frac{1}{1 + \eta^3}$$

The integral is equal to

$$I = \frac{\pi/3}{\sin(\pi/3)} = \frac{\pi}{3} \frac{2}{\sqrt{3}} = 1.209$$

It follows that

$$Sh = \frac{1}{\Pi(\infty) - \Pi(0)} = 0.057 Re Sc^{1/3} \sqrt{f/2}$$

If the Blasius expression is used for the friction factor we obtain

$$Sh = 0.0108 Re^{7/8} Sc^{1/3}$$

which is within about 5% of the above value. This is good agreement.

21B.4: Deposition of silver from a turbulent stream.

(a) We may write immediately from the results of the previous problem that

$$\frac{d\Pi}{d\eta} = \frac{14.5}{\text{Re} \text{Sc}^{1/3} \sqrt{f/2}} \frac{1}{1+\eta^3}$$

where  $\eta$  is defined as in the last example. In our situation. However, for our initial purposes it is most convenient to write

$$(D_{eq} v_* / \nu) = \text{Re} \sqrt{f/2} = \frac{2.54 \text{cm} \cdot 11.4 \text{cm/s}}{0.0101 \text{cm}^2 / \text{s}} = 2,863$$

The corresponding Schmidt number is 952 as stated in Fig.21B.3(b). The concentration gradient is then defined by

$$\frac{d\Pi}{d\eta} = \frac{1}{1942} \int_0^\eta \frac{d\eta}{1+\eta^3}$$

and we are now able to calculate the concentration gradient explicitly in terms of  $\eta$ .

We may now calculate the concentration gradient, and the results are shown in Fig.

21B.3(b). However, the abscissa is written in terms of

$$s^+ = s v_* / \nu$$

where  $s$  is distance measured into the fluid from the surface under consideration. This is done to facilitate comparison with velocity profiles. We can calculate the concentration profile by integration of the concentration gradient with respect to  $s^+$ , but this result is not shown on the figure. It rises so rapidly to a limiting value

$$\Pi(\infty) - \Pi(0) = 1.209/1942 = 6.23 \cdot 10^{-4}$$

that the initial slope appears infinite on the scale of the figure, and the ordinate is 0.000623 for all readable positions.

$$Sh = \frac{2864 \cdot 9.84}{1.209 \cdot 14.5} = 1606$$
 Under these conditions the cathode is completely

polarized, i.e. the silver ion concentration there is essentially. This is also the situation of maximum silver flux and the corresponding maximum, or *limiting* current.

The corresponding Sherwood Number is

and the mass transfer coefficient for  $Ag^+$  is

$$k_c = \left( \frac{D_{Ag-W}}{D} \right) Sh = \frac{1.06 \cdot 10^{-5} \text{ cm}}{2.54} \frac{1606}{s} = 6.7 \cdot 10^{-3} \text{ cm/s}$$

The corresponding silver ion flux

$$N_{Ag^+} = 6.7 \cdot 10^{-3} \frac{\text{cm}}{\text{s}} \cdot 10^{-9} \frac{\text{g-eqts}}{\text{cm}^3} = 6.7 \cdot 10^{-12} \frac{\text{g-eqts}}{\text{cm}^2 \text{s}}$$

## 21B.5 Mixing-length expression for the velocity profile.

(a) For steadily driven turbulent flow in a tube, Eq. 5.5-3 gives

$$\frac{d}{dr}(r\bar{\tau}_{rz}) = \frac{r(\mathcal{P}_0 - \mathcal{P}_L)}{L}$$

in which  $\bar{\tau} = \bar{\tau}^{(v)} + \bar{\tau}^{(t)}$ . Integration gives

$$r\bar{\tau}_{rz} = \frac{r^2}{2} \frac{(\mathcal{P}_0 - \mathcal{P}_L)}{L} + C_0$$

in which the integration constant  $C_0$  is zero because the other terms vanish at  $r = 0$ . Hence,

$$\bar{\tau}_{rz} = \frac{r}{2} \frac{(\mathcal{P}_0 - \mathcal{P}_L)}{L}$$

and the wall shear stress is

$$\tau_0 = \frac{R}{2} \frac{(\mathcal{P}_0 - \mathcal{P}_L)}{L}$$

Combining the last two equations, we get

$$\bar{\tau}_{rz} = \tau_0 \frac{r}{R} = \tau_0 \frac{R-y}{R} = \tau_0 \left(1 - \frac{y}{R}\right) \text{ for } 0 \leq y \leq R \quad (21B.5-1)$$

(b) Inserting the viscous momentum-flux expression

$$\bar{\tau}_{rz}^{(v)} = \mu \frac{d\bar{v}_z}{dy}$$

and the mixing-length model

$$\bar{\tau}_{rz}^{(t)} = \rho \ell^2 \left(\frac{d\bar{v}_z}{dy}\right)^2$$

into the result of (a), we get the differential equation

$$\rho \ell^2 \left(\frac{d\bar{v}_z}{dy}\right)^2 + \mu \frac{d\bar{v}_z}{dy} = \tau_0 \left(1 - \frac{y}{R}\right) \text{ for } 0 \leq y \leq R \quad (21B.5-2)$$

for the time-smoothed velocity distribution  $\bar{v}_z(r)$ .

(c) Setting  $v_* = \sqrt{\tau_0/\rho}$ ,  $\bar{v}_z = v_* v^+$ ,  $y = \nu y^+/v_*$ , and  $\ell = \nu \ell^+/v_*$  in Eq. 21B.5-2 gives

$$\rho \left(\frac{\nu \ell^+}{v_*}\right)^2 \left(\frac{d(v_* v^+)}{d(\nu y^+/v_*)}\right)^2 + \mu \frac{d(v_* v^+)}{d(\nu y^+/v_*)} = \tau_0 \left(1 - \frac{y^+}{R^+}\right) \text{ for } 0 \leq y^+ \leq R^+$$

Division of the terms of this equation by their common factor  $\tau_0 = \rho v_*^2 = (\mu/\nu)v_*^2$  gives

$$(\ell^+)^2 \left(\frac{dv^+}{dy^+}\right)^2 + \frac{dv^+}{dy^+} = \left(1 - \frac{y^+}{R^+}\right) \text{ for } 0 \leq y^+ \leq R^+$$

in agreement with Eq. 21.4-13.

22A.1 Prediction of mass transfer coefficients in closed channels

- a) Neglect the velocity of the water film surface.

$$\text{Re} = \frac{D(v\rho)}{\mu} = \frac{D(4W/\pi D^2)}{\mu} = \frac{4W}{\pi \mu D}$$

To a presently acceptable approximation the viscosity of air (in cp) at low density is given by

$$\mu = 0.0716 + 4.94 \cdot 10^{-5} T - 3.71 \cdot 10^{-8} T^2$$

where T is degrees centigrade. It follows that at 25 C

$$\mu = 0.0184 \text{cp} = 0.000184 \text{g/cm-s}$$

$$\text{Re} = \frac{4 \cdot 1570 \cdot 453.6 \cdot 0.032808}{\pi \cdot 0.000184 \cdot 0.5 \cdot 3600} = 89,820$$

At 2 atmospheres the kinematic viscosity is given approximately by

$$\nu = (1/2)[0.13269 + 8.73 \cdot 10^{-4} T + 9.8 \cdot 10^{-7} T^2] \text{ in cm}^2/\text{s}$$

or  $\nu = 0.0775 \text{cm}^2/\text{s}$

Then

$$\text{Sc} = \nu / D_{AW} = 0.60$$

It follows that the Sherwood number

$$\text{Sh} = 0.023 [89,820^{0.83} \cdot 0.6^{0.44}] = 237$$

and

$$k_c = 2.02 \text{cm/s}$$

- b) Here we must go back to Section 14.5 and the mass transfer analogs to the heat transfer expressions of Table 22.2-1.

We begin by writing

$$j_D = j_H = 2.19 \text{Re}^{-2/3} + 0.78 \text{Re}^{-0.381}$$

with

$$\text{Re} = \frac{6G_0}{a\mu} = 89,820 \cdot \frac{6}{(100/\text{ft})(0.5\text{ft})} = 10,778$$

Then

$$j_D = \frac{2.19}{10,788^{2/3}} + \frac{0.78}{\text{Re}^{0.381}} = 0.0272$$

We now turn to Table. 22.2-1 to write

$$j_D = \frac{k_c}{v_0} Sc^{2/3} = (0.6)^{2/3} \frac{k_c}{v_0}; k_c = \frac{0.0272}{0.6} v_0 = 0.0382 v_0$$

and it only remains to find the superficial velocity

$$v_0 = \frac{1570 \text{lb/hr}}{(\pi/4)(1/4 \text{ft}^2) \rho_{air}}$$

with air density given by the ideal gas law as

$$\rho_{air} = \frac{M_{air} p}{RT} = \frac{(28.97 \text{lbs/lb-mol})(2 \text{atm})}{(538 \text{R})(0.73 \text{atm-ft}^3/\text{lb-mol-R})} = 0.1475 \text{lbs/ft}^3$$

Then

$$v_0 = \frac{1570 \text{lb/hr}}{(\pi/4)(1/4 \text{ft}^2)(0.1475 \text{lbs/ft}^3)} \cdot \frac{\text{hr}}{3600 \text{s}} = 15.1 \text{ft/s}$$

or  $v_0 = 460 \text{cm/s}$

Then  $k_c = 17.6 \text{cm/s}$

22A.2 Calculation of gas composition from psychrometric data.

Solution is conveniently started with Eq. 22.3-39, with  $n$  equal to 0.44 (see Prob. 22A.1 statement). The molar heat capacity at the mean "film" temperature of 105 F is 6.98 Btu/lb-F (see Ex. 22.3-2), and the heat of vaporization at 80 F is 18,851 Btu/lb-mol. The vapor pressure of water at 80 F, 26.7 C, is 26.0 mm Hg. [Erratum: the coefficient of  $T^2$  in Fig. 22B.7 should be  $-7.98 \cdot 10^{-5}$ ]. It follows that the water vapor mole fraction at the water surface

$$x_{w0} = 26/800 = 0.0325$$

We may then write:

$$\frac{0.0325 - x_{w\infty}}{(130 - 80)(1 - 0.0325)} = \frac{6.98}{18,851} \left( \frac{0.58}{0.74} \right)^{0.56} = 3.23 \cdot 10^{-4}$$

It then follows that  $x_{w\infty} = 0.0158$

This differs from the answer given in the text primarily because I used a value of 0.56 for  $n$ , not 2/3. This corresponds to assuming  $Sh \propto Sc^{0.44}$ ,  $Nu \propto Pr^{0.44}$ .



### 22A.3 Calculating the inlet air temperature for drying in a fixed bed.

For water at  $60^\circ\text{F} = 15.56^\circ\text{C}$ , the fitted equation in Fig. 22B.7 gives  $p_{A,\text{vap}} = 13.15$  mm Hg. The resulting mole fraction of  $\text{H}_2\text{O}$  in the interfacial air, assuming local equilibrium and ideal gas behavior, is  $x_{A0} = (p_{A,\text{vap}}/p) = 13.15/(1.1 \times 760) = 0.0157$ . The film composition in the shallow bed is then  $x_{Af} = 0.5(0 + 0.0157) = 0.0079$ . The molar enthalpy of vaporization of water at this temperature, from Lange's Handbook (1999), is 19,044 Btu/lb-mol.

At the estimated film temperature  $T_f$  of  $90^\circ\text{F}$ , the molar heat capacities of dry air and of water vapor are found as 6.96 and 8.01, respectively, in Btu/lb-mol $\cdot$ F in Fig. 60 of Hougen Watson and Ragatz, *Chemical Process Principles Charts*, 2nd Ed., Wiley, New York (1960). Thus, the humid air at film conditions has a heat capacity  $\tilde{C}_p$  of  $0.0079 \times 8.01 + .9921 \times 6.96 = 6.97$  btu/lb-mol $\cdot$ F. The Prandtl number and Schmidt number at the film condition are taken as 0.74 and 0.58, respectively, as in Example 22.3-1.

The development in Example 22.3-2 can then be paralleled, with these comments:

- (i) For a shallow bed,  $x_{Ab}$  and  $T_b$  reduce to the inlet conditions  $x_{A1}$  and  $T_1$ .
- (ii) The exponent  $n = 1/3$  in Eq. 14.5-3, and in the analogous function  $j_D$ , is supported for this geometry by the data analysis reported in §14.5. The exponent  $1 - n = 0.56$ , reported by Bedingfield and Drew and cited on page 684, is for flow across a single cylinder in a large duct.

Therefore, subject to the indicated neglect of radiation, Eq. 22.3-38 can be taken over to calculate the inlet temperature as follows, with physical properties evaluated at  $(T_f, x_{Af})$ :

$$\begin{aligned} T_1 &= T_0 + \left( \frac{x_{A0} - x_{A1}}{1 - x_{A0}} \right) \left( \frac{\text{Sc}}{\text{Pr}} \right)^{-2/3} \frac{\Delta \hat{H}_{\text{vap}}}{\tilde{C}_p} \\ &= 60 + \left( \frac{0.0157 - 0}{1 - 0.0157} \right) \left( \frac{0.74}{0.58} \right)^{2/3} \left( \frac{19,091}{6.97} \right) \\ &= 111.4^\circ\text{F} \end{aligned}$$

#### 22A.4 Rate of drying of granular solids in a fixed bed.

The calculations made in the solution of Problem 22A.3 are applicable here, along with the comments (i) and (II). Note also that the flux ratio  $R_x$  of Table 22.8-1 has the value

$$R_x = \frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} = \frac{0.0157 - 0}{1 - 0.0157} = 0.0160$$

here, when the solubility of species B (air) in the interstitial liquid water is neglected. At this small value of  $R_x$ , the mass-transfer coefficient  $k_{x,loc}$  is negligibly affected by the net molar transfer, as shown in Fig. 22.8-1 on page 710.

Then the binary analog of Eq. 14.5-1 gives the rate of water removal per unit volume of bed as

$$\frac{dW_{A0}}{Sdz} = (k_{x,loc}a) \frac{(x_{A0} - x_{Ab})}{(1 - x_{A0})}$$

and the Chilton-Colburn analogy  $j_H = j_D$  in Eq. 22.3-23, when applied to Eqs. 14.5-2,3,4, gives the following binary mass-transfer formula in molar units (see also Table 22.2-1):

$$j_D = \frac{k_{x,loc}}{cv_0} (Sc)^{2/3} = 2.19Re^{-2/3} + 0.78Re^{-0.381}$$

in which

$$Re = \frac{6\rho v_0}{a\mu\psi} = \frac{6v_0}{a\nu\psi}$$

Insertion of numerical values for this problem (including  $\nu = 0.162 \text{ cm}^2/\text{s} = 0.000174 \text{ ft}^2/\text{s}$  from Table 1.2.1 and §F.3,  $\psi = 0.92$  for cylinders from page 441, and  $c = p/RT = 0.00275 \text{ lb-mol}/\text{ft}^3$ ) gives

$$Re = \frac{(6)(15)}{(180)(0.000174)(0.92)} = 3.123 \times 10^3$$

$$j_D = (2.19)(3123)^{-2/3} + (0.78)(3123)^{-0.381} = 0.0466$$

$$\begin{aligned} k_{x,loc} &= j_D cv_0 (Sc)^{-2/3} \\ &= (0.0466)(0.00275)(15)(0.58)^{-2/3} = 0.00276 \text{ lb-mol}/\text{s}\cdot\text{ft}^2 \end{aligned}$$

and finally, the initial rate of water removal per unit volume of bed is

$$\begin{aligned} \frac{dW_{A0}}{Sdz} &= (0.00276 \text{ lb-mol}/\text{s}\cdot\text{ft}^2)(180 \text{ ft}^2/\text{ft}^3) \frac{0.0157 - 0}{1 - 0.0157} \\ &= 7.9 \times 10^{-3} \text{ lb-mol}/\text{s}\cdot\text{ft}^3 \\ &= 28.5 \text{ lb-mol}/\text{hr}\cdot\text{ft}^3 \end{aligned}$$

### 22B.1 Evaporation of a freely falling drop

Begin by noting that acceptable approximations for all needed physical properties have been provided in the above solutions except water density which is  $0.998 \text{ g/cm}^3$ .

(a) From Eq. 6.1-7 we may write

$$\text{Re}^2 f = \frac{4 D^3 g \Delta \rho}{3 \mu}$$

and for this problem

$$D = 0.1 \text{ cm}, g = 980 \text{ cm/s}^2, \Delta \rho = (0.998 - 0.0014) \text{ g/cm}^3, \mu = 1.84 \cdot 10^{-4} \text{ g/cm}\cdot\text{s}$$

so that

$$\text{Re} \sqrt{f} = 212.5$$

A plot of this  $f(\text{Re})$  relation on Fig. 6.3-1 is line of slope minus 2 which intersects the friction factor-Re curve at a Reynolds number of 250. It follows that

$$v = 250 \mu / D \rho \approx 390 \text{ cm/s}$$

(b) To the accuracy of this problem we may use the simple approximation of Eq. 14.4-5 and its mass transfer counterpart

$$Nu_m = 2 + 0.6 \text{Re}^{1/2} \text{Pr}^{1/3} = 10.6$$

$$Sh_m = 2 + 0.6 \text{Re}^{1/2} Sc^{1/3} = 10$$

It follows that to a reasonable approximation

$$\frac{h}{k_x} = \frac{10.6}{10} C_p \left( \frac{Sc}{Pr} \right) \approx 6$$

cal/g-mole, C or Btu/lb-mole, F. We may then write approximately

$$\frac{x_{w0} - 0}{(100 - T_0)(1 - x_{w0})} \approx \frac{6}{19,100} \approx 3.2 \cdot 10^{-4} F^{-1}$$

This equation is to be solved simultaneously with the equilibrium relation

$$x_{w0} = p_w^\circ / 1 \text{ atm}$$

with the vapor pressure of water  $p_w^\circ$  obtained for example from Fig. 22B.6. This process yields a surface temperature

$$T_0 \approx 54F \text{ and } x_{w0} \approx 0.0141$$

(c) A mass balance over the sphere gives

$$-\frac{d}{dt} \left( \frac{4}{3} \pi R^3 c_L \right) = 4\pi R^2 N_{wr0}$$

This equation is easily rewritten as

$$-\frac{dD}{dt} = \frac{2k_{xm} x_{w0} - x_{w\infty}}{c_L (1 - x_{w0})}$$

We now assume pseudo-steady condition such that sphere surface temperature is that given by the above analysis, and we use the following parameter values

$$c_G = p/RT = 1/(82.05 \cdot 285) = 4.28 \cdot 10^{-5} \text{ g} = \text{moles/cm}^3$$

$$v_G = 0.13269 + 0.0008729 + 9.82 \cdot 10^{-7}$$

$$= 0.1433 \text{ cm}^2 / \text{s}$$

$$D_{WA} = v_G / Sc = (0.1433 \text{ cm}^2 / \text{s}) / 0.625$$

$$= 0.229 \text{ cm}^2 / \text{s}$$

$$k_{xm} = 10 \frac{(cD_{wa})_G}{D} = \frac{10 \cdot (4.06 \cdot 10^{-5}) \cdot 0.229}{0.1}$$

$$= 9.3 \cdot 10^{-4} \text{ g} - \text{mols/cm}^2, \text{s}$$

Then

$$-\frac{dD}{dt} = \frac{2 \cdot 9.3 \cdot 10^{-4} \text{ g} - \text{mols/cm}^2 \cdot 0.0141}{0.0555 \text{ g} - \text{mols/cm}^3 \cdot 0.9859} = 4.79 \cdot 10^{-4} \text{ cm/s}$$

## 22B.2 Effect of radiation on psychrometric measurements

- (a) Only convective and radiant heat transfer occur for the dry-bulb thermometer, and we may write

$$h_{db}(T_{\infty} - T_{db}) + \sigma [a_{db}T_s^4 - e_{db}T_{db}^4]$$

Here the subscripts db,  $\infty$  and s refer to the mean dry bulb temperature, the air

temperature of the surroundings, respectively.

This equation permits determining the bulk air temperature,  $T_{\infty}$ , from the dry-bulb reading and  $T_s$ , presumed known.

- (b) Here we must consider convective heat transfer and write

$$\begin{aligned} N_{w0} \Delta \tilde{H}_{w,vap} &= k_{xwm} \frac{x_{w0} - x_{w\infty}}{1 - x_{w0}} \Delta \tilde{H}_{w,vap} \\ &= h_{wb}(T_{\infty} - T_{wb}) + \sigma [a_{wb}T_s^4 - e_{wb}T_{wb}^4] \end{aligned}$$

$$j_H \approx 0.57 / \sqrt{\text{Re}} = 0.57 / \sqrt{621} = 0.023$$

Here kinematic air viscosity is calculated for 60 C (140 F) from the equation

$$\nu_{air} = 0.1327 + 0.00087T + 9.82 \cdot 10^{-7} T^2$$

where  $\nu$  is in cp, T is in C, and the pressure is one atmosphere. It then follows from the gas law and the other data given that

$$h_{db} \approx 24 \text{ Btu/hr, ft}^3, ^\circ \text{F}$$

$$\text{Then } T_\infty \approx 140 + \frac{0.1712 \cdot 0.93}{24} \left[ \left( \frac{600}{100} \right)^4 - \left( \frac{590}{100} \right)^4 \right] = 140.6 \text{ F}$$

This is a quite minor correction.

Following the same approach we find that

$$h_{wb} \approx 20 \text{ Btu/hr, ft}^2, ^\circ \text{F}$$

and

$$\frac{h_{wb}}{k_{xw} \Delta \tilde{H}} = \frac{\tilde{C}_{p,w}}{\Delta \tilde{H}} \left[ \frac{Sc}{Pr} \right]^{2/3} = 3.14 \cdot 10^{-4} / ^\circ \text{F}$$

Putting this result into the first equation of (c) yields

$$x_{w\infty} = 0.0021$$

which is significantly <sup>smaller</sup> than the result in Ex. 22.3-2.

### 22B.3 Film theory with variable transport properties

Begin with Eq. 19.4-10 and rearrange to

$$cD_{AB} \frac{dx_A}{dy} = x_A(N_{A0} + N_{B0}) - N_{A0}$$

and separate variables to obtain

$$\begin{aligned} \frac{dy}{cD_{AB}} &= \frac{dx_A}{x_A(N_{A0} + N_{B0}) - N_{A0}} \\ &= \frac{d \ln[x_A(N_{A0} + N_{B0}) - N_{A0}]}{(N_{A0} + N_{B0})} \end{aligned}$$

$$I \equiv (N_{A0} + N_{B0}) \int_0^y \frac{dy}{cD_{AB}} = \ln[x_A(N_{A0} + N_{B0}) - N_{A0}] \Big|_{x_{A0}}$$

or

$$e^I = \frac{x_A(N_{A0} + N_{B0}) - N_{A0}}{x_{A0}(N_{A0} + N_{B0}) - N_{A0}}$$

Then

$$I = \frac{N_{A0} - x_A(N_{A0} + N_{B0})}{N_{A0} - x_{A0}(N_{A0} + N_{B0})}$$

Now subtract

$$\frac{N_{A0} - x_{A0}(N_{A0} + N_{B0})}{N_{A0} - x_{A0}(N_{A0} + N_{B0})}$$

from both sides to obtain the desired result:

$$\frac{(N_{A0} + N_{B0})(x_A - x_{A0})}{N_{A0} - x_{A0}(N_{A0} + N_{B0})} = 1 - \exp \left[ (N_{A0} + N_{B0}) \int_0^y \frac{dy}{cD_{AB}} \right]$$

The heat transfer analog can be obtained by a similar procedure. Parts (b) and (c) are left to the reader.

## 22B.4 An evaporative ice maker

Here we are only interested in a preliminary study so will assume steady behavior. We will also accept the boundary layer simplifications introduced in this chapter and the simplified boundary conditions that go with it. We begin by neglecting the differences in  $Sc$  and  $Pr$  so that we can use the additivity of Grashof numbers introduced in Ex. 22.6-1, and we apply this concept to the horizontal plate with flow inward from the surroundings. For illustrative processes we use the laminar-flow expression for a horizontal plate. Now the flow of fluid will be toward the plate and out at the periphery, and this is the situation of a cooled plate: the surface is cooler than the surroundings. We thus begin with Eq. 14.6-7:

$$Nu_m = \frac{0.527}{[1 + (1.9/Pr)^{9/10}]^{2/9}} (Gr Pr)^{1/5}$$

For our present purposes  $Gr$  is replaced by  $(Gr + Gr_{AB})$ , but in this situation  $Gr_{AB}$  is quite small and can be neglected. Moreover, it should be noted that the denominator has the magnitude

$$[1 + (1.9/0.74)^{9/10}]^{2/9} = 1.30$$

and the corresponding expression for  $Sc$  of 0.58 is 1.35, which is not significantly different for our present purposes.

We may thus write

$$Nu_m \approx \frac{0.57}{1.3} 0.74^{1/5} Gr^{1/5} = 0.412 Gr^{1/5}$$

$$Sh_m \approx \frac{0.57}{1.35} 0.58^{1/5} = 0.379 Gr^{1/5}$$

and

$$h/k_{xw} = \frac{0.412 Sc}{0.379 Pr} \tilde{C}_p \approx 0.85 \tilde{C}_p$$

It follows that



$$\frac{(x_{w0} - x_{w\infty})}{(T_\infty - T_0)(1 - x_{w0})} = 0.85 \frac{\tilde{C}_p}{\Delta\tilde{H}_{vap}}$$

Heat of vaporization should be calculated at the freezing point and is about

$$\Delta\tilde{H}_{vap} = 19,313 \text{ Btu/lb-mol} = 10,735 \text{ cal/g-mol}$$

The molar heat capacity should be evaluated at a somewhat higher but unknown temperature. Since its temperature sensitivity is small we shall use a value of

$$\tilde{C}_p \approx 8 \text{ Btu/lb-mole, } F = 8 \text{ cal/g-mole, } F$$

which corresponds to about 40 F or approximately 5 C.

Using the vapor pressure data of Fig. 22B.6 we find the relation between surrounding mole fraction and temperature is

$$\frac{0.00626 - x_{w\infty}}{T_\infty(1 - 0.00626)} = 0.85 \frac{8}{10,735}$$

or

$$x_{w\infty} = 0.00676 - 6.29 \cdot 10^{-4} T \quad x_w = 0.00626 - 6.29 \cdot 10^{-4} T$$

This equation is plotted on the attached psychrometric chart. It may be seen here that the maximum possible temperature is about 5.5 C or about 42 F, and that even for extremely dry air, the maximum is a bit below 10 C or 50 F.

We must now see how effective radiation to the night sky can be, and we start with a result already obtained in Prob. 22B.2:

$$\frac{0.00626 - x_{w\infty}}{T_\infty(1 - 0.00626)} = 0.85 \frac{8}{10,735} \left\{ 1 + \left[ \frac{\sigma e(T_s^4 - T_0^4)}{hT_\infty} \right] \right\}$$

Note though that radiation now opposes convective heat transfer, and that the radiation flux is independent of local ambient temperature. For the given conditions and a grey surface, with absorptivity equal to emissivity of 0.93, as in Prob. 22B.2, we find

$$q_{rad} = 1.355 \cdot 0.93 (0.15^4 - 0.273^4) = -5.04 \cdot 10^{-3} \frac{\text{cal}}{\text{cm}^2, \text{s}}$$

We must now calculate the free convection heat transfer coefficient from

$$h_m = 0.412 \frac{k}{D} Gr^{0.2}$$

$$\text{with } Gr = \frac{D^3 g \beta \Delta T}{\nu^2}$$

$k \approx 5.9 \cdot 10^{-5} \text{ cal/cm}\cdot\text{s}\cdot^\circ\text{K}$  (Bejan),  $D = 50 \text{ cm}$ ,  $g = 980 \text{ cm/s}^2$ ,  $\beta = 1/T \approx 1/273 = 0.00366$ ,  $\nu \approx 0.133 \text{ cm}^2/\text{s}$

$$Gr \approx \frac{50^3 \cdot 980 \cdot \Delta T}{273 \cdot (0.133)^2} = 2.54 \cdot 10^7 \Delta T$$

$$\text{and } Gr^{1/5} = 30.2 (\Delta T)^{0.2} (^\circ\text{C})^{-0.2}$$

$$\text{Then } h = 0.412 \frac{6 \cdot 10^{-5}}{50} 30.2 (\Delta T)^{0.2} = 1.46 \cdot 10^{-5} \frac{\text{cal}}{\text{cm}^2 \cdot \text{s} \cdot (^\circ\text{C})^{0.2}}$$

and the convective heat transfer rate is

$$q_{conv} = 1.46 \cdot 10^{-5} (\Delta T)^{1.2} \text{ cal/cm}^2 \cdot \text{s} \cdot (^\circ\text{C})^{1.2}$$

We may now calculate the local ambient temperature for which no net evaporation takes place: where radiation out just balances convection in to the water surface.

From the left side of the wet-bulb expression this is the temperature at which 30% saturated air has a water vapor mole fraction of 0.00626. From our psychrometric chart this is about 20 C. However, at this temperature

$$q_{conv} = 4.2 \cdot 10^{-4} \text{ cal/cm}^2 \cdot \text{s}$$

which is insufficient to supply the radiative loss. Water vapor must now condense to supply the radiative loss, and local ambient temperature must be well above 20 C.

We could go further, but already it is clear that radiation is very powerful, and that the prediction is greatly at variance with observation. Ice is never found at ambient temperatures even of 20 C. There are many possible reasons for this discrepancy between this simple theory and actual observation. They include

conduction from the ground, forced convection in the form of wind and turbulence in the boundary layer. This last is unlikely as flows about a cold plate facing upwards are very stable (Rohsenow et al, p. 4.17). However, one of the most important is fog formation (see Ex. 19.5-2), very often seen on still nights. Fog very effectively inhibits radiation. Ice can form at very high ambient temperatures in a desert.

Finally we note that the efficiency of our device can be significantly improved by the presence of a small lip as this adds a convective heat transfer resistance without appreciably affecting radiation. A stagnant film has a thermal resistance which can be calculated from

$$Nu = hD/k = D/\delta$$

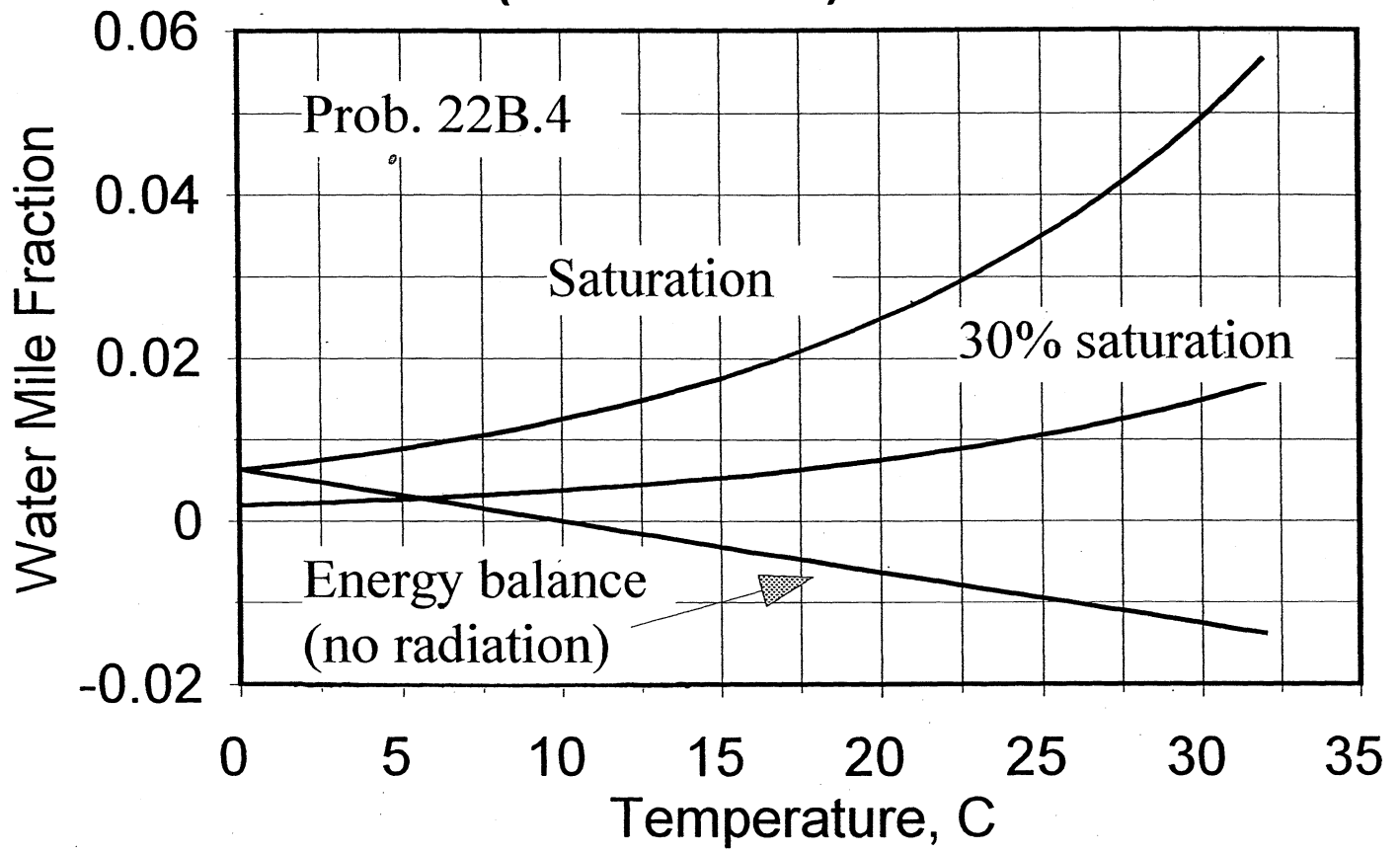
where  $\delta$  is the film thickness. Then for 2 mm film

$$h = k/\delta = (5.9 \cdot 10^{-5} \text{ cal/cm}\cdot\text{s}\cdot^{\circ}\text{C})/0.2\text{cm}$$

or 
$$h_{film} = 2.95 \cdot 10^{-5} \text{ cal/cm}^2\cdot\text{s}\cdot^{\circ}\text{C}$$

and its resistance is the reciprocal of this quantity.

# Evaporative Ice maker (no radiation)



## 22B.5 Oxygen stripping

Once again we must begin by determining terminal velocity, and we begin here with the fundamental momentum balance

$$F = \frac{4}{3}\pi R^3 \Delta\rho g = \frac{1}{2}\pi R^2 \rho_w v^2 f$$

and rearranging as before we find

$$\text{Re}^2 f = \frac{4 D^3 \rho_w \Delta\rho g}{3 \mu_w^2}$$

Looking ahead to the inaccuracies involved in using the graphical form of the  $f(\text{Re})$  relation shown in Fig. 6.3-1 we make the approximations

$$\Delta\rho \approx \rho_w; \mu_w^2 / \rho_w \Delta\rho \approx v_w^2 \approx 10^{-4} \text{ cm}^4 / \text{s}^2$$

It follows that

$$\text{Re}^2 f = \frac{4 \cdot 10^{-3} \cdot 980}{3 \cdot 10^{-4}} = 1.3 \cdot 10^4$$

Sketching this  $f$ - $\text{Re}$  relation on Fig. 6.3-1 shows that the Reynolds number is of the order of 10, where

$$f \approx 18.5 / \text{Re}^{3/5}$$

Eliminating the friction factor between these two expressions yields

$$\text{Re}^{7/5} = 1.3 \cdot 10^4 / 18.5; \text{Re} \approx 108$$

We are now ready to estimate mass transfer rates, and we begin by anticipating the results of Prob. 22B.8 by assuming that essentially all mass transfer resistance occurs in the water phase.

The best available correlation is then that

$$\text{Sh}_m \approx 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} = k_{cm} D / D_{AW}$$

and it remains to determine magnitudes of key system properties. Here we shall assume oxygen solubility to be given by

$$c_{O_2} = [2.17 - 0.0507T + 5.604 \cdot 10^{-4} T^2](p/1\text{atm})$$

where concentration is mmols/L, and temperature is in degrees centigrade [regression of data in J. E. Bailey and D. F. Ollis, Biochemical Engineering Fundamentals, 2nd Ed., McGraw-Hill, 1986 -- p. 463]. Then for our circumstances, the entering oxygen concentration is about

$$c_{O_2} \approx 1.38 \text{ mmols} / L = 1.38 \cdot 10^{-6} \text{ g - mols} / \text{cm}^3$$

For oxygen-water diffusivity we shall use

$$D_{O_2W} \approx (1.04 + 0.053T) \cdot 10^{-5} \text{ cm}^2 / \text{s}$$

[This is a regression of data at 37 C by E. E. Spaeth and S. K. Friedlander, Biophys. J. 1967, p.827 and data at 25 C reported in T. K. Sherwood, et al, Mass transfer 1975, Wiley] It follows that

$$D_{O_2W} \approx 2.1 \cdot 10^{-5} \text{ cm}^2 / \text{s}$$

Then the Schmidt number

$$Sc \approx 0.0100137 / [2.1 \cdot 10^{-5}] = 476$$

and

$$k_c = \frac{2.1 \cdot 10^{-5} \text{ cm}^2 / \text{s}}{0.1 \text{ cm}} \left[ 2 + 0.6 \cdot 108^{1/2} \cdot 476^{1/3} \right] \approx 0.0106 \text{ cm} / \text{s}$$

The inward directly oxygen flux at the bubble surface is then

$$-N_{O_2r} \Big|_{r=R} = k_c \Delta c_{O_2} = 0.010106 \cdot 1.38 \cdot 10^{-8} \text{ gmoles} / \text{cm}^2, \text{s}$$

## 22B.6 Controlling diffusional resistances

No first of all because there is no diffusional resistance in pure oxygen. However, the same answer would be true even if the gas phase were any nitrogen-oxygen mixture. The gas phase contribution is truly negligible, so it is only necessary to recognize that the gas phase diffusivity is in the range of

$$0.1 < D_{GM} < 1.0 \text{ cm}^2 / \text{s}$$

where G is "any" gas in a gas containing "M" and "G" for these conditions. To show this begin by writing

$$N_{O_2,0} = k_{cL}(c_{Lb} - c_{L0}) = k_{cG}(c_{G0} - c_{Gb}) = K_{cL}(c_{Lb} - c_{Le})$$

Now define

$$(c_{G0} - c_{Gb}) = \frac{1}{m}(c_{L0} - c_{Le})$$

to write

$$\frac{1}{k_{cL}} + \frac{m}{k_{cG}} = \frac{1}{K_{cL}} \quad \text{or} \quad \frac{k_{cL}}{K_{cL}} = 1 + m \frac{k_{cL}}{k_{cG}}$$

Noting that

$$Sh = Dk_c / D_{im}$$

we may write

$$\frac{k_{cL}}{K_{cL}} = 1 + m \frac{D_{O_2W} Sh_L}{D_{O_2A} Sh_A}$$

and to an order of magnitude approximation

$$(Sh_L / Sh_G) \ll (D_{O_2A} / D_{2OW})^n$$

where "n" is 1/3 for the situation being considered here.

Note that for our conditions

$$c_G = p / RT = \frac{1 \text{ atm, g = mole}}{82.05 \text{ cm}^3 \cdot 293.16} \cdot 10^6 \frac{\text{mmols, cm}^3}{\text{g - mole, L}} = 41.6 \text{ mmols / L}$$

so that

$$m \approx 0.03$$

## 22B.7 Determination of diffusivity

The basic problem here is to calculate the quantity  $\psi$ . this may be shown as follows:

For the actual situation,

$$\frac{dV}{dt} = S\phi\sqrt{D_{WA}/t}$$

whereas in the absence of convection

$$\frac{dV}{dt} = Sx_{W0}\sqrt{D_{WA}/\pi t}$$

The ratio of these two quantities is then just  $\psi$ .

Determination of  $\psi$  is difficult, as stated in Ex. 20.1-1, but the inverse is straightforward. Examples in the supplement attached show that significant corrections are needed even for mole fractions as low as 0.03. These calculations were made using the approximation of the error function

$$\text{erf}(x) \approx 1 - (a_1t + a_2t^2 + a_3t^3)e^{-x^2}$$

$$t = 1/1 + 0.47047x$$

$$a_1 = 0.34802$$

$$a_2 = -0.09587$$

$$a_3 = 0.74785$$

with

(Abramowitz and Stegun, 7.1.25.)

Mole fractions can be related to temperature using Fig. 22B.6.

Now just looking at Table 20.1-1 we see that  $\psi$  begins to increase very rapidly with interfacial water vapor mole fraction, and this means that heat supply can become a problem.



Now the oxygen-air diffusivity is to the approximations of Chap. 17 equal to oxygen-air diffusivity, and from Table 17.1-1 this is  $0.181 \text{ cm}^2/\text{s}$ . From Eq. 17.2-1

$$D_{O_2A} = (0.18)(293.2/273.2)^{1.82} = 0.205 \text{ cm}^2 / \text{s}$$

We then find that

$$\frac{k_{cL}}{K_{cL}} \ll 0.03 \left( \frac{2.1 \cdot 10^{-5}}{2.05 \cdot 10^{-1}} \right)^{2/3} = 6.6 \cdot 10^{-5}$$

which is truly negligible. Similar remarks hold or almost all systems of sparingly soluble gases.

## 22B.8 Marangoni effects in condensation of vapors

We begin by calculating film thickness in the absence of surface tension gradients as

$$\begin{aligned}\delta &= k/h = (0.73/5,000)m \\ &= 1.46 \cdot 10^{-4} m\end{aligned}$$

From Eq.2.2-19

$$\langle v \rangle = g\delta^2 / 3\nu = 24.0 \text{ cm/s}$$

and the mass flow rate per unit width

$$\rho \langle v \rangle = 24.0 \cdot 0.96 = 23.1 \text{ g/cm, s}$$

We may now parallel the development of Ex. 2.2 and write

$$\tau_{xz} = \rho gx + C_1$$

but now the integration constant is to be evaluated from the new BC so that

$$\tau_{xz} = \rho gx + \tau_s = -\mu dv_z / dx$$

Integrating this equation with respect to  $x$ , and using the BC

$$v_z|_{x=\delta} = 0$$

yields

$$\rho \langle v \rangle = \left[ \frac{\rho^2 g \delta^2}{3\mu} \right] \left( 1 + \frac{3}{2} \frac{\tau_s}{\rho g \delta} \right)$$

The term in  $\tau_s$  represents the effect of surface tension gradients, and where this term is small its denominator will be about that for no gradient. Now for our circumstances  $\rho g \delta \doteq 14.3 \text{ dyne/cm}^2$ . Surface tension effects will thus be small for systems like ours where surface tension increases downwards. In the reverse case however, even small gradients can cause hydrodynamic instabilities and thus have major effects.

22B.9 and 22B.10 Film models for spheres and cylinders.

For all three of our basic coordinate systems we may write

$$N_A - x_A (N_A + N_B) = -cD_{AB} \frac{dx_A}{dr}$$

where  $r$  represents distance,  $y$  for rectangular coordinates and  $r$  for cylindrical and spherical. A subscript "r" is understood for each of the molar fluxes.

It is necessary for this development that the left side of the equation become independent of  $r$ , so we rewrite it as

$$r^n [N_A - x_A (N_A + N_B)] = -cD_{Ab} r^n \frac{dx_A}{dr}$$

where  $n = 0$  for slabs, 2 for spheres and 1 for cylinders. Now for all three

$$r^n N_i = R^n N_i(R)$$

a constant, and  $R$  is any convenient value of  $r$ . We may then write

$$\begin{aligned} R^n [N_{AR} - x_A (N_{AR} + N_{BR})] \\ = \frac{cD_{AB}}{R^n [N_{AR} + N_{BR}]} r^n \frac{d \ln [R^n (N_{AR} + N_{BR})]}{dr} \end{aligned}$$

with boundary conditions

$$x_A = x_{A0} \text{ at } r = R_0$$

$$x_A = x_{A\delta} \text{ at } r = R_\delta$$

Here the subscript "R" denotes evaluation at  $r = R$ .

Separation of variables and integration gives

$$\frac{R^n [N_{AR} - x_{A\delta} (N_{AR} + N_{BR})]}{R^n [N_{AR} - x_{A0} (N_{AR} + N_{BR})]} = \exp \left[ \frac{R^n (N_{AR} + N_{BR})}{cD_{AB}} \int_{R_0}^{R_\delta} \frac{dr}{r^n} \right] \equiv E$$

$$E = \frac{(N_{A0} + N_{B0}) R_0}{cD_{Ab} R_\delta} (R_\delta - R_0)$$

Note now that  $R$  cancels out on the left side of this equation. We can this eliminate it and, just for convenience, replace the “ $R$ ” subscripts by “ $0$ ”, referring to conditions at  $R_0$ .

Moreover we can add  $1 + -1$  to the left side in the form of

$$1 - \frac{N_{A0} - x_{A0}(N_{A0} + N_{B0})}{N_{A0} - x_{A0}(N_{A0} + N_{B0})}$$

We thus obtain

$$1 + \frac{(N_{A0} + N_{B0})(x_{A0} - x_{A\delta})}{N_{A0} - x_{A0}(N_{A0} + N_{B0})} = E$$

as required. Moreover,  $E$  can be expressed as

$$E = \exp\left[(N_{A0} + N_{B0})/k_{x,loc}\right]$$

to complete the development. Remember that we are using the mass transfer coefficient for negligible convection, so that

$$x_{A0}(N_{A0} + N_{B0}) \ll N_{A0}$$

To show this for spheres, start with a spherical shell and write

$$\nabla^2 x_A = 0 = \frac{1}{r^2} \frac{d}{dr} r^2 \frac{dx_A}{dr}$$

For the above boundary conditions this yields

$$\frac{x_A - x_{A0}}{x_{A\delta} - x_{A0}} = \frac{R_\delta - R_0}{R_\delta} \left(1 - \frac{R_0}{r}\right)$$

$$N_{A0} = \left[ cD_{AB} \left( \frac{R_\delta}{R_0} \frac{1}{(R_\delta - R_0)} \right) \right] (x_{A0} - x_{A\delta}) = k_{x,loc} (c_0 - c_\delta)$$

The cylindrical result is obtained similarly, and the heat transfer results can be obtained directly by analogy:

$$N_A \rightarrow N_A \tilde{C}_{pA}$$

$$cD_{AB} \rightarrow k$$

$$x_A \rightarrow T$$

$$J_{A0}^* \rightarrow q_0$$

Moreover, one can extend this result to variable properties by including the transport properties inside the integral.

## 22C.1 Calculation of ultrafiltration rates

The calculational technique is described in detail on pages 714 and 715, and the results are shown in Fig. 22.8-9.

Prob. 23A.1 Expansion of a gas mixture: very slow reaction rate

We first the gas composition from Eqs. 23.5-56 through 59:

$$K_H = \frac{(x_{H_2O})(x_{CO})}{(x_{H_2})(x_{CO_2})} = \frac{(x_{CO})^2}{(x_{CO_2})^2} = \left( \frac{x_{CO}}{0.5 - x_{CO_2}} \right)^2$$

$$x_{CO} = \frac{0.5\sqrt{K}}{1 + \sqrt{K}}; \quad \sqrt{K} = 10^{-0.15/2} = 0.841;$$

$$x_{CO} = x_{H_2O} = \frac{0.5 \cdot 0.841}{1 + 0.841} = 0.228;$$

$$x_{H_2} = x_{CO_2} = 0.5 - 0.228 = 0.272$$

It follows that

$$\sum_i x_i M_i = 0.228(28.01 + 18.02) + 0.272(2.016 + 44.01) = 23.01$$

$$\begin{aligned} \sum_i x_i \tilde{C}_{pi} &= 0.228(7.93 + 9.86) + 0.272(7.217 + 12.995) \\ &= 9.554 \text{ cal} / \text{g} - \text{mol}, ^\circ \text{K} \end{aligned}$$

Substitution of this last result in Eq. 23.5-54 yields

$$T_2 = T_1 (p_2 / p_1)^{R / \sum x_i \tilde{C}_{pi}} = 1000(1/1.5)^{(1.987/9.55)} = 920 \text{ K}$$

Substitution of the above values in Eq. 23.5-55, using Table F3.3, yields

$$\begin{aligned} v_2 &= \left\{ 2(T_1 - T_2) \frac{\sum x_i \tilde{C}_{pi}}{\sum x_i M_i} \right\}^{1/2} \\ &= \left[ 2(1000 - 920) \frac{9.554 \cdot 4.1840 \cdot 10^7}{23.01} \right]^{1/2} \\ &= 2.78 \cdot 10^9 \text{ cm} / \text{s} = 1726 \text{ ft} / \text{s} \end{aligned}$$

The speed of sound can be determined from Eq. 9.4-4 as

$$\begin{aligned}
v_s &= \sqrt{\gamma RT_2 / M} = \sqrt{\frac{\tilde{C}_p}{\tilde{C}_p - R} \cdot \frac{RT_2}{M}} \\
&= \sqrt{\frac{9.554}{9.554 - 1.987} \cdot \frac{1.987 \cdot 4.184 \cdot 10^7 \cdot 920}{23.01}} \\
&= 6.48 \cdot 10^9 \text{ cm/s} = 2126 \text{ ft/s}
\end{aligned}$$

The flow is therefore subsonic, and the assumption that  $p_2$  is equal to the ambient pressure is justified.



## 23A.2 Height of a packed-tower absorber

Begin by completing the mass balance as shown on the accompanying figure.  
The cyclohexane free gas stream rate in lb-moles/hr

$$W_G = (363 \text{ ft}^3 / \text{min})(60 \text{ min/hr}) \left( 1.05 \cdot \frac{273 \text{ lb-mole}}{303 \cdot 359 \text{ ft}^3} \right) \cdot 0.99$$
$$= 56.8 \text{ lb-moles/hr}$$

and

$$Y_{H2} = 0.01/0.99 = 0.0101$$

The corresponding exit mole ratio is

$$Y_{H1} = 0.0101 \cdot 0.1 = 0.00101$$

The exit liquid mole ratio is now obtained from the macroscopic mass balance

$$X_{H2} = X_{H1} - (-56.8/19.94)(0.00909)$$
$$= 0.0289$$

More generally we may write

$$Y = 0.00101 + (19.94/56.8)(X - 0.003)$$
$$= 0.351X - 0.00043$$

This is the answer to part (a).

We now begin with Raoult's law in the form

$$y_0 = \frac{P_{vap}}{P_{tot}} x_0 = \frac{121}{1.05 \cdot 760} x_0 = 0.1516 x_0$$

This result can be used along with the definition of the mole ratio to obtain an equilibrium expression in terms of mole ratio:

$$Y = y/(1-y) = \alpha x/[1-\alpha x]; \quad x = X/(1+X)$$

where  $\alpha$  equals 0.1516. This expression is also drawn on the accompanying figure, and it may be seen to effectively straight, because all solutions are so dilute. This is the solution to part (b).

We may now determine the interface conditions from the relation

$$\frac{Y - Y_0}{X - X_0} = - \left( \frac{0.32}{14.2} \right) = -0.0225$$

Since both the equilibrium and operating lines are linear to the accuracy of the technique we can simplify this expression to

$$Y_0 = 0.15X_0; Y = 0.351X - 0.00043$$

We thus find

$$X_0 \approx \frac{Y + 0.0225X}{0.15 + 0.0225}$$

$$Y_0 \approx 0.15X_0$$

These results are tabulated on the attached spread sheet, and they include the answer to part (c).

We may next calculate the tower height from the expression

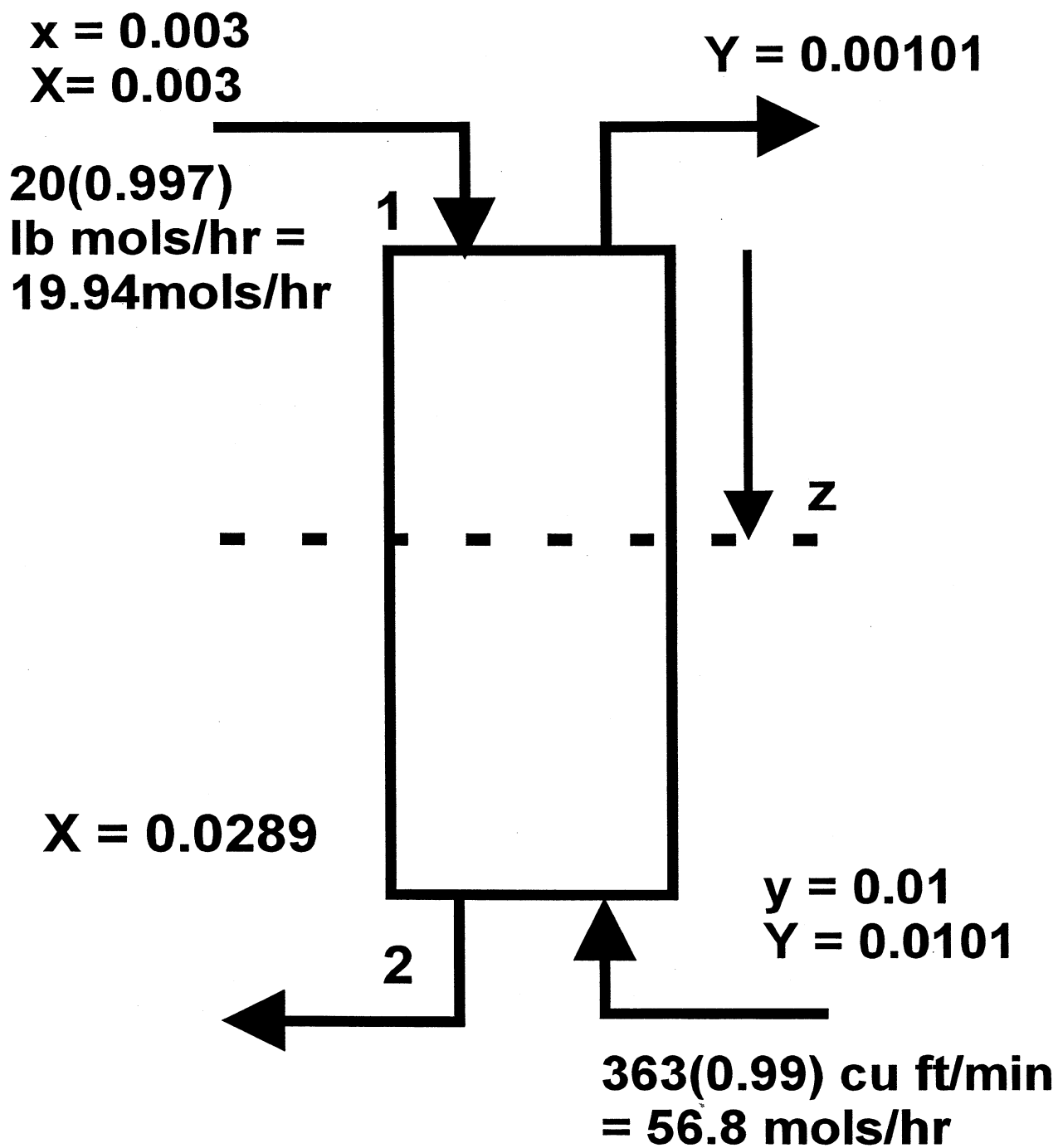
$$Z = -\frac{W_G}{S(k_y a)} \int_{Y_1}^{Y_2} \frac{dY}{(Y - Y_0)} = -\left(\frac{56.8}{2 \cdot 14.2}\right) I$$

Numerical integration gives about 62 ft, which is the answer to part (d). Use of the log mean approximation yields

$$I \approx \frac{(Y_2 - Y_1)}{(Y - Y_0)_{\ln}}$$

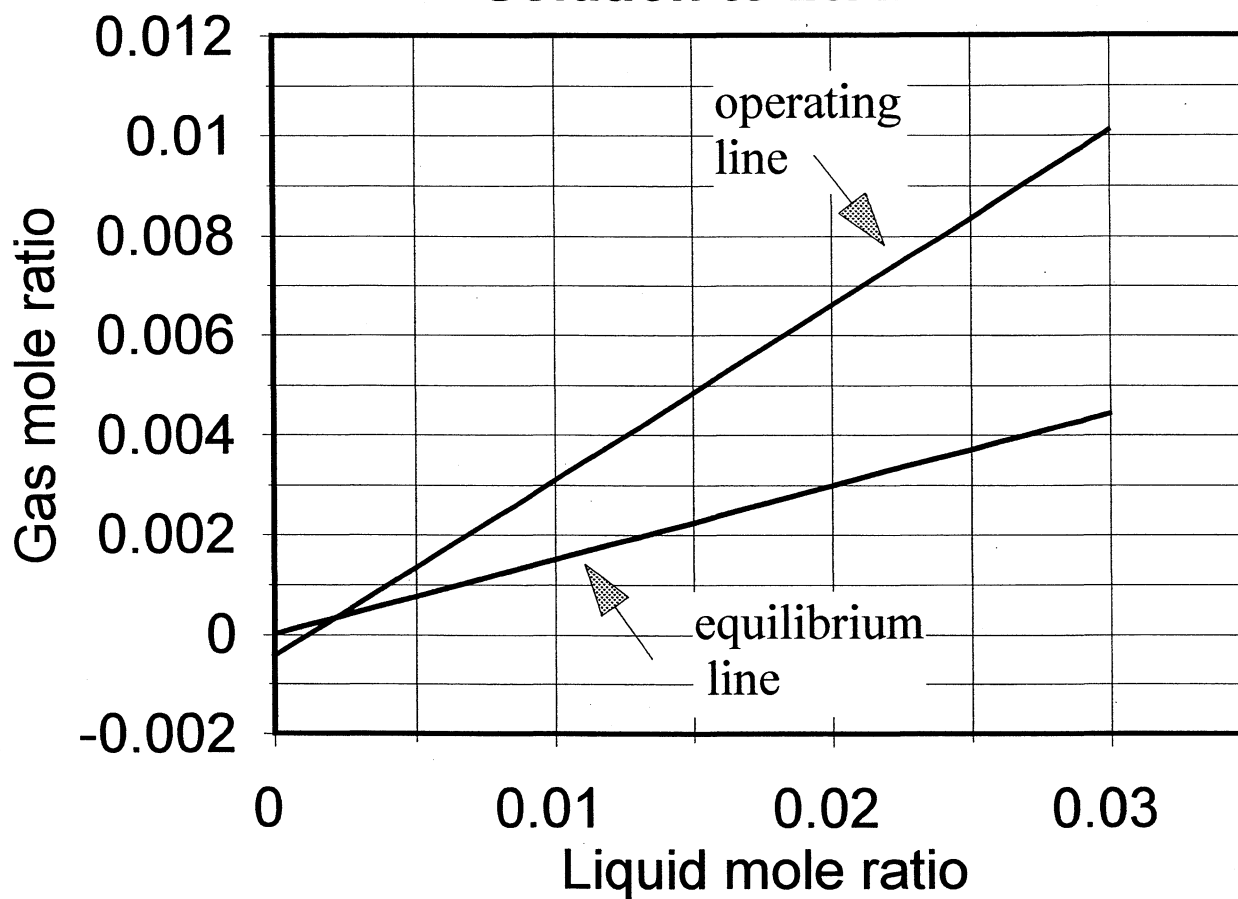
with  $Y_2 - Y_1 = 0.00909$ ;  $(Y - Y_0)_{\ln} = 0.0003$

and a packed height of 60 ft.



**23A.2: Mass balances**

## A Packed-tower Absorber Solution to 23A.2



23A.2 Graphical constructions

X	Y	x	y*	Y*	X/0	Y/0
0	-0.00043	0	0	0	0	0
0.001	-7.9E-05	0.000999	0.0001514	0.000151	0	0
0.002	0.000272	0.001996	0.0003026	0.000303	0	0
0.003	0.000623	0.002991	0.0004534	0.000454	0.004003	0.0006
0.004	0.000974	0.003984	0.000604	0.000604	0.006168	0.000925
0.005	0.001325	0.004975	0.0007542	0.000755	0.008333	0.00125
0.006	0.001676	0.005964	0.0009042	0.000905	0.010499	0.001575
0.007	0.002027	0.006951	0.0010538	0.001055	0.012664	0.0019
0.008	0.002378	0.007937	0.0012032	0.001205	0.014829	0.002224
0.009	0.002729	0.00892	0.0013522	0.001354	0.016994	0.002549
0.01	0.00308	0.009901	0.001501	0.001503	0.019159	0.002874
0.011	0.003431	0.01088	0.0016495	0.001652	0.021325	0.003199
0.012	0.003782	0.011858	0.0017976	0.001801	0.02349	0.003523
0.013	0.004133	0.012833	0.0019455	0.001949	0.025655	0.003848
0.014	0.004484	0.013807	0.0020931	0.002097	0.02782	0.004173
0.015	0.004835	0.014778	0.0022404	0.002245	0.029986	0.004498
0.016	0.005186	0.015748	0.0023874	0.002393	0.032151	0.004823
0.017	0.005537	0.016716	0.0025341	0.002541	0.034316	0.005147
0.018	0.005888	0.017682	0.0026806	0.002688	0.036481	0.005472
0.019	0.006239	0.018646	0.0028267	0.002835	0.038646	0.005797
0.02	0.00659	0.019608	0.0029725	0.002981	0.040812	0.006122
0.021	0.006941	0.020568	0.0031181	0.003128	0.042977	0.006447
0.022	0.007292	0.021526	0.0032634	0.003274	0.045142	0.006771
0.023	0.007643	0.022483	0.0034084	0.00342	0.047307	0.007096
0.024	0.007994	0.023438	0.0035531	0.003566	0.049472	0.007421
0.025	0.008345	0.02439	0.0036976	0.003711	0.051638	0.007746
0.026	0.008696	0.025341	0.0038417	0.003857	0.053803	0.00807
0.027	0.009047	0.02629	0.0039856	0.004002	0.055968	0.008395
0.028	0.009398	0.027237	0.0041292	0.004146	0.058133	0.00872
0.029	0.009749	0.028183	0.0042725	0.004291	0.060299	0.009045
0.03	0.0101	0.029126	0.0044155	0.004435	0.062464	0.00937

23B.1: Effective average driving forces in a gas absorber.

This problem has really been solved in the above discussion of Prob. 23A.2, but perhaps a more detailed analysis is in order. (a) We therefore begin by writing

$$Y_e = m_1 X + b_1$$

$$Y = m_2 X + b_2$$

It follows that  $Y_e - Y = (m_2 - m_1)X + (b_2 - b_1)$

which is the required linear relation. It follows directly that

$$Y - Y_e = C_1 Y + C_2$$

(b) We now write directly from Eq. 23.5-21

$$Y - Y_0 = m_3 (X - X_0)$$

and

$$Y_0 = m_1 X_0 + b_1$$

It follows that

$$Y - Y_0 = m_3 \left[ \frac{Y - b_2}{m_2} - \frac{Y_0 - b_1}{m_1} \right]$$

which is the required linear relation between Y and Y<sub>0</sub>. It follows that there is also a linear relation between (Y-Y<sub>0</sub>) and Y so that

$$Y - Y_0 = C_3 Y + C_4$$

where C<sub>3</sub> and C<sub>4</sub> are constants, obtainable from the above relations.

(c) We now begin with the relation

$$Z = -\frac{W_G}{S(k_y a)} \int_{Y_1}^{Y_2} \frac{dY}{C_3 Y + C_4}$$

For C<sub>3</sub> non-zero and a finite denominator

$$Z = -\frac{1}{C_3} \frac{W_G}{S(k_y a)} \ln \left[ \frac{C_3 Y_2 + C_4}{C_3 Y_1 + C_4} \right]$$

Now

$$C_3 Y_2 + C_4 = (Y - Y_0)_2$$

$$C_3 Y_1 + C_4 = (Y - Y_0)_1$$

$$C_3 = \frac{(Y - Y_0)_2 - (Y - Y_0)_1}{(Y_2 - Y_1)}$$

and 
$$Z = -\frac{W_G}{S(k_y a)} \frac{(Y_2 - Y_1)}{(Y - Y_0)_2 - (Y - Y_0)_1} \ln \left[ \frac{(Y - Y_0)_2}{(Y - Y_0)_1} \right]$$

or 
$$Z = -\frac{W_G}{S(k_y a)} \frac{(Y_2 - Y_1)}{(Y - Y_0)_{\ln}}$$

This result also holds for the degenerate of  $C_3$  equal to zero where  $(Y - Y_0)_{\ln}$  becomes equal to the driving force at any position in the column.

The corresponding expression in terms of  $(K_y a)$  follows by analogy.

23B.2 Expansion of a gas mixture: very fast reaction rate.

Begin by computing the temperature distribution of  $\tilde{H}$  as follows:

	900 K	950 K	1,000 K
$\sqrt{K}$	0.676	0.754	0.841
$x_{H_2} = x_{CO_2} = 0.5/\sqrt{K}$	0.298	0.285	0.272
$x_{CO} = x_{H_2O} = 0.5 - x_{H_2}$	0.202	0.215	0.228
$\tilde{H}_{H_2} = 6340 + 7.217(T - 900)$	6340	6701	7062
$\tilde{H}_{CO_2} = -83,242 + 12.995(T - 900)$	-83,242	-82,592	-81,942
$\tilde{H}_{CO} = -16,636 + 7.932(T - 900)$	-16,636	-16,239	-15,843
$\tilde{H}_{H_2O} = -49,378 + 9.861(T - 900)$	-49,378	-48,885	-48,392
$\tilde{H} = \sum x_i \tilde{H}_i, cal / g - mole$	-36,252	-35,631	-35,013
$\Delta\tilde{H} / \Delta T$		12.42	12.36

The proposed value of 12.4 is clearly adequate. This is the answer to part (a).

(b) From Eq. 23.5-53, which holds for constant mean molecular weight we get

$$\ln\left(\frac{T_2}{T_1}\right) - \frac{1.987}{12.40} \ln\left(\frac{1}{1.5}\right) = -0.065$$

so that 
$$T_2 = 1,000 \cdot e^{-0.056} = 937K$$

(c) For consistency with (b) we do not interpolate for  $\tilde{H}_2$ . Rather we set

$$\tilde{H}_2 - \tilde{H}_1 \approx 12.4(937 - 1,000) = -781 cal / g - mole$$



Then 
$$\hat{H}_1 - \hat{H}_2 = \frac{\tilde{H}_1 - \tilde{H}_2}{\sum x_i M_i} = \frac{781 \cdot 4.184 \cdot 10^7}{23.01}$$

$$= 1.42 \cdot 10^9 \text{ erg/g} = 1.42 \cdot 10^9 \text{ cm}^2/\text{s}^2$$

and 
$$v_2 = \sqrt{2(\hat{H}_1 - \hat{H}_2)} = 5.33 \cdot 10^4 \text{ cm/s} = 1748 \text{ ft/s}$$

### 23B.3 Startup of a chemical reactor

It is convenient to start by scaling moles of B by defining

$$u \equiv M_{B,tot} \cdot \frac{\rho k_{1c}'''}{w C_{A0}}$$

and to write

$$u \equiv u_{tr} + u_{\infty}$$

where the subscripts “tr” and “∞” refer to transient and steady contributions, respectively.

We then find that

$$\frac{d^2 u}{dt^2} + \Sigma \frac{du}{dt} + P u = 1$$

where  $\Sigma = (k_{1A}''' + k_{1B}''' + k_{1C}'')$  and  $P = k_{1B}''' k_{1C}'''$ . It also follows that

$$u_{\infty} = 1/P; \quad \frac{d^2 u}{dt^2} + \Sigma \frac{du}{dt} = 0$$

with the initial conditions that at time zero

$$u_{tr} = -1/P; \quad du_{tr}/dt = 0$$

We now assume solutions of the form

$$u_{tr} = a_{\pm} e^{s_{\pm} t}$$

Putting this trial solution into the differential equation gives

$$s^2 + s\Sigma + P = 0$$

Solving for  $s$  using the quadratic formula gives Eq. 23.6-9, and use of the boundary conditions yields Eq. 23.6-28, with  $u_{\infty}$  included, thus completing the formal solution to part (a).

Using the identity in the hint shows that the argument of the radical is indeed real, and smaller than  $\Sigma$ . Both of the exponents are thus negative as required for part (b).

We also have the explicit expression for B required in part (c) and need only that for A.

This latter can be obtained directly from Eq. 23.6-3 as

$$M_{A,tot} = \frac{1}{k_{1B}''} \left[ \frac{dM_{B,tot}}{dt} + (k_{1A}''' + k_{1C}''') M_{B,tot} \right]$$

with

$$\frac{dM_{B,tot}}{dt} = \frac{wC_{A0}}{\rho k_{1C}^m} \cdot \frac{s_+ s_-}{(s_+ - s_-)} [\exp(s_+ t) - \exp(s_- t)]$$

which completes the solution.

### 23B.4 Irreversible first-order reaction in a continuous reactor

The unsteady state mass balance on substance  $A$  over the reactor is (see Eq. 21.1-3)

$$\frac{d}{dt}M_{A,\text{tot}} = W_{A1} - W_{A2} - W_{A,0} + R_{A,\text{tot}}$$

Into this we substitute  $M_{A,\text{tot}} = Vc_A$ ,  $W_{A1} = (w/\rho)c_{A0}$ ,  $W_{A2} = (w/\rho)c_A$ , and  $R_{A,\text{tot}} = -(k_1'''c_A)V$ . Then division by  $V$  gives

$$\frac{dc_A}{dt} = \left(\frac{w}{\rho V}\right)c_{A0} - \left(\frac{w}{\rho V} + k_1'''\right)c_A$$

Designate the coefficient of the last term by  $t_0^{-1}$ , where  $t_0$  has dimensions of time. Then the separable first-order equation may be integrated to give

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{(t_0^{-1} - k_1''')c_{A0} - t_0^{-1}c_A} = \int_0^t dt$$

Performing the integration gives

$$-t_0 \ln \frac{(t_0^{-1} - k_1''')c_{A0} - t_0^{-1}c_A}{-k_1'''c_{A0}} = t \quad \text{or} \quad \ln \frac{c_A - (1 - k_1'''t_0)c_{A0}}{k_1'''t_0c_{A0}} = -\frac{t}{t_0}$$

Taking the antilogarithm of both sides then yields

$$\frac{c_A}{c_{A0}} = (1 - k_1'''t_0) + k_1'''t_0 \exp\left(-\frac{t}{t_0}\right)$$

Then, transforming back to the original variables, we get

$$\frac{c_A}{c_{A0}} = \frac{w/\rho V}{(w/\rho V) + k_1'''} + \left(1 - \frac{w/\rho V}{(w/\rho V) + k_1'''}\right) \exp[-((w/\rho V) + k_1''')t]$$

which is the same as Eq. 23B.4-1.

23B.4 Irreversible first-order reaction in a continuous reactor (Alternative Solution)

A balance on species "A" in the reactor gives

$$\frac{d}{dt}M_{A,tot} = W_{A1} - W_{A2} - W_{A0} + R_{A,tot}$$

For  $t > 0$ , this equation is to be integrated as

$$V \int_{c_{A0}}^{c_A} \frac{dc_A}{Qc_{A0} - (Q + k_1^m V)c_A} = t$$

from which we may write

$$\left( c_A - \frac{Qc_{A0}}{Q + k_1^m V} \right) = \left( c_{A0} - \frac{Qc_{A0}}{Q + k_1^m V} \right) \cdot \exp \left[ - \left( \frac{Q + k_1^m V}{V} \right) t \right]$$

or

$$\frac{c_A}{c_{A0}} = \frac{Q}{Q + k_1^m V} + \left( 1 - \frac{Q}{Q + k_1^m V} \right) \exp \left[ - \left( \frac{Q + k_1^m V}{V} \right) t \right]$$

23B.5 Math and enthalpy balances in an adiabatic splitter

The conservation relations for this systems are:

Total mass balance:  $F = P + W = 100$

Mass of ammonia:  $zF = yP + xW = 40$

Enthalpy:  $HF = HP + hW = 42,000$

Equilibrium:  $Y = 10^{1.4} X^{1.53} = 25.12X^{1.53}$

We now write explicit expressions for the conditions of the problem, beginning by using the overall balance in the ammonia balance to write:

$$y\Theta + x(1 - \Theta) = 0.4$$

or

$$\Theta = \frac{0.4 - x}{y - x}$$

where  $\Theta = P/F$  is the product (fractional) *cut*. We next eliminate P and W in the enthalpy balance by writing

$$(1,210 - 465y - 115y^{12})\Theta + (330 - 950x + 740x^2)(1 - \Theta) = 420$$

or

$$(2.88 - 1.107y - 0.2378y^{12})\Theta + (0.7857 - 2.26x + 1.762x^2)(1 - \Theta) = 1$$

or

$$A\Theta + B(1 - \Theta) = 1$$

which can be rearranged to 
$$\Theta = \frac{1 - B}{A - B}$$

Clearly a numerical solution is required, and the following approach is used here:

- 1) assume a value of x, and compute the corresponding values of X and Y.
- 2) calculate the cut corresponding to these choices from the species mass balance, and plot  $\Theta(x)$ , and

3) do the same for the enthalpy balance.

4) The desired solution occurs when these two equations give the same cut.

This process is shown on the attached spread sheet, where it I found that

$$\mathbf{x = 0.22; y = 0.713; \Theta = 0.365}$$

Enthalpies can then be obtained from the thermal data just given:

$$\hat{h} = 330 - 950 \cdot 0.22 + 740 \cdot (0.22^2) = 157 \text{ Btu/lb}$$

$$\hat{H} = 1210 - 465y - 115y^2 \quad \hat{H} = 1210 - 465y - 115y^2 = 877 \text{ Btu/lb}$$

These results vary significantly from the answers given in the problem statement.

Mass and energy balances for Prob. 23B.5

x	X	Y	y	Theta-x	A	B	Theta-h	H-E
0.1	0.1111111	0.741344	0.425731	0.9210058	2.408708	0.57732	0.230798	-0.69021
0.11	0.123596	0.85773	0.461709	0.8245463	2.368866	0.55842	0.243907	-0.58064
0.12	0.136364	0.979867	0.494915	0.746835	2.332077	0.539873	0.256738	-0.4901
0.13	0.149425	1.107524	0.525509	0.6826638	2.298156	0.521678	0.269253	-0.41341
0.14	0.162791	1.240496	0.55367	0.6285198	2.26689	0.503835	0.281423	-0.3471
0.15	0.176471	1.378603	0.579585	0.5819568	2.238058	0.486345	0.29323	-0.28873
0.16	0.190476	1.52168	0.603439	0.5412245	2.211439	0.469207	0.304663	-0.23656
0.17	0.204819	1.669577	0.625409	0.5050407	2.186821	0.452422	0.315716	-0.18932
0.18	0.219512	1.82216	0.645662	0.4724462	2.164005	0.435989	0.326392	-0.14605
0.19	0.234568	1.979305	0.664351	0.4427099	2.142805	0.419908	0.336696	-0.10601
0.2	0.25	2.140896	0.681619	0.4152656	2.123055	0.40418	0.346634	-0.06863
0.21	0.265823	2.306828	0.697595	0.3896674	2.104604	0.388804	0.356216	-0.03345
0.22	0.282051	2.477002	0.712396	0.3655595	2.087315	0.373781	0.365455	-0.0001
0.23	0.298701	2.651327	0.726127	0.3426542	2.071068	0.35911	0.374361	0.031707
0.24	0.315789	2.829716	0.738884	0.3207158	2.055758	0.344791	0.382946	0.062231
0.25	0.333333	3.012089	0.750753	0.2995487	2.041292	0.330825	0.391224	0.091675
0.26	0.351351	3.198371	0.761812	0.2789887	2.027587	0.317211	0.399204	0.120215
0.27	0.369863	3.38849	0.772131	0.2588965	2.014572	0.30395	0.406899	0.148002
0.28	0.388889	3.582378	0.781773	0.2391521	2.002185	0.291041	0.414319	0.175167
0.29	0.408451	3.779972	0.790794	0.2196513	1.990369	0.278484	0.421475	0.201823
0.3	0.428571	3.981211	0.799246	0.2003022	1.979078	0.26628	0.428375	0.228073
0.31	0.449275	4.186037	0.807175	0.181023	1.968268	0.254428	0.43503	0.254007
0.32	0.470588	4.394395	0.814622	0.1617395	1.957904	0.242929	0.441447	0.279708
0.33	0.492537	4.606234	0.821627	0.1423843	1.947952	0.231782	0.447635	0.305251
0.34	0.515152	4.821502	0.828223	0.1228947	1.938384	0.220987	0.453601	0.330706
0.35	0.538462	5.040153	0.834441	0.1032117	1.929174	0.210545	0.459352	0.35614
0.36	0.5625	5.262141	0.84031	0.0832795	1.920299	0.200455	0.464894	0.381614
0.37	0.587302	5.487421	0.845856	0.0630443	1.91174	0.190718	0.470234	0.407189
0.38	0.612903	5.715952	0.851101	0.0424538	1.903477	0.181333	0.475377	0.432923
0.39	0.639344	5.947692	0.856067	0.0214561	1.895495	0.1723	0.480329	0.458873
0.4	0.666667	6.182604	0.860775	-4.82E-16	1.887778	0.16362	0.485095	0.485095
0.41	0.694915	6.420649	0.865241	-0.0219664	1.880313	0.155292	0.48968	0.511646
0.42	0.724138	6.661792	0.869482	-0.0444956	1.873088	0.147317	0.494088	0.538584



### 23B.6 Flow Distribution in an ideal cascade

Begin with a mole fraction of  $x_W = x_0 = 0.1$  in liquid downflow. Then

$$X_0 = x_0 / (1 - x_0) = 0.1 / 0.9 = 0.1111$$

and a relative volatility of 2.5. Then

$$X_{n+1} = \sqrt{2.5} X_n = 1.581 X_n$$

Values through  $X_{11}$  are given on the attached spread sheet. These in turn may be expressed as mole fractions. Thus

$$\text{Plate "0" (reboiler): } x_0 = 0.1; y_0 = 0.217391$$

because the upflow stream leaving the reboiler must be in equilibrium with the downflowing stream, which is the product. Compositions are shown in the attached spread sheet. It may be seen there that the mole ratio for stage 9, the tenth stage is 17.1428, corresponding to a mole fraction of 0.9488. [The large numbers of digits being carried is to ensure agreement with ideal stage theory. Note that 13 stages are provided for in the spread sheet. There is no upper limit at this stage of the calculations.]

These compositions must be correct for any ideal cascade with a bottoms mole fraction of 0.1 and constant relative volatility of 2.5. It remains however, to make mass balances for this system, and for convenience we shall assume saturated liquid feed of mole fraction 0.523249, the predicted composition of  $x_5$ .

We can then make mass balances for the column as a whole, using as basis a feed rate of unity:

$$1 = P + W$$

$$0.5232 = 0.9449P + 0.1W$$

We thus find that

$$P = 0.501$$

$$W = 0.499$$

$$F = 1.000$$

and we are now ready to calculate intermediate stream rates. This done via overall and solute mass balances. Thus for the section below the feed plate, the "exhausting" section, we begin by writing mass balances on plate "0":

$$D_1 - U_0 = W$$

$$x_1 D_1 - y_0 U_0 = x_0 W$$

or

$$D_1 = W \left( \frac{y_0 - x_0}{y_0 - x_1} \right)$$

More generally

$$D_{n+1} = W \left( \frac{x_w - y_n}{x_{n+1} - y_n} \right)$$

The results are shown in the attached spread sheet.

At the top of the column, plate 12, part of the upflow is removed as product and the remainder converted to a downflow. The mass balances are then

$$P = U_n - D_{n+1}$$

$$y_p P = y_n U_n - x_{n+1} D_{n+1}$$

$$D_n = P \left( \frac{y_p - y_{n-1}}{y_{n-1} - x_n} \right)$$

These results are also shown in the spread sheet.

Prob. 23B.6 solutions

n	Xn	Yn	xn	yn	D	-f	U
0	0.111111	0.277778		0.1	0.217391	0.499	-0.499
1	0.175666	0.439166	0.149419	0.305153	0.861792	-0.86179	
2	0.277729	0.694322	0.217361	0.409793	1.166069	-1.16607	
3	0.439089	1.097723	0.305116	0.523293	1.476794	-1.47679	
4	0.6942	1.7355	0.409751	0.634436	1.860312	-1.86031	
5	1.09753	2.743825	0.523249	0.732894	2.398508	-2.39851	
6	1.735195	4.337987	0.634395	0.812663	1.078348	-1.07835	
7	2.743343	6.858358	0.732859	0.872747	0.830161	-0.83016	
8	4.337226	10.84306	0.812637	0.915562	0.601373	-0.60137	
9	6.857154	17.14288	0.872727	0.944882	0.343134	-0.34313	
10	10.84116	27.1029	0.915549	0.964416			
11	17.13987	42.84969	0.944873	0.977195			
12	27.09814	67.74535	0.96441	0.985454			
13			0.985454				

Note: P = 0.501 and W = 0.499

23B.7 Isotope fractionation and the value function

The fundamental equation needed for this comparison are

$$\Delta / F = \Theta V(y) + (1 - \Theta)V(x) - V(z) \quad (1)$$

$$z = y\Theta + x(1 - \Theta) \quad (2)$$

$$V(w) = (2w - 1)\ln[w/(1 - w)] \quad (3)$$

We must first calculate the material balances for the two processes using Eq. 2:

Process 1:

$$0.1 = 0.9\Theta + 0.01(1 - \Theta); \Theta = 0.101$$

Process 2:

$$0.1 = 0.95\Theta + 0.02(1 - \Theta); \Theta = 0.86$$

We next need values for each of these compositions:

w	0.01	0.02	0.1	0.9	0.95
V	4.503	3.736	1.758	1.758	2.650

We may then calculate the separative work done by the two processes as:

Process 1:

$$\Delta / F = 0.101 \cdot 1.758 + 0.899 \cdot 4.503 - 1.758 = 2.47$$

Process 2:

$$\Delta / F = 0.86 \cdot 2.650 + 0.14 \cdot 3.736 - 1.758 = 1.04$$

The first process is the more effective.

< end >



$$\text{At } t = 0: \quad u = c_{A0} + \frac{1}{2k_2'''} \left( \frac{w}{\rho V} \right) (1 + Z)$$

c. We now make the change of variable  $v = 1/u$ , which converts the Bernoulli equation into a linear first-order differential equation:

$$\frac{dv}{dt} + \left( \frac{w}{\rho V} \right) Zv = k_2'''$$

This can be solved at once to give

$$v = C \exp \left( - \left( \frac{w}{\rho V} \right) Zt \right) + k_2''' \left( \frac{\rho V}{wZ} \right)$$

The constant of integration is obtained by using the initial condition given in (b)

$$\frac{1}{c_{A0} + (1/2k_2''')(w/\rho V)(1 + Z)} = C + k_2''' \left( \frac{\rho V}{wZ} \right)$$

When we insert this constant into the solution and then revert to the original variable, we get

$$\begin{aligned} & \frac{1}{c_A + (1/2k_2''')(w/\rho V)(1 + Z)} \\ &= \left( \frac{1}{c_{A0} + (1/2k_2''')(w/\rho V)(1 + Z)} - k_2''' \left( \frac{\rho V}{wZ} \right) \right) \exp \left( - \left( \frac{w}{\rho V} \right) Zt \right) + k_2''' \left( \frac{\rho V}{wZ} \right) \end{aligned}$$

When the expression for Z is inserted, we then have the final concentration vs. time expression in terms of the original variables.

**Prob. 23C.2 Protein Purification**

(a)  $Y = N_1 / N_2 = cvS_1x_1 / cvS_2 / x_2 = (S_1 / S_2)X_1$

(b) Begin with writing material balances over the column:

$$0.99P = 0.95 \cdot 0.9F; P = 0.8636F$$

$$W = (1 - 0.8636)F = 0.1364F$$

$$x_W = 0.05 \cdot 0.9F / 0.1364F = 0.3300$$

We thus find that

$$Y_P = 0.99 / 0.01 = 99; X_W = 0.33 / 0.67 = 0.4925$$

Then, counting from the bottom, so that stage 1 produces the product W, we find that

$$Y_1 = \alpha X_W = 0.4925\alpha; Y_N = Y_P = 99$$

$$Y_N / Y_1 = (99 / 0.4925) = 201 = (\sqrt{\alpha})^N = \alpha^{N/2}$$

or

$$N = 2 \cdot \ln 201 / \ln \alpha$$

The relation between N and  $\alpha$  is calculated on the attached spread sheet and shown on the attached graph.

(c) For a 3-stage ideal cascade, the down flow from the top stage and the up flow from the bottom must both have the composition of the feed: a mole fraction of 0.9 and a mole ratio of 9. The product mole ratio must then be

$$Y_P = 40 \cdot 9 = 360; y_P = 360 / 361 = 0.997$$

and the bottoms must be

$$X_W = 9 / 40 = 0.225; x_W = 0.225 / 1.225 = 0.184$$

The over up and down flows from the feed stage in turn are

$$Y_F = Y_P / \sqrt{40} = 56.92; y_F = 56.92 / 57.92 = 0.983$$

$$X_F = Y_F / 40 = 1.423; x_F = 1.423 / 1.423 = 0.590$$

which completes the determination of stage compositions.

Calculation of stage stream flows is calculated as follows:

$$P, W: \begin{aligned} F &= P + W \\ 0.9F &= 0.997P + 0.184W \end{aligned}$$

It follows that

$$P = 0.8807F; W = 0.1193F$$

$$U_F, D_P:$$

$$U_F = P + D_P$$

$$0.983U_F = 0.997P + 0.9D_P$$

Thus

$$U_F = 1.1687P = 1.029F$$

$$D_P = 0.1687P = 0.1485F$$

Similarly

$$D_F = W + U_W$$

$$x_F D_F = x_W W + y_W U_W$$

so that

$$D_F = 2.31W = 0.275F$$

$$U_W = 1.31W = 0.156F$$

These results can be summarized as follows:

Stream	to product	to top stage	to feed stage	to bottom stage	to bottoms
Rate/F	0.8807	1.029	1.30	0.275	0.1193

The sum of flows into the three stages is then

$$\text{Sum of stage inflows} = 2.60 F$$

which determines the total membrane requirement. The yield is

$$\text{Yield} = 0.997 \cdot 0.8807 / 0.9 = 0.9756$$

(d) For a simple single stage operation the defining equations are

$$F = P + W$$

$$zF = yP + xW$$

$$Y = 40X$$

For  $P = 0.8807 F$  we may write



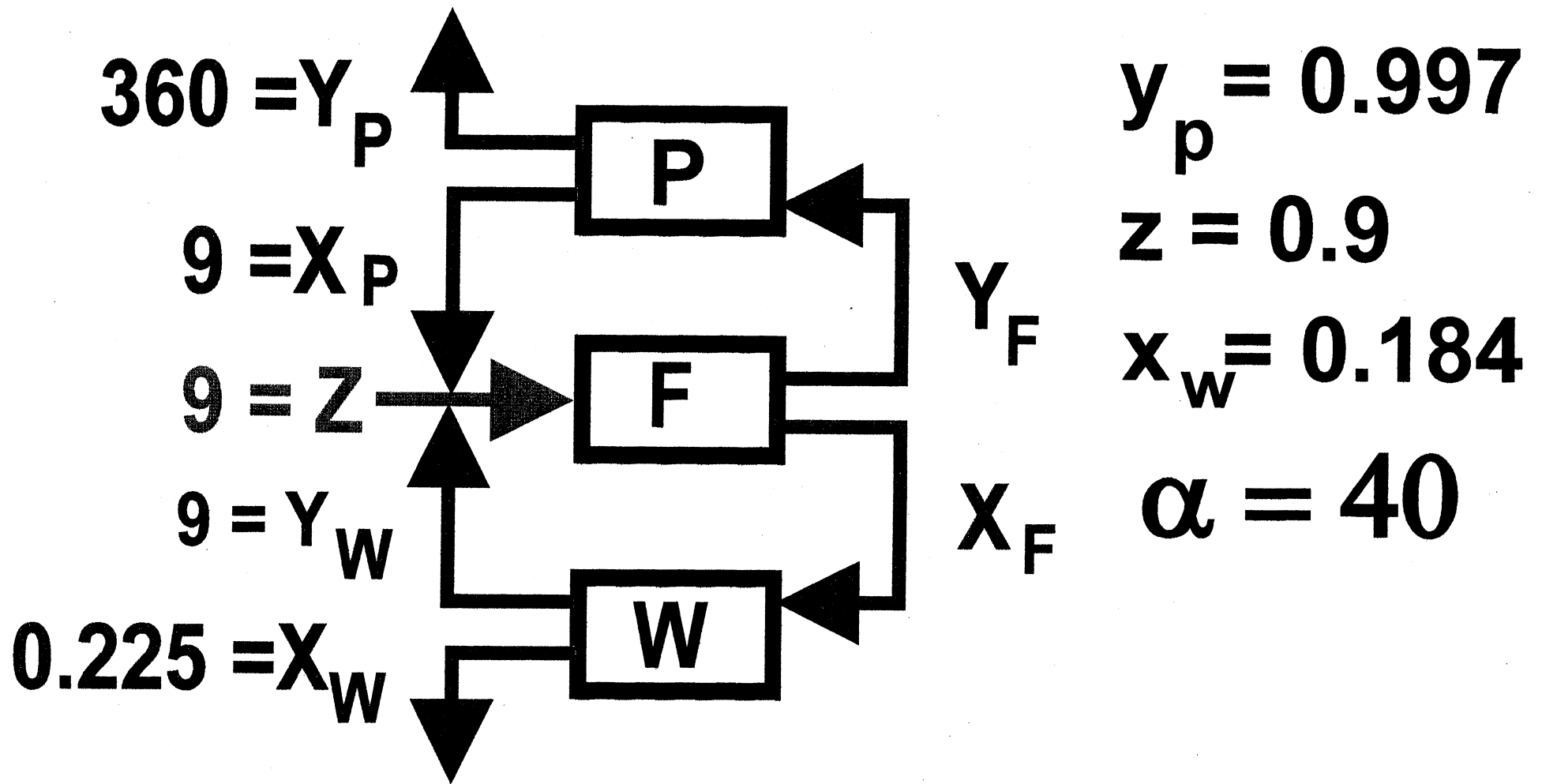
$$y = \frac{0.9 - 0.1193x}{0.8807}; x = \frac{y}{40 - 39y}$$

and therefore since y must be less than unity,

0.974

$$\text{Yield} = 0.974 \cdot 0.8807 / 0.9 = 0.953$$

Both results are quite good, but product purity is substantially higher for the 3-stage cascade.



## A Three-stage Protein Fractionator

(X, Y, Z = mole ratios of desired to undesired component;  
 x, y, z = corresponding mole fractions)

### 23C.3 Physical significance of the zeroth and first moments

There is no end to the systems that can be examined, but one must limit behavior to a single inlet and single outlet with negligible diffusion across both, and effectively uniform concentration across both inlet and outlet. Here we merely summarize the key findings. These two moments enable calculation of the *effective* volume of an otherwise ill defined system and the flow rate of fluid through it.

For the zeroth moment one can relax all constraints except those of time independent flow and both uniform concentration and negligible diffusion across the outlet. The tracer must also be introduced over a finite time interval. Then

$$\int_{-\infty}^{\infty} Qc dt = Q \int_{-\infty}^{\infty} c dt = QM_0 = m$$

over any flow cross-section meeting the above requirements. It follows that

$$Q = m / M_0$$

with what are often minimal reservations.

We may generalize the treatment of the first moment to

$$\frac{M_1|_{out} - M_1|_{in}}{M_0} = t_{res} \equiv \frac{V_{eff}}{Q}$$

where the *effective volume*

$$V_{eff} = \int_V K_D dV$$

where  $K_D$  is the equilibrium ratio of local tracer concentration to that in the stream flowing into, through and out of the system under investigation. For tissue permeated by blood vessels for example

$$K_D = \frac{c_{tissue}}{c_{blood}}$$

This generalization is very important in pharmacokinetics for example.

23C.4 Analogy between the unsteady operation of an adsorption column and a cross-flow heat exchanger.

There are three basic cross flow exchanger morphologies: both streams mixed, only one mixed and neither mixed. The analog sought here is the last of these, and it was first described by Nusselt (W. Nusselt, Z. Ver. deut. Ing., 1911, **55**, 2021; Tech. Mech. Thermodynam., 1930, **1**, 417; Jakob, Max, "Heat Transfer", Wiley, 1957, pp. 217-227 and 253). It is difficult to find more than graphical representations of the solution because of numerical difficulties. Moreover, even Jakob's detailed analysis is cumbersome and difficult to follow. Now however many available programs can handle functions like the integral in Eq. 25 quite simply and effectively.

The analogs of Eq. 23.6-10 and 11 are

$$v_{x0} \rho_s \hat{C}_{pS} \frac{\partial T_S}{\partial x} = (Ua)(T_M - T_S)$$

$$v_{z0} \rho_m \hat{C}_{pM} \frac{\partial T_M}{\partial z} = -(Ua)(T_M - T_S)$$

Here the subscript "S" refers to the analog of the stationary phase, and x replaces t. The terms  $v_{x0}$  and  $v_{z0}$  are the superficial velocities in the x and z directions respectively, and they are defined by

$$v_{x0} = v_x / (1 - \varepsilon); \quad v_{z0} = v_z / \varepsilon$$

where the unadorned velocities are the mean velocities in the "x" and "z" channels, which occupy fractions  $\varepsilon$  and  $(1-\varepsilon)$  of the total fluid space respectively. These differ from their mass transfer analogs primarily in that there are convective terms in both regions, and no transient terms in either. However, they have the same basic mathematical forms as Eqs. 23.6-15 and 16 respectively. They are to be solved with the boundary conditions

$$\text{At } x = 0, T_S = T_{S0}; \quad \text{At } z = 0, T_M = T_{M0}$$

We may thus write the description in the form

$$\frac{\partial \Theta_S}{\partial \xi} = (\Theta_M - \Theta_S); \quad \frac{\partial \Theta_M}{\partial \zeta} = -(\Theta_M - \Theta_S)$$

$$\text{with} \quad \Theta_S(\zeta, 0) = 0 \quad \Theta_M(0, \xi) = 1$$

where

$$\Theta = (T - T_{S0}) / (T_{M0} - T_{S0})$$

$$\xi = x(Ua)(T_{M0} - T_{S0}) / v_{x0} \rho_S \hat{C}_{pS}$$

$$\zeta = z(Ua)(T_{M0} - T_{S0}) / v_{z0} \rho_M \hat{C}_{pM}$$

The solution to the  $T_M$  profile is then given directly by Eq. 23.6-25 with  $\tau$  replaced by  $\xi$ .

However, the outlet temperature varies with position, and the average outlet temperature is given by

$$\bar{\Theta}_M(\Xi) = \frac{1}{\Xi} \int_0^\Xi \left[ 1 - \int_0^Z \exp\left(-(\xi + Z)J_0\left(i\sqrt{4\zeta\xi}\right) d\zeta\right) \right] d\xi$$

where  $\Xi$  is the width of the exchanger (in the  $\xi$  direction).

### 23D.1 Unsteady-state operation of a packed column

The suggested solution is in effect just reverse engineering, and it seems more useful to show how the result can be obtained. Here we follow A. Anzelius (of Stockholm, *Z. angew. Math u. Mech.* 1926, 6, #4, 291-293) who provides a clear and elegant proof, as well as the first of many. In our notation he starts with Eqs. 23.6-23 and 24:

$$\frac{\partial X}{\partial \zeta} = Y - X; \quad \frac{\partial Y}{\partial \tau} = X - Y$$

The key to Anzelius' solution is to define a function

$$G(\zeta, \tau) = e^{\zeta + \tau}(X - Y)$$

which satisfies the relation

$$\frac{\partial^2 G}{\partial \tau \partial \zeta} = G$$

as can be shown by differentiation with the aid of Eqs. 23.6-23 and 24. To show this note that

$$\frac{\partial^2 Y}{\partial \zeta \partial \tau} = \frac{\partial}{\partial \zeta}(X - Y)$$

and similarly for the mixed second derivative of X.

We now look again at Eq. 23.6-23 and consider initial conditions at the column entrance:

$$\left. \frac{\partial X}{\partial \zeta} \right|_{\zeta, 0} = Y(\zeta, 0) - X(\zeta, 0) = -X(\zeta, 0)$$

or 
$$X(\zeta, 0) = e^{-\zeta}$$

Similarly 
$$Y(0, \tau) = 1 - e^{-\tau}$$

It follows that the boundary conditions on G are

$$G(\zeta, 0) = G(0, \tau) = 1$$

Anzelius obtained G by an iterative process in series form

$$G = G_0 + G_1 + G_2 + \dots$$

for which  $\frac{\partial^2 G_n}{\partial \tau \partial \zeta} = G_{n-1}$  and  $G_0 = 1$

and  $G_n = \int_0^\zeta \cdots \int_0^\zeta d\zeta^n \cdot \int_0^\tau \cdots \int_0^\tau d\tau^n = \frac{(\zeta\tau)^n}{(n!)^2}$

This series converges to  $G = \sum_{n=0}^{\infty} \frac{(\zeta\tau)^n}{(n!)^2} = J_0(2i\sqrt{\zeta\tau})$

and it follows that  $X - Y = e^{-(\tau+\zeta)} J_0(2i\sqrt{\zeta\tau})$

The desired concentration profiles can now be obtained directly from Eqs. 23.6-23 and 24:

$$X = 1 - \int_0^\zeta e^{-(\tau+s)} J_0(2i\sqrt{\tau s}) ds$$

$$Y = \int_0^\tau e^{-(\zeta+u)} J_0(2i\sqrt{\zeta u}) du$$

Note that this elegant and concise solution requires no special skill beyond recognizing the infinite series as a well characterized function.

### 23D.2 Additivity of the lower moments

[For background see Bracewell, Ron, "The Fourier Transform and its Applications", McGraw-Hill, 3<sup>rd</sup> Ed, 1999]

- (i) It was already shown in Prob. 23C.3 that the zeroth moment

$$M_0 = m / Q$$

where  $m$  is the mass of tracer fed, and  $Q$  is the solvent flow rate. This quantity is thus the same for all input and output streams in a series of units, which need not be identical.

- (ii) We now begin with the first absolute moment for one system

$$M_1 = \frac{h'}{h}$$

For two systems in series

$$M_1 = \frac{F'(0)}{F(0)} = \frac{h_1 h'_2 + h'_1 h_2}{h_1 h_2} = \frac{h'_2}{h_2} + \frac{h'_1}{h_1} = (M_1)_1 + (M_1)_2$$

as required. For the second central moment we may write for one system

$$\mu_2 = \frac{h''}{h} - \left(\frac{h'}{h}\right)^2$$

while for two systems in series  $\mu_2 = \left[ \frac{h''}{h} - \left(\frac{h'}{h}\right)^2 \right]_1 + \left[ \frac{h''}{h} - \left(\frac{h'}{h}\right)^2 \right]_2$

as required. The second central moment with respect to time is the variance of the distribution and thus the measure of dispersion about the mean. The third central moment

is given by

$$\mu_3 = -\frac{h'''}{h} + 3\frac{h'h''}{h^2} - 2\left(\frac{h'}{h}\right)^3$$

Again we find

$$\mu_3 = (\mu_3)_1 + (\mu_3)_2$$

This third central moment is the primary measure of skewness.

Additivity does not, however, occur for the fourth and higher central moments. As a practical matter this is not very important because these moments are usually not obtainable from experimental data with useful accuracy.

It should be noted that additivity is not restricted to two systems in series but holds for any number.



### 23D.3 Startup of a chemical reactor

Taking the Laplace transform of Eqs. 23.6-2 and 3, we get

$$p\bar{M}_{A,\text{tot}} - M_{A,\text{tot}}(0) = \frac{wc_{A0}/\rho}{p} - k_{1B}'''\bar{M}_{A,\text{tot}} + k_{1A}'''\bar{M}_{B,\text{tot}}$$

$$p\bar{M}_{B,\text{tot}} - M_{B,\text{tot}}(0) = -(k_{1A}''' + k_{1C}''')\bar{M}_{B,\text{tot}} + k_{1B}'''\bar{M}_{A,\text{tot}}$$

Both  $M_{A,\text{tot}}$  and  $M_{B,\text{tot}}$  are zero at  $t = 0$ . The above pair of algebraic equations can be rearranged thus:

$$(p + k_{1B}''')\bar{M}_{A,\text{tot}} - k_{1A}'''\bar{M}_{B,\text{tot}} = \frac{wc_{A0}/\rho}{p}$$

$$-k_{1B}'''\bar{M}_{A,\text{tot}} + (p + k_{1A}''' + k_{1C}''')\bar{M}_{B,\text{tot}} = 0$$

These equations can be solved for  $\bar{M}_{A,\text{tot}}$  and  $\bar{M}_{B,\text{tot}}$ . We are interested only in  $\bar{M}_{B,\text{tot}}$ , which can be written down immediately:

$$\bar{M}_{B,\text{tot}} = \frac{\begin{vmatrix} p & wc_{A0}/\rho \\ -k_{1B}''' & 0 \end{vmatrix}}{\begin{vmatrix} p + k_{1B}''' & -k_{1A}''' \\ -k_{1B}''' & p + k_{1A}''' + k_{1C}''' \end{vmatrix}} = \frac{k_{1B}''' \frac{wc_{A0}/\rho}{p}}{(p + k_{1B}''')(p + k_{1A}''' + k_{1C}''') - k_{1A}'''k_{1B}'''} \\ = \left( k_{1B}''' \frac{wc_{A0}}{\rho} \right) \left( \frac{1}{p(p - p_+)(p - p_-)} \right)$$

The second expression gives the form of the result, and  $p_+$  and  $p_-$  may be found by equating the first and second expressions:

$$2p_{\pm} = -(k_{1A}''' + k_{1B}''' + k_{1C}''') \pm \sqrt{(k_{1A}''' + k_{1B}''' + k_{1C}''')^2 - 4k_{1B}'''k_{1C}'''}$$

which is Eq. 23.6-9.

Next we recognize that the above expression for  $\bar{M}_{B,\text{tot}}$  is of the form of a "numerator function"  $N(p)$  divided by a "denominator

function"  $D(p)$ , which can be expanded in partial fractions (the "Heaviside partial fractions expansion theorem), thus:

$$\frac{N(p)}{D(p)} = \sum_k \frac{N(a_k)}{D'(a_k)} \frac{1}{p - a_k}$$

Then the inverse transform is taken:

$$\mathfrak{F}^{-1} \left\{ \frac{N(p)}{D(p)} \right\} = \sum_k \frac{N(a_k)}{D'(a_k)} \exp(a_k t)$$

Therefore

$$M_{B,\text{tot}} = \left( k_{1B}''' \frac{wC_{A0}}{\rho} \right) \left( \frac{1}{(0 - p_+)(0 - p_-)} + \frac{1}{p_+(p_+ - p_-)} \exp p_+ t \right. \\ \left. + \frac{1}{p_-(p_- - p_+)} \exp p_- t \right)$$

Then, since  $p_+ p_- = k_{1B}''' k_{1C}'''$ , the above expression may be rewritten thus:

$$M_{B,\text{tot}} = \left( \frac{wC_{A0}}{\rho k_{1C}'''} \right) \left( 1 + \frac{p_- \exp p_+ t - p_+ \exp p_- t}{(p_+ - p_-)} \right)$$

which is Eq. 23.6-8.

### 23D.4 Transient behavior of N reactors in series

Begin by redefining subscripts to facilitate generalization and to follow Acrivos and Amundson:

$$A \Rightarrow 1; B \Rightarrow 2; C \Rightarrow 3$$

$$k_{1AB}''' \equiv k_1; k_{1BA}''' \equiv k_1'; k_{1BC}''' \equiv k_2; k_{1CB}''' \equiv k_2'$$

where  $c_1(0)$  is the concentration at which solute 1 (A) enters the first tank. One can write similar equations for the two remaining solutes, but it is simpler to write a single matrix equation

$$c(2) = h^2 \left( I - e^{-\bar{B}t} - \bar{B}t e^{-\bar{B}t} \right) \bar{B}^{-2} c(0)$$

and for any tank n

$$c(n) = h^n \left( I - e^{-\bar{B}t} \sum_{i=0}^{n-1} \frac{(\bar{B}t)^i}{i!} \right) \bar{B}^{-n} c(0)$$

This expression may be written out explicitly using Sylvester's theorem as

$$c(n) = h^n \sum_{k=1}^3 \left( \frac{1}{\lambda_k} \right)^n \left\{ \left( 1 - e^{-(\lambda_k t)} \right) \sum_{i=1}^{n-1} \frac{(\lambda_k t)^i}{i!} \right\} \frac{\text{adj} (\lambda_k I - \bar{B})}{\pi_{i \neq k} (\lambda_k - \lambda_i)} c(0)$$

where the  $\lambda_k, (1 \leq k \leq 3)$ , are the characteristic roots of  $\bar{B}$ .

Agriyas and Amundson provide the following numerical example to illustrate use

of this approach:

$$h = 1; k_1 = 0.2; k'_1 = 0.05; k_2 = 0.10; k'_2 = 0.05$$

$$c_1(0) = 1; c_2(0) = 0; c_3(0) = 0$$

Then

$$\bar{B} = \begin{pmatrix} 1.2 & -0.05 & 0 \\ -0.2 & 1.15 & -0.05 \\ 0 & -0.1 & 1.05 \end{pmatrix}$$

and the characteristic equation for  $\bar{B}$  is

$$|\lambda I - \bar{B}| = \lambda^3 - 3.4000\lambda^2 + 3.8325\lambda - 1.4325 = 0$$

The roots of this equation are then

$$\lambda_1 = 1.2866; \lambda_2 = 1.1133; \lambda_3 = 1.0000$$

Therefore

$$c(n) = (0.7772)^n \left[ 1 - e^{-1.2866t} \sum_{i=0}^{n-1} \frac{(1.2866)^i}{i!} \right] \begin{pmatrix} 0.5501 \\ -0.9527 \\ 0.4027 \end{pmatrix}$$

$$+(0.8982)^n \left[ 1 - e^{-1.1133t} \sum_{i=0}^{n-1} \frac{(1.1133t)^i}{i!} \right] \begin{pmatrix} 0.3730 \\ 0.6448 \\ -1.0186 \end{pmatrix}$$

$$+ \left[ 1 + e^{-t} \sum_{i=0}^{n-1} \frac{t^i}{i!} \right] \begin{pmatrix} 0.0769 \\ 0.3080 \\ 0.6159 \end{pmatrix}$$

### 24A.1 Thermal diffusion

a. From Table 24.2-3 it can be seen that, for positive  $k_T$  and the conditions shown, hydrogen must be designated as species A. Then Eq. 24.2-13 gives:

$$x_{A2} - x_{A1} = -k_T \ln \frac{T_2}{T_1} = 0.0166 \ln \frac{600}{200} = 0.0183$$

Thus there is a higher concentration of A (hydrogen) in the bulb at temperature  $T_1$ , the mole fraction difference being 0.0183.

b. The recommended mean temperature is obtained from Eq. 24.2-14:

$$T_m = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{T_2}{T_1} = \frac{(200)(600)}{600 - 200} \ln \frac{600}{200} = 330\text{K}$$

## 24A.2 Ultracentrifugation of proteins

Recognizing that  $x_B$  is very nearly equal to  $x_{B0}$ , and taking the  $1/\bar{V}_B$  power of both sides of Eq. 24.2-22, we get

$$\frac{x_A}{x_{A0}} = \exp\left[\left(\frac{\bar{V}_A}{\bar{V}_B} M_B - M_A\right) \frac{g_\Omega z}{RT}\right]$$

The values of the quantities in this equation are for this problem

$$M_A = 45,000 \text{ g/g - mole}$$

$$\bar{V}_A = \frac{M_A}{M_A/\bar{V}_A} = \frac{45,000}{1.34} = 33,582 \text{ cm}^3/\text{g - mole}$$

$$\frac{M_B}{\bar{V}_B} = 1.00 \text{ g/cm}^3$$

$$g_\Omega = (50,000)(980.665) = 4.903 \times 10^7 \text{ cm/s}$$

$$R = 8.314 \times 10^7 \text{ g} \cdot \text{cm}^2/\text{s}^2 \text{ g - mole} \cdot \text{K}$$

$$T = 75^\circ\text{F} = 297\text{K}$$

Substitution into the above equation gives

$$\frac{x_A}{x_{A0}} = \exp\left[\frac{((33,582)(1.00) - 45,000) \frac{(4.903 \times 10^7) z}{(8.314 \times 10^7)(297)}}{RT}\right] = e^{-22.7z}$$

in which  $z$  has units of centimeters.

A somewhat more accurate results may be obtained by accounting for the variation of  $x_B$ . Then taking the  $1/\bar{V}_B$  power of Eq. 24.2-22 (with no approximations) gives:

$$\frac{x_A}{x_{A0}} = \left(\frac{1-x_A}{1-x_{A0}}\right)^{\bar{V}_A/\bar{V}_B} \exp\left[\left(\frac{\bar{V}_A}{\bar{V}_B} M_B - M_A\right) \frac{g_\Omega z}{RT}\right]$$

This differs from the foregoing solution only by the first factor on the right side. For positive  $z$  the two solutions agree within 0.93% for the conditions given.

24A.2 Ultracentrifugation of Proteins (Alternative Solution)

It is preferable here to begin with Eq. 24.4-18, and, in the absence of further information, to assume concentration independent activity coefficient. This is probably a reasonable assumption.

Now begin by writing the equation of motion in the form

$$\partial p / \partial r = \rho g_{eff}; g_{eff} = (1g / cm^3) \cdot 50,000 \cdot 980cm / s^2$$

$$\partial p / \partial r = 4.9 \cdot 10^7 g / cm^2 s^2$$

Next note that 75 F = 23.8C = 297 K.

Then, neglecting the effect of pressure on the density of water we find from App. F, p. 867, that

$$cRT =$$

$$(55.5 \cdot 10^{-3} g - moles / cm^3) \cdot 297K \cdot (8.31451 \cdot 10^7 \frac{g - cm^2}{s^2 - gmole - K})$$

$$\text{or } cRT = 1.371 \cdot 10^9 g / s^2 - cm.$$

Finally we note that

$$M_P / M_W = 2,500; \hat{V}_P / \hat{V}_W = 1 / 1.34 = 0.746$$

Putting all of these results into Eq. 24.4-18 gives

$$\partial \ln x_P / \partial r = 22.68 / cm$$

Integrating this expression with the given BC at a reference value, z, of r yields

$$x_P = (5.6 \cdot 10^{-6}) e^{22.68z / cm}$$

which completes the solution.



Prob. 24A.3 Ionic diffusivities.

---

Ion:	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	
Diffusivity:	1.33	1.95	2.00	$\times 10^{-5} \text{ cm}^2/\text{s}$

---

Prob. 24B.1 Dimensions of the Lorentz force

In the international system of units,

$c_i$  [=] g-moles/m<sup>3</sup>,  $z_i$  [=] g-equivalents/g-mole,  $F = 96,500$  coulombs/g-equivalent

$v_i$  [=] m/s

It follows that

$c_i z_i F [v_i \times B]$  [=] Newtons/m<sup>3</sup>.

This is in agreement with the definition of the  $d_i$ .

## 24B.2 Junction potentials.

Integrating across the stagnant region gives

$$\phi_2 - \phi_1 = \left( \frac{RT}{F} \right) \left[ \frac{\mathcal{D}_{mw} - \mathcal{D}_{xw}}{\mathcal{D}_{mw} + \mathcal{D}_{xw}} \right] \ln \left( \frac{c_1}{c_2} \right)$$

For 25 C,  $(RT/F) = 25.692$  mV,  $\ln(c_1/c_2) = 2.303$ . It follows that the junction potential  $(\phi_2 - \phi_1)$  is  $-11.8$  mV for the sodium chloride and  $0.75$  for the potassium chloride. The sign of this potential arises from the tendency of the chloride ion to move faster than either cation. The very small junction potential for KCl leads to the use of saturated KCl solutions (salt bridges) between electrodes and the point in a physiological solution where potential is to be measured. The concentrated KCl tends to overwhelm the effects of solution electrolytes, which are typically on about  $0.15$  N.

Prob. 24B.3 Donnan Exclusion

The external salt mole fraction is

$$x_{NaCl} = x_{Na^+} = x_{Cl^-} = 0.00180$$

The internal molar concentrations are

$$c_{NaR} = 1.03 \text{ eqts} / L$$

$$c_{NaCl} = 0.001$$

$$c_W = 13.2$$

Then total molar concentration is

$$c_{tot} = 14.23$$

$$x_{Na^+} = 1.03 / 14.23 = 0.072$$

$$x_{Cl^-} = 0.01 / 14.23 = 0.0007027$$

It follows that

$$K_D = (0.0018^2) / [(0.000703)(0.0724)] \\ \doteq 0.064$$

#### 24B.4 Osmotic Pressure

Begin with Eq. 24.5-4, and limit consideration to equilibrium between two electrically uncharged solutions. Under these conditions the equation reduces to

$$\nabla \ln(a_w)_{T,p} = -(\bar{V}_w / RT) \nabla p$$

where the subscript “T,p” is a reminder that the activities are to be evaluated at the same reference temperature and pressure. Next note that for all practical purposes water may be considered incompressible and the sea water quite dilute. Then

$$\bar{V} \doteq 1/c$$

and we may write

$$(a_{w1})_{T,p} = (a_{w2})_{T,p} = p_{w1}^0 / p_{w2}^2 = e^{(p_2 - p_1) / cRT}$$

where  $p_{wi}^0$  is the vapor pressure of water over phase “i”, and  $p_i$  is the hydrostatic pressure on phase “i”. This equation then relates the pressures on pure water and sea water required to make them in equilibrium with each other. This could be accomplished for example by pressing down on the sea water with a hydrophobic screen with holes large enough to permit free passage of vapor but small enough that surface tension forces prevent movement of liquid. This would be one type of ideal membrane.

The osmotic pressure,  $\pi$ , is  $(p_2 - p_1)$  if “2” refers to the sea water and “1” to pure water. Then

$$\pi = cRT \ln(1 / 0.9816)$$

No temperature was specified, and 300 K will be assumed here for illustrative purposes. Then, from App. F, p.867, we may write

$$\begin{aligned} \pi &= (55.5 \cdot 10^{-3})(300)(82.0578) \text{ atm} (\ln(1 / 0.9816)) \\ &= 1366 \cdot 0.0185 \doteq 25 \text{ atm} \end{aligned}$$

This will of course vary with salinity as well as temperature.

Prob. 24B.5 Permeability of a perfectly selective filtration membrane.

$$x_w = c \bar{V}_w = 1$$

$$x_s = N_s = 0$$

Any ultrafiltrate will now be pure water, and the single operative diffusion equation reduces to

$$\frac{d}{dz} \ln a_w + \frac{p \bar{V}_w}{RT} = -N_w / \mathcal{D}'_{wm}$$

with

$$a_w = 1$$

at

$$z = \delta$$

It follows that

$$K_H = (\mathcal{D}'_{wm})_{avg} / RT \delta$$

where  $\delta$  is membrane thickness, and

$$(\mathcal{D}'_{im}) = \left[ \frac{1}{\delta} \int_0^\delta \frac{dz}{\mathcal{D}'_{im}} \right]^{-1}$$

In practice  $K_H$  is just an empirical quantity.

## 24B.6 Model insensitivity

The ratio of fluxes predicted by Eqs. 1 and 2 is

$$\frac{N_A(\text{pore})}{N_A(\text{Diff})} = \frac{2\pi}{3} \frac{(1 - \varepsilon)}{(1 + \pi/8)} \doteq 1.5(1 - \varepsilon)$$

At a porosity of 0.4 this ratio is about 0.9. Thus, although the two expressions predict different void fraction dependence they give nearly the same predictions for this common void fraction as well as the same dependence on particle diameter, temperature and molecular weight. Moreover, both fail to take into account the distributions of diameter and uniformity. From a practical standpoint they are closely equivalent.

### 24C.1 Expressions for the mass flux

a. First rewrite the left side of Eq. 24.2-8 thus

$$\begin{aligned} \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (\mathbf{v}_\alpha - \mathbf{v}_\beta) &= \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (\mathbf{v}_\gamma - \mathbf{v}_\beta) + x_\alpha (\mathbf{v}_\alpha - \mathbf{v}_\gamma) \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\beta}{D_{\alpha\beta}} \\ &= \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (\mathbf{v}_\gamma - \mathbf{v}_\beta) + x_\alpha (\mathbf{v}_\alpha - \mathbf{v}_\gamma) \sum_{\substack{\beta=1 \\ \text{(all } \beta)}}^N \frac{x_\beta}{D_{\alpha\beta}} + x_\alpha (\mathbf{v}_\gamma - \mathbf{v}_\alpha) \frac{x_\alpha}{D_{\alpha\alpha}} \end{aligned}$$

in which  $\mathbf{v}_\gamma$  is the velocity of an arbitrarily chosen species. In the last step, we have introduced  $D_{\alpha\alpha}$ , which has not been defined. We now define it as follows:

$$\frac{x_\alpha}{D_{\alpha\alpha}} = - \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\beta}{D_{\alpha\beta}} \quad \text{or} \quad \sum_{\substack{\beta=1 \\ \text{(all } \beta)}}^N \frac{x_\beta}{D_{\alpha\beta}} = 0 \quad (*)$$

Then, in the last expression (for the left side of Eq. 124.2-8) the second term drops out, and the third term can be combined with the first, so that we obtain

$$\sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (\mathbf{v}_\alpha - \mathbf{v}_\beta) = \sum_{\beta=1}^N \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (\mathbf{v}_\gamma - \mathbf{v}_\beta)$$

Thus the first term of Eq. 24.2-9 is now obtained, along with the auxiliary relation (designated by (\*)), which now has to be included because of the introduction of the  $D_{\alpha\alpha}$ .

b. In (a) we have not included the thermal diffusion terms. This is easy to do if, in the above development, we replace  $\mathbf{v}_\beta$  by  $\mathbf{v}_\beta + (D_\beta^T / \rho_\beta) \nabla \ln T$ . Then the procedure in (a) can be followed exactly to get Eq. 24.2-9, including the thermal diffusion terms.



## 24C.2 Differential centrifugation.

Yes. From Eq. 24.4-22, migration velocities are proportional to

$$v_{migr} \propto R_p^2 \Delta \rho$$

Begin by noting that protein mass is equal to

$$\begin{aligned} m_p &= (\text{mass / mole}) \cdot (\text{moles / molecule}) \\ &= (40,000 \text{g/mole}) / \tilde{N} = [40,000 / (6.022 \cdot 10^{23})] g \\ &= 5.64 \cdot 10^{-20} g \end{aligned}$$

Next note that, if we assume the particles to be spherical

$$\begin{aligned} m_p &= (4/3) \pi \rho_p R_p^3 \\ R_p^2 &\propto (m_p / \rho_p)^{2/3} \end{aligned}$$

Then taking the migration velocity of the cells as unity, we find the relative migration velocities to be 1, 0.0122 and 0.0000102 respectively, and diffusion is negligible for both cells and inclusion bodies. Shape will be a secondary consideration under these circumstances.

### 24C.3 Transport characteristics of sodium chloride

First put all data on the same concentration scale by writing in the molar equivalents of molality using the formula provided. Next put the diffusivities and conductances in comparable units of  $10^5 \text{ cm}^2/\text{s}$  by noting that

Faraday's constant (F or more commonly  $\mathcal{F}$ ) equals 96,485 coulombs/g-eqt.

$$R = 8.3145 \text{ joules/g-mol}\cdot\text{K}$$

$$1 \text{ joule} = 1 \text{ volt-coulomb} = 1 \text{ volt-ampere}\cdot\text{s}$$

$$1 \text{ volt/ampere} = 1 \text{ ohm}$$

It follows that  $\mathcal{F}^2 / RT = 3.755 \cdot 10^6 \text{ ohm} - \text{eqt}$

It also follows that conductance is the sum of the two ionic conductances while diffusivity is the average defined by Eq. 24.4-32. Therefore conductances should be divided by 71.1 relative to diffusivities which are given by the table of the problem statement in units of  $10^5 \text{ cm}^2/\text{s}$ .

In the accompanying spread sheet and graph three quantities are given in terms of molality: diffusivity/activity, diffusivity and conductance. It may be seen that all three are equal to each other at the limit of infinite dilution to the accuracy of the figure.

However, conductance decreases rapidly with increasing concentration, because of an increasing effect of diffusional ion-ion interaction.

There is no such interaction for diffusivity, and the observed diffusivity of salt can be predicted surprisingly well from ionic conductances at infinite dilution. Salt diffusivity is equal to  $1.54 \pm 0.07$  over the whole range of salt concentrations from zero to 3 N. Clearly ionic diffusivities are not changing much with concentration.

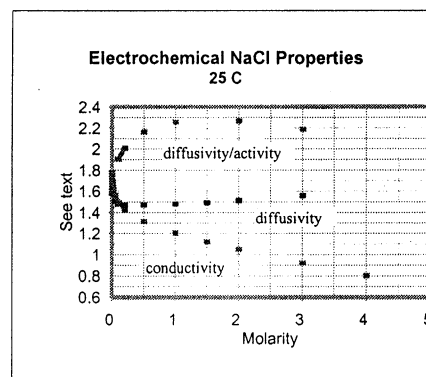
At the same time it can be seen that the activity correction is significant and masks some of the variation in transport properties.

Electrochemical Characteristics of Aqueous NaCl at 25 C

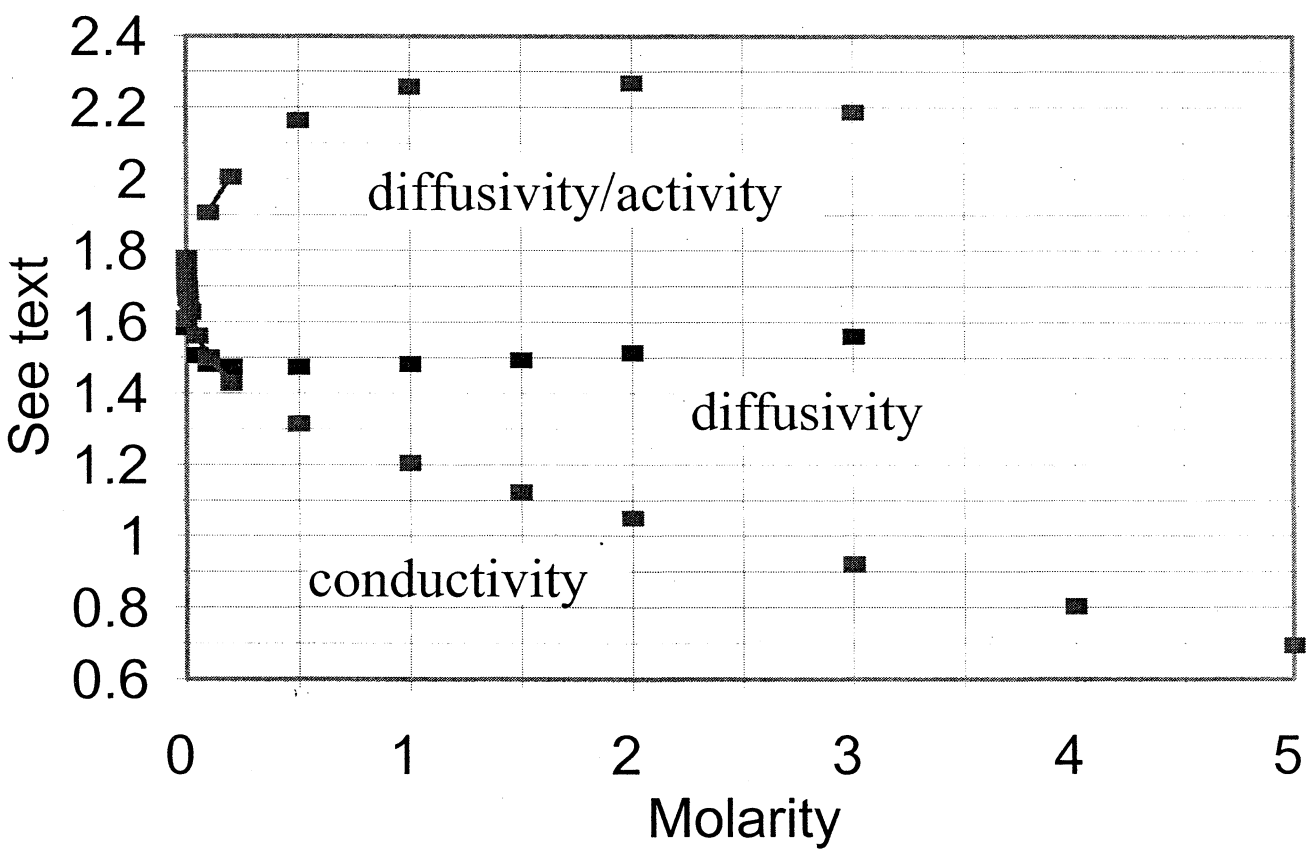
Diffusivity is in (cm<sup>2</sup>/s)\*10<sup>5</sup>

Lambda = equivalent conductance in cm<sup>2</sup>/ohm-equivalent

c(molar)	Lambda	Diffusivity	c(molal)	Act. coeff.	dif/act	B/71.1
0	126.45	1.61	0	1	1.61	1.778481
0.00055	124.51		0.00055			1.751195
0.001	123.74	1.585	0.001			1.740366
0.005	120.64		0.005			1.696765
0.01	118.53		0.01			1.667089
0.02	115.76		0.02			1.628129
0.05	111.06	1.507	0.05			1.562025
0.1	106.74	1.483	0.1	0.778	1.90617	1.501266
0.2	101.71	1.475	0.2	0.735	2.006803	1.43052
0.298			0.3	0.71		
0.39696			0.4	0.693		
0.5	93.62	1.474	0.5	0.681	2.164464	1.316737
0.59316			0.6	0.673		
0.69069			0.7	0.667		
0.78784			0.8	0.659		
0.88461			0.9	0.657		
1	85.76	1.484		0.657	2.258752	1.206188
1.17264			1.2	0.654		
1.36276			1.4	0.655		
1.5	79.86	1.495				1.123207
1.55136			1.6	0.657		
1.73844			1.8	0.662		
2	74.71	1.516		0.668	2.269461	1.050774
2.38125			2.5	0.688		
3	65.57	1.563		0.714	2.189076	0.922222
3.26725			3.5	0.746		
4	57.23		4	0.783		0.804923
4.11525			4.5	0.826		
5	49.46		5	0.874		0.69564



# Electrochemical NaCl Properties 25 C



Prob. 24C.4 Departures from electroneutrality

Begin by writing

$$d\phi/dz = \frac{d\phi}{dc_s} \frac{dc_s}{dz} = -\left(\frac{RT}{F}\right) \left[ \frac{\mathcal{D}_{mw} - \mathcal{D}_{xw}}{\mathcal{D}_{mw} + \mathcal{D}_{xw}} \right] \left( \frac{1}{c_s} \right) \frac{dc_s}{dz}$$

$$d^2\phi/dz^2 = \left(\frac{RT}{F}\right) \left[ \frac{\mathcal{D}_{mw} - \mathcal{D}_{xw}}{\mathcal{D}_{mw} + \mathcal{D}_{xw}} \right] \left( \frac{1}{c_s^2} \right) \left( \frac{dc_s}{dz} \right)^2$$

Now for NaCl,

$$\left(\frac{RT}{F}\right) \left[ \frac{\mathcal{D}_{mw} - \mathcal{D}_{xw}}{\mathcal{D}_{mw} + \mathcal{D}_{xw}} \right] = 25.692mV \cdot 0.2875 = 7.3878mV$$

while

$$(dc_s/dz)^2 = 0.81(\text{eqts/liter})^2 / L^2$$

$$c_s^2 = [1 - 0.9(z/L)]^2 (\text{eqts/liter})^2$$

It follows that for our system

$$\frac{d^2\phi}{dz^2} = 7.3878mV \left( \frac{0.81}{L^2} \right) [1 - (0.9z/L)]^2$$

or, at the center of the stagnant region

$$\frac{d^2\phi}{dz^2} = 1.788mV / L^2$$

$$c_+ - c_- = (1.788 \cdot 10^{-3} V)(1/L^2) / (1.392 \cdot 10^{16} V - cm / \text{eqt})$$

$$= 1.128 \cdot 10^{-18} \text{eqts/L}^2 \text{ cm}$$

This tends to be a very small number, but for thin membranes, it can become appreciable.

## 24C.5 Dielectrophoretic Driving Forces

Begin by writing

$$\nabla^2 \phi = \frac{1}{r} \frac{d}{dr} \left( r \frac{d\phi}{dr} \right) = 0$$

with the boundary conditions that

$$\text{At } r = R_1, \phi = \phi_1, \text{ and at } r = R_2, \phi = \phi_2,$$

It then follows directly that

$$\frac{\phi - \phi_1}{\phi_2 - \phi_1} = \frac{\ln(r/R_1)}{\ln(R_2/R_1)}$$

and that

$$E = \nabla \phi = \underline{\delta}_r \frac{d\phi}{dr} = \underline{\delta}_r \frac{(\phi_2 - \phi_1)}{\ln(R_2/R_1)} \frac{1}{r}$$

Next note from Eq. S, Table A.7-2

$$\nabla \underline{E} = \delta_r \delta_r \frac{d}{dr} \frac{d\phi}{dr} = \underline{\delta}_r \underline{\delta}_r \left( \frac{\phi_2 - \phi_1}{\ln(R_2/R_1)} \right) \left( \frac{-1}{r^2} \right)$$

and, finally

$$[\underline{E} \cdot \nabla \underline{E}] = -\delta_r \left( \frac{\phi_2 - \phi_1}{\ln(R_2/R_1)} \right)^2 \left( \frac{1}{r^3} \right)$$

We see then that the dielectrophoretic force is in the negative  $r$ -direction, whatever the direction of  $\underline{E}$ , and that it increases very strongly with decrease in  $r$ .

24C.6 Effects of small inclusions in a dielectric medium

The first requirement here is to complete the problem statement by adding:  
 "Develop an expression for  $\phi_s$  if  $\phi_c \rightarrow \Phi z$  at large  $r$  with  $\Phi$  a constant."

One must next recognize that for an uncharged medium

$$(\nabla \cdot E) = \nabla^2 \phi = 0$$

This equation and the given boundary conditions make an exact analog of the corresponding heat conduction problem, treated for example in Carslaw and Jaeger, Sect. 16.4 I, p. 426. We thus proceed with trial solutions of the form

$$\phi_c = \Phi r \cos \theta + \frac{B}{r^2} \cos \theta$$

$$\phi_s = A r \cos \theta$$

and the boundary condition

$$\epsilon_s \left. \frac{d\phi_s}{dr} \right|_{r=R} = \epsilon_c \left. \frac{d\phi_c}{dr} \right|_{r=R}$$

where  $R$  is the radius of the inclusion. This boundary condition plus that at large  $r$  permit determination of  $A$  and  $B$ , and the final result is

$$\phi_c = \Phi \left[ r \cos \theta + \frac{(\epsilon_c - \epsilon_s) R^3 \cos \theta}{r^2 (2\epsilon_c + \epsilon_s)} \right]$$

$$\phi_s = \frac{3\Phi \epsilon_c r \cos \theta}{2\epsilon_c + \epsilon_s} = \frac{3\Phi \epsilon_c z}{2\epsilon_c + \epsilon_s}$$

This result can be used to obtain the effective dielectric constants of composite media just as was done for thermal conductivity in Section 9.6.

### 24C.7 Frictionally induced selective filtration

The first step is to review the development of Section 24.5 and to obtain a directly useable set of equations for pressure and activity gradients. Begin by adding Eqs. 24.5-16 and 17 with the aid of Eq. 24.5-19 in the form

$$x_s \nabla_{T,p} \ln a_s + x_w \nabla_{T,p} \ln a_w = 0$$

The result is

$$\frac{N_s}{c\mathcal{D}'_{sm}} + \frac{N_w}{c\mathcal{D}'_{wm}} = -\frac{(\phi_s + \phi_w)}{cRT} \nabla p = -\frac{\nabla p}{cRT}$$

Next this expression for pressure gradient should be put into Eq. 24.5-16 to obtain

$$\begin{aligned} \frac{x_w N_s - x_s N_w}{c\mathcal{D}'_{sw}} + \frac{N_s}{c\mathcal{D}'_{sm}} &= -x_s \nabla_{T,p} \ln a_s \\ &+ \phi_s \left[ \frac{N_s}{c\mathcal{D}'_{sm}} + \frac{N_w}{c\mathcal{D}'_{wm}} \right] \end{aligned}$$

This expression can be rearranged to

$$N_s \left[ \frac{x_w}{c\mathcal{D}'_{sw}} + \frac{\phi_w}{c\mathcal{D}'_{sm}} \right] - N_w \left[ \frac{x_s}{c\mathcal{D}'_{sw}} + \frac{\phi_s}{c\mathcal{D}'_{wm}} \right] = - \left( 1 + \frac{\partial \ln \gamma_s}{\partial \ln x_s} \right) \frac{dx_s}{dz}$$

The solution will always be dilute enough that the activity coefficient can be considered constant. Moreover, for this system there is no change in activity or concentration across the solution membrane interface, so our concentration boundary condition is just that

$$z = 0, x_s = 0.01$$

The imposed pressure drop across the membrane, which is the same as that between the upstream and downstream fluid phases, determines the flow rate. Limiting behavior is readily determined.

For very low flow rates, both convective terms are very small. Hence the diffusional term and concentration changes across the membrane, are also very small. Then, as for all but truly ideal membranes the filtrate has the same composition as the feed. This is a general characteristic of all non-ideal membranes.



For very high flow rates, the two convective terms are both very large but nearly equal, and Eq. 24.5-26 governs, except for a very thin boundary layer near the downstream end of the membrane. The two may then be equated, and for high flow rates the filtrate composition is expressible as

$$Y_s = \frac{y_s}{y_w} = \frac{N_s}{N_w} = \left( \frac{x_s}{x_w} \right) \left[ \frac{1 + c \bar{V}_s \mathcal{D}_{sw} / \mathcal{D}'_{wm}}{1 + c \bar{V}_w \mathcal{D}_{sw} / \mathcal{D}'_{sm}} \right]$$

Here  $Y_s$  and  $y_s$  refer to mole ratio and mole fraction of solute respectively in the filtrate. Now in our specific case, "S" equals "G", and, because the solution is mostly water "c" equals  $\bar{V}_w$ . Then with

$$\mathcal{D}_{GW} / \mathcal{D}'_{Gm} = 25; \mathcal{D}'_{wm} = 100 \mathcal{D}'_{Gm}$$

$$Y_s / X_s = 2 / 26 = 1 / 13 = 0.00076$$

where  $X_s$  is feed mole ratio.

The concentration profile and filtrate compositions at intermediate pressure gradients can be obtained by replacing  $N_w$  in Eq. 24.5-16 using Eq. 24.5-20.

### 24C.8 Thermodynamically induced selective filtration.

Consider now internal behavior so that the  $x'_i$  are defined as the mole fractions in the matrix-free solution just inside the upstream surface of the membrane. Then for the conditions described in the problem statement at high flow rates, where concentration gradients are confined to a thin boundary layer just inside the downstream surface

$$Y_S = \frac{N_S}{N_W} = X'_S = \frac{x'_S}{x'_W}$$

However, for the dilute solutions normal in these systems

$$X'_S = 0.1X_S$$

and

$$Y_S = 0.1X_A$$

Again for very slow flow there is no enrichment, and for intermediate flows one must carry out the integration suggested for the previous problem.

## 24C.9 Facilitated Transport

The defining equations are

$$N_C = -N_{CS}$$

$$N_C = \mathcal{D}_{Cm} (c_{C0} - c_{C\delta}) / \delta$$

$$N_{CS} = \mathcal{D}_{CSm} (c_{CS0} - c_{CS\delta}) / \delta$$

These fluxes are to be determined with the aid of the boundary conditions

$$c_{CS0} / c_{C0} = K_D c_{S0}$$

$$c_{CS\delta} / c_{C\delta} = K_D c_{S\delta}$$

and the conservation constraint

$$\frac{1}{\delta} \int_0^\delta (c_C + c_{CS}) d\delta = \bar{c}$$

Here  $\bar{c}$ , the sum of free and complexed carrier, is position invariant. For our present purposes it and the two external concentrations will be assumed known.

Normally the carrier is much larger than the solute, and the diffusivities of the carrier and carrier-solute complex are assumed to be equal. This is done both for lack of data and because the model is so oversimplified that its chief use is to gain insight.

We will now make this assumption, in order to concentrate on the qualitative aspects of system behavior:

$$\mathcal{D}_{Cm} = \mathcal{D}_{CSm} = D$$

We may now replace the above summational constraint with

$$c_C + c_{CS} = \bar{c}$$

Flux of the solute-carrier complex can then be determined by noting

## 24D.1 Entropy flux and entropy production

a. From Eq. 24.1-2 we get for a moving fluid element

$$\frac{D\hat{U}}{Dt} = T \frac{D\hat{S}}{Dt} - p \frac{D\hat{V}}{Dt} + \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} \frac{D\omega_\alpha}{Dt}$$

We now solve this for  $D\hat{S}/Dt$  and multiply by the density to obtain

$$\rho \frac{D\hat{S}}{Dt} = \frac{\rho}{T} \frac{D\hat{U}}{Dt} + \frac{p\rho}{T} \frac{D\hat{V}}{Dt} - \frac{\rho}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} \frac{D\omega_\alpha}{Dt}$$

Next we rewrite each of the terms on the right side by using the equations of change:

$$\frac{\rho}{T} \frac{D\hat{U}}{Dt} = -\frac{1}{T} (\nabla \cdot \mathbf{q}) - \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) - \frac{p}{T} (\nabla \cdot \mathbf{v}) + \sum_{\alpha=1}^N (\mathbf{j}_\alpha \cdot \mathbf{g}_\alpha)$$

$$\frac{p\rho}{T} \frac{D\hat{V}}{Dt} = \frac{p\rho}{T} \frac{D}{Dt} \left( \frac{1}{\rho} \right) = -\frac{p}{\rho T} \frac{D\rho}{Dt} = \frac{p}{T} (\nabla \cdot \mathbf{v})$$

$$-\frac{\rho}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} \frac{D\omega_\alpha}{Dt} = \frac{1}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} [(\nabla \cdot \mathbf{j}_\alpha) - r_\alpha]$$

Then the entropy equation becomes

$$\rho \frac{D\hat{S}}{Dt} = -\frac{1}{T} (\nabla \cdot \mathbf{q}) - \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) + \sum_{\alpha=1}^N (\mathbf{j}_\alpha \cdot \mathbf{g}_\alpha) + \frac{1}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} [(\nabla \cdot \mathbf{j}_\alpha) - r_\alpha]$$

We next want to force this equation into the form of Eq. 24.1-1 by creating a divergence term on the right side and then adding compensating terms (the dashed-underlined terms):

$$\rho \frac{D\hat{S}}{Dt} = -\left( \nabla \cdot \frac{1}{T} \left\{ \mathbf{q} - \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} \mathbf{j}_\alpha \right\} \right) - \left( \frac{1}{T^2} \mathbf{q} \cdot \nabla T \right) - \sum_{\alpha=1}^N \left( \mathbf{j}_\alpha \cdot \nabla \left( \frac{1}{T} \frac{\bar{G}_\alpha}{M_\alpha} \right) \right)$$


---

$$+ \frac{1}{T} \sum_{\alpha=1}^N (\mathbf{j}_\alpha \cdot \mathbf{g}_\alpha) - \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) - \frac{1}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} r_\alpha$$

This is now of the form of Eq. 24.1-1, so that the entropy flux and entropy generation terms may be identified as in Eqs. 24.1-3 and 4.

b. Going from Eq. 24.1-5 to Eq. 24.1-3 is straightforward:

$$\mathbf{s} = \frac{1}{T} \mathbf{q}^{(h)} + \sum_{\alpha=1}^N \frac{\bar{S}_\alpha}{M_\alpha} \mathbf{j}_\alpha = \frac{1}{T} \left( \mathbf{q} - \sum_{\alpha=1}^N \frac{\bar{H}_\alpha}{M_\alpha} \mathbf{j}_\alpha \right) + \frac{1}{T} \sum_{\alpha=1}^N \frac{T\bar{S}_\alpha}{M_\alpha} \mathbf{j}_\alpha$$

Then use of the relation  $\bar{G}_\alpha = \bar{H}_\alpha - T\bar{S}_\alpha$  gives Eq. 24.1-3.

Substitution of Eq. 24.1-7 and the first line of Eq. 21.4-8 into Eq. 24.1-6 gives

$$g_s = - \left( \mathbf{q} \cdot \frac{1}{T^2} \nabla T \right) + \frac{1}{T^2} \left( \sum_{\alpha=1}^N \frac{\bar{H}_\alpha}{M_\alpha} \mathbf{j}_\alpha \cdot \nabla T \right)$$

(1) (2)

$$- \frac{1}{T} \sum_{\alpha=1}^N \left( \mathbf{j}_\alpha \cdot \left\{ T \nabla \frac{\bar{G}_\alpha}{M_\alpha T} + \frac{\bar{H}_\alpha}{M_\alpha T} \nabla T - \frac{1}{\rho} \nabla p - g_\alpha + \frac{1}{\rho} \sum_{\beta=1}^N \rho_\beta \mathbf{g}_\beta \right\} \right)$$

(3) (4) (5) (6) (7)

$$- \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) - \frac{1}{T} \sum_{\alpha=1}^N \frac{\bar{G}_\alpha}{M_\alpha} r_\alpha$$

(8) (9)

Term (1) gives the first term in Eq. (24.1-4), and terms (8) and (9) are the same as the third and fourth term. Term (5) is the same has the second part of the second term. Terms (6) and (7) are identically zero because the sum of the mass fluxes is zero. This leaves us with terms (2), (3), and (4), which we have to show gives the first term in Eq. 24.1-4. That is, we have to verify that

$$\frac{1}{T^2} \left( \sum_{\alpha=1}^N \frac{\bar{H}_\alpha}{M_\alpha} \mathbf{j}_\alpha \cdot \nabla T \right) - \frac{1}{T} \sum_{\alpha=1}^N \left( \mathbf{j}_\alpha \cdot T \nabla \frac{\bar{G}_\alpha}{M_\alpha T} \right) - \frac{1}{T} \sum_{\alpha=1}^N \left( \mathbf{j}_\alpha \cdot \frac{\bar{H}_\alpha}{M_\alpha T} \nabla T \right)$$

$$= -\sum_{\alpha=1}^N \left( \mathbf{j}_{\alpha} \cdot \nabla \left( \frac{1}{T} \frac{\bar{G}_{\alpha}}{M_{\alpha}} \right) \right)$$

This is indeed an identity, and therefore the equivalence of Eqs. 24.1-1 and 24.1-6 has been affirmed.

Appendix A: p. 810, Ex. 1

a.  $(\mathbf{v} \cdot \mathbf{w})$

The order is  $1+1-2=0$ , the 1s for the vectors and the  $-2$  for the single dot. The result is a scalar.

b.  $(\mathbf{v} - \mathbf{u})\mathbf{w}$

The order is  $1+1=2$ . The result is a second-order tensor.

c.  $(\mathbf{ab}:\mathbf{cd})$

The order is  $1+1+1+1-4=0$ , the 1s for the vectors and the  $-4$  for the double dot. The result is a scalar.

d.  $[\mathbf{v} \cdot \rho \mathbf{w} \mathbf{u}]$

The order is  $1+0+1+1-2=1$ , so that the result is a vector.

e.  $[[\mathbf{a} \times \mathbf{f}] \times [\mathbf{b} \times \mathbf{g}]]$

The order is  $1+1+1+1-1-1-1=1$ , so that the result is a vector. There are four 1s for the four vectors and three crosses for the three cross-products.

**Appendix A: p. 810, Ex. 2**

Verify, by example, the inequality

$$(\mathbf{u} \cdot \mathbf{v})\mathbf{w} \neq \mathbf{u}(\mathbf{v} \cdot \mathbf{w})$$

by means of a specific illustration.

Let us take  $\mathbf{u}$  to be a unit vector in the  $x$  direction, and call this vector  $\delta_x$ . Then take  $\mathbf{v}$  to be  $\delta_x$  also. Further take  $\mathbf{w}$  to be a unit vector in the  $y$  direction, calling it  $\delta_y$ . Then the equality becomes

$$(\delta_x \cdot \delta_x)\delta_y \neq \delta_x(\delta_x \cdot \delta_y)$$

Since, by the definition of the dot product  $(\delta_x \cdot \delta_x) = 1$  and  $(\delta_x \cdot \delta_y) = 0$ , the above inequality becomes

$$\delta_y \neq 0$$

This is a true statement, inasmuch as  $\delta_y$  is a vector of unit length in the  $y$  direction.

If all three vectors are equal

$$\mathbf{u} = \mathbf{v} = \mathbf{w} = \mathbf{A}$$

then the above "inequality" becomes

$$\mathbf{A}^2 \mathbf{A} = \mathbf{A} \mathbf{A}^2$$

which is clearly an equality.

If the three vectors are mutually perpendicular, then one gets the equality  $0 = 0$ .



**Appendix A: p. 810, Ex. 3**

The volume rate of flow of a fluid flowing through a surface is given by the product of the surface area  $S$  and the component of the velocity that is perpendicular to the surface. The components of velocity parallel to the surface contribute nothing to the volume rate of flow.

Since the unit normal vector for the surface is  $\mathbf{n}$ , the component of the fluid velocity  $\mathbf{v}$  in the direction perpendicular to the surface is  $(\mathbf{v} \cdot \mathbf{n})$  and the volume rate of flow through the surface is  $(\mathbf{v} \cdot \mathbf{n})S$ .

When the volume rate of flow is multiplied by the fluid density, we get the mass rate of flow  $\rho(\mathbf{v} \cdot \mathbf{n})S$ .

#### Appendix A: p. 810, Ex. 4

Let us establish a coordinate system in the rotating body at some time  $t = t_0$ , such that the  $z$  axis is along the axis of rotation and pointing in the direction of the  $\mathbf{W}$  vector. This is a coordinate system fixed in space.

Select now a point  $P$  in the rotating body with coordinates  $x, y, z$  at time  $t = t_0$ . As the body rotates, the point  $P$  will have the same value of  $z$  at all times, but  $x$  and  $y$  will change. Let the instantaneous location of point  $P$  be given by its  $z$  coordinate and a vector  $\mathbf{s}$  perpendicular to the axis of rotation. The vector  $\mathbf{s}$  changes with time, although its magnitude is constant.

The instantaneous velocity vector  $\mathbf{v}$  for the point  $P$  will have a magnitude equal to the product of the magnitude of the  $\mathbf{W}$  vector and the magnitude vector  $\mathbf{s}$ , and its direction will be perpendicular to the vectors  $\mathbf{W}$  and  $\mathbf{s}$ . That is, the vector  $\mathbf{v}$  will increase proportionately to an increase in  $\mathbf{W}$ , and will also increase as point  $P$  moves outward from the axis of rotation. The relation

$$\mathbf{v} = [\mathbf{W} \times \mathbf{s}]$$

captures the ideas in the paragraph above. It not only shows the linear dependence of  $\mathbf{v}$  on  $\mathbf{W}$  and  $\mathbf{s}$ , but also gives the direction of the velocity correctly (which  $[\mathbf{s} \times \mathbf{W}]$  would not).

The location of the point  $P$  with respect to the origin of coordinates is  $\mathbf{r} = \delta_z z + \mathbf{s}$  so that the velocity of the point is given by

$$\mathbf{v} = [\mathbf{W} \times \mathbf{s}] = [\mathbf{W} \times (\mathbf{r} - \delta_z z)]$$

Since  $\mathbf{W}$  and  $\delta_z z$  are vectors with the same direction, their cross product will be zero. Therefore we are left with

$$\mathbf{v} = [\mathbf{W} \times \mathbf{r}]$$

This, then, gives the instantaneous velocity of a point in the rotating solids in terms of the instantaneous position vector of the point with respect to the origin of coordinates located on the axis of rotation.

**Appendix A: p. 810, Ex. 5**

The formal expression for the differential amount work done on an object as it is moved through a differential displacement  $d\mathbf{r}$  by a force  $\mathbf{F}$  is

$$dW = (\mathbf{F} \cdot d\mathbf{r})$$

Note that, if the force acts in a direction perpendicular to the displacement vector, no work is done.

The rate of doing work is then

$$\frac{dW}{dt} = \left( \mathbf{F} \cdot \frac{d\mathbf{r}}{dt} \right) = (\mathbf{F} \cdot \mathbf{v})$$

since the velocity is given by the time rate of change of the position vector (see Exercise 1, p. 839). This expression for the rate of doing work is used in §9.8 in connection with developing the rate of doing work on a fluid element (see Eq. 9.8-4), an essential ingredient in the combined energy flux vector  $\mathbf{e}$ .

**Appendix A: p. 814, Ex. 1**

$$a. \sum_{k=1}^3 k^2 = 1^2 + 2^2 + 3^2 = 14$$

$$b. \sum_{k=1}^3 a_k^2 = a_1^2 + a_2^2 + a_3^2$$

$$c. \sum_{j=1}^3 \sum_{k=1}^3 a_{jk} b_{kj} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31} \\ + a_{21}b_{12} + a_{22}b_{22} + a_{23}b_{32} + a_{31}b_{13} + a_{32}b_{23} + a_{33}b_{33}$$

$$d. \left( \sum_{j=1}^3 a_j \right)^2 = \sum_{j=1}^3 \sum_{k=1}^3 a_j a_k = a_1 a_1 + a_1 a_2 + a_1 a_3 \\ + a_2 a_1 + a_2 a_2 + a_2 a_3 + a_3 a_1 + a_3 a_2 + a_3 a_3 \\ = a_1^2 + a_2^2 + a_3^2 + 2a_1 a_2 + 2a_2 a_3 + 2a_3 a_1$$

**Appendix A: p. 814, Ex. 2**

$$a. (\mathbf{v} \cdot \mathbf{w}) = (1)(3) + (2)(-1) + (-5)(1) = -4$$

$$\begin{aligned} b. [\mathbf{v} \times \mathbf{w}] &= \delta_x [(2)(1) - (-5)(-1)] + \delta_y [(-5)(3) - (1)(1)] \\ &\quad + \delta_z [(1)(-1) - (2)(3)] \\ &= \delta_x (-3) + \delta_y (-16) + \delta_z (-7) \end{aligned}$$

$$c. v = \sqrt{(1)^2 + (2)^2 + (-5)^2} = \sqrt{30}; w = \sqrt{(3)^2 + (-1)^2 + (1)^2} = \sqrt{11}$$

$$d. (\delta_x \cdot \mathbf{v}) = v_x = 1$$

$$\begin{aligned} e. [\delta_x \times \mathbf{w}] &= \delta_x [(0)(1) - (0)(-1)] + \delta_y [(0)(3) - (1)(1)] \\ &\quad + \delta_z [(1)(-1) - (0)(3)] \\ &= \delta_y (-1) + \delta_z (-1) \end{aligned}$$

f. From Eq. A.1-6,

$$\cos \phi_{\mathbf{vw}} = \frac{(\mathbf{v} \cdot \mathbf{w})}{vw} = \frac{-4}{\sqrt{(30)(11)}} = \frac{-4}{\sqrt{330}} = \frac{-4}{18.166} = -0.220$$

Hence  $\phi_{\mathbf{vw}} = 77.29^\circ$ . The minus sign is not affixed to  $\phi_{\mathbf{vw}}$  since the angle is defined only as the angle *between*  $\mathbf{v}$  and  $\mathbf{w}$  and therefore has no sign.

$$\begin{aligned} g. [\mathbf{r} \times \mathbf{v}] &= \delta_x [(y)(-5) - (z)(2)] + \delta_y [(z)(1) - (x)(-5)] \\ &\quad + \delta_z [(x)(2) - (y)(1)] \end{aligned}$$

**Appendix A: p. 814, Ex. 3**

a.  $\left([\delta_x \times \delta_y] \cdot \delta_z\right) = (\delta_z \cdot \delta_z) = 1$

b.  $\left[[\delta_y \times \delta_z] \times [\delta_x \times \delta_z]\right] = [\delta_x \times (-\delta_y)] = -\delta_z$

**Appendix A: p. 815, Ex. 4**

$$a. \quad \sum_{j=1}^3 \sum_{k=1}^3 \varepsilon_{1jk} \varepsilon_{2jk} = \varepsilon_{111} \varepsilon_{211} + \varepsilon_{112} \varepsilon_{212} + \varepsilon_{113} \varepsilon_{213} \\ + \varepsilon_{121} \varepsilon_{221} + \varepsilon_{122} \varepsilon_{222} + \varepsilon_{123} \varepsilon_{223} + \varepsilon_{131} \varepsilon_{231} + \varepsilon_{132} \varepsilon_{232} + \varepsilon_{133} \varepsilon_{233} = 0$$

since every term contains a permutation symbol with two indices the same.

$$b. \quad \sum_{k=1}^3 \varepsilon_{11k} \varepsilon_{12k} = \delta_{11} \delta_{12} - \delta_{21} \delta_{11}$$

The left side is zero, because each term contains a permutation symbol with two indices the same. The right side is zero, because every term contains a Kronecker delta with two indices that are different

**Appendix A: p. 815, Ex. 5**

This result (where  $\varepsilon_{ijk}$  is defined by Eqs. A.2-3 to 5) is used quite a lot in proofs involving cross products. In the sum on  $j$  and  $k$ , there are nine terms:

$$\begin{aligned}\sum_{j=1}^3 \sum_{k=1}^3 \varepsilon_{ijk} \alpha_{jk} &= \varepsilon_{i11} \alpha_{11} + \varepsilon_{i12} \alpha_{12} + \varepsilon_{i13} \alpha_{13} \\ &\quad + \varepsilon_{i21} \alpha_{21} + \varepsilon_{i22} \alpha_{22} + \varepsilon_{i23} \alpha_{23} \\ &\quad + \varepsilon_{i31} \alpha_{31} + \varepsilon_{i32} \alpha_{32} + \varepsilon_{i33} \alpha_{33}\end{aligned}$$

The terms containing epsilon with two indices equal are zero by definition. The remaining terms may be written as follows, using the fact that the epsilons change sign if any two indices are reversed:

$$\begin{aligned}\sum_{j=1}^3 \sum_{k=1}^3 \varepsilon_{ijk} \alpha_{jk} &= \varepsilon_{i12} \alpha_{12} + \varepsilon_{i13} \alpha_{13} + \varepsilon_{i23} \alpha_{23} - \varepsilon_{i12} \alpha_{21} - \varepsilon_{i13} \alpha_{31} - \varepsilon_{i23} \alpha_{32} \\ &= \varepsilon_{i12} (\alpha_{12} - \alpha_{21}) + \varepsilon_{i13} (\alpha_{13} - \alpha_{31}) + \varepsilon_{i23} (\alpha_{23} - \alpha_{32})\end{aligned}$$

But the quantities  $\alpha_{jk}$  are symmetrical, and therefore the coefficients  $(\alpha_{12} - \alpha_{21})$ , etc., are zero. Therefore the entire sum is zero.



Appendix A : p. 815, Ex. 6

The cross product, being a vector quantity, can be written as the sum of products of unit vectors and scalar components thus:

$$[\mathbf{v} \times \mathbf{w}] = \sum_{i=1}^3 \delta_i [\mathbf{v} \times \mathbf{w}]_i$$

From Eq. A.2-21 we have

$$[\mathbf{v} \times \mathbf{w}] = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 \epsilon_{ijk} \delta_i v_j w_k = \sum_{i=1}^3 \delta_i \left( \sum_{j=1}^3 \sum_{k=1}^3 \epsilon_{ijk} v_j w_k \right)$$

the second form being obtained by rearranging the original expression.

Now we can equate the coefficients of the unit vectors to get

$$[\mathbf{v} \times \mathbf{w}]_i = \sum_{j=1}^3 \sum_{k=1}^3 \epsilon_{ijk} v_j w_k$$

which just states that the  $i$ th component of  $[\mathbf{v} \times \mathbf{w}]$  is given by the double sum on the right side. This result is used in the first line of Eq. A.2-25.

**Appendix A: p. 815, Ex. 7**

First all terms in the "identity of Lagrange" are expanded in component form, thus

$$\sum_i \sum_j \sum_k \sum_m \sum_n \varepsilon_{ijk} v_j w_k \varepsilon_{imn} v_m w_n + \left( \sum_i v_i w_i \right) \left( \sum_j v_j w_j \right) = \left( \sum_i v_i v_i \right) \left( \sum_j w_j w_j \right)$$

Then perform the sum on  $i$  and use Eq. A.2-7 in the first term on the left side to get

$$\sum_j \sum_k \sum_m \sum_n (\delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}) v_j v_m w_k w_n + \sum_i \sum_j v_i v_j w_i w_j = \sum_i \sum_j v_i v_i w_j w_j$$

Next, perform the sums on  $m$  and  $n$  in the first term on the left side:

$$\sum_j \sum_k (v_j v_j w_k w_k - v_j v_k w_k w_j) + \sum_i \sum_j v_i v_j w_i w_j = \sum_i \sum_j v_i v_i w_j w_j$$

Make the change of indices  $i \rightarrow j$  and  $j \rightarrow k$  in the second term on the left side and in the term on the right side to get:

$$\sum_j \sum_k (v_j v_j w_k w_k - v_j v_k w_k w_j) + \sum_j \sum_k v_j v_k w_j w_k = \sum_j \sum_k v_j v_j w_k w_k$$

which completes the proof.

**Appendix A: p. 819, Ex. 1**

$$\begin{aligned} a. \quad [\boldsymbol{\tau} \cdot \mathbf{v}]_x &= (3)(5) + (2)(3) + (-1)(-2) = 23 \\ [\boldsymbol{\tau} \cdot \mathbf{v}]_y &= (2)(5) + (2)(3) + (1)(-2) = 14 \\ [\boldsymbol{\tau} \cdot \mathbf{v}]_z &= (-1)(5) + (1)(3) + (4)(-2) = -10 \end{aligned}$$

$$\begin{aligned} b. \quad [\mathbf{v} \cdot \boldsymbol{\tau}]_x &= (5)(3) + (3)(2) + (-2)(-1) = 23 \\ [\mathbf{v} \cdot \boldsymbol{\tau}]_y &= (5)(2) + (3)(2) + (-2)(1) = 14 \\ [\mathbf{v} \cdot \boldsymbol{\tau}]_z &= (5)(-1) + (3)(1) + (-2)(4) = -10 \end{aligned}$$

Note that these results are the same as those in part (a). Normally  $[\boldsymbol{\tau} \cdot \mathbf{v}] \neq [\mathbf{v} \cdot \boldsymbol{\tau}]$ , but since  $\boldsymbol{\tau}$  is symmetric, the two operations give identical results.

$$c. \quad (\boldsymbol{\tau} : \boldsymbol{\tau}) = \sum_i \sum_j \tau_{ij} \tau_{ji} = \sum_i \sum_j \tau_{ij}^2$$

since  $\boldsymbol{\tau}$  is symmetric. Then

$$\begin{aligned} (\boldsymbol{\tau} : \boldsymbol{\tau}) &= (3)^2 + (2)^2 + (-1)^2 + (2)^2 + (2)^2 + (1)^2 \\ &\quad + (-1)^2 + (1)^2 + (4)^2 = 41 \end{aligned}$$

$$\begin{aligned} d. \quad (\mathbf{v} \cdot [\boldsymbol{\tau} \cdot \mathbf{v}]) &= \sum_i v_i [\boldsymbol{\tau} \cdot \mathbf{v}]_i \\ &= (5)(23) + (3)(14) + (-2)(-10) = 117 \end{aligned}$$

$$\begin{aligned} e. \quad \mathbf{v}\mathbf{v} &= \boldsymbol{\delta}_x \boldsymbol{\delta}_x (25) + \boldsymbol{\delta}_x \boldsymbol{\delta}_y (15) + \boldsymbol{\delta}_x \boldsymbol{\delta}_z (-10) \\ &\quad + \boldsymbol{\delta}_y \boldsymbol{\delta}_x (15) + \boldsymbol{\delta}_y \boldsymbol{\delta}_y (9) + \boldsymbol{\delta}_y \boldsymbol{\delta}_z (-6) \\ &\quad + \boldsymbol{\delta}_z \boldsymbol{\delta}_x (-10) + \boldsymbol{\delta}_z \boldsymbol{\delta}_y (-6) + \boldsymbol{\delta}_z \boldsymbol{\delta}_z (4) \end{aligned}$$

$$\begin{aligned} f. \quad [\boldsymbol{\tau} \cdot \boldsymbol{\delta}_x]_x &= (3)(1) + (2)(0) + (-1)(0) = 3 \\ [\boldsymbol{\tau} \cdot \boldsymbol{\delta}_x]_y &= (2)(1) + (2)(0) + (1)(0) = 2 \\ [\boldsymbol{\tau} \cdot \boldsymbol{\delta}_x]_z &= (-1)(1) + (1)(0) + (4)(0) = -1 \end{aligned}$$

Appendix A: p. 819, Ex. 2

$$a. \quad [[\delta_1 \delta_2 \cdot \delta_2] \times \delta_1] = [\delta_1 \times \delta_1] = 0$$

$$b. \quad (\delta : \delta_1 \delta_2) = \sum_m \sum_n \delta_{mn} \delta_{1n} \delta_{2m} = \sum_m \delta_{m1} \delta_{2m} = \delta_{12} = 0$$

$$c. \quad (\delta : \delta) = \sum_m \sum_n \delta_{mn} \delta_{nm} = \sum_m \delta_{mm} = 3$$

$$\begin{aligned} d. \quad \{\delta \cdot \delta\} &= \left\{ \left( \sum_m \sum_n \delta_m \delta_n \delta_{mn} \right) \cdot \left( \sum_p \sum_q \delta_p \delta_q \delta_{pq} \right) \right\} \\ &= \sum_m \sum_n \sum_p \sum_q \{ \delta_m \delta_n \cdot \delta_p \delta_q \} \delta_{mn} \delta_{pq} \\ &= \left( \sum_m \sum_n \sum_p \sum_q \delta_m \delta_q \delta_{mn} \delta_{np} \delta_{pq} \right) \\ &= \sum_m \sum_n \sum_p \sum_q \delta_m \delta_q \delta_{mn} \delta_{np} \delta_{pq} \\ &= \sum_m \sum_n \delta_m \delta_q \delta_{mq} = \delta \end{aligned}$$

This is just a special case of  $\{\delta \cdot \tau\} = \{\tau \cdot \delta\} = \tau$ . Note also Eq. A.3-20.

**Appendix A: p. 819, Ex. 3**

According to Eq. A.3-14

$$(\boldsymbol{\alpha}:\boldsymbol{\beta}) = \sum_m \sum_n \alpha_{mn} \beta_{nm}$$

Now we make use of the fact that  $\boldsymbol{\alpha}$  is symmetric:

$$(\boldsymbol{\alpha}:\boldsymbol{\beta}) = \frac{1}{2} \sum_m \sum_n (\alpha_{mn} + \alpha_{nm}) \beta_{nm} = \frac{1}{2} \sum_m \sum_n \alpha_{mn} \beta_{nm} + \frac{1}{2} \sum_m \sum_n \alpha_{nm} \beta_{nm}$$

In the second summation we now use the fact that  $\boldsymbol{\beta}$  is antisymmetric, so that

$$(\boldsymbol{\alpha}:\boldsymbol{\beta}) = \frac{1}{2} \sum_m \sum_n \alpha_{mn} \beta_{nm} - \frac{1}{2} \sum_m \sum_n \alpha_{nm} \beta_{mn}$$

Next, in the second summation we interchange the indices  $m$  and  $n$  to obtain

$$(\boldsymbol{\alpha}:\boldsymbol{\beta}) = \frac{1}{2} \sum_m \sum_n \alpha_{mn} \beta_{nm} - \frac{1}{2} \sum_m \sum_n \alpha_{mn} \beta_{nm} = 0$$

Alternatively, one can use the method of Example 5 on p. 815.

**Appendix A: p. 819, Ex. 4**

When the tensor  $\{\sigma \cdot \tau\}$  on the left side of Eq. A.3-17 is expanded in terms of its components, we have

$$\{\sigma \cdot \tau\} = \sum_i \sum_l \delta_i \delta_l \{\sigma \cdot \tau\}_{il}$$

But the last expression in Eq. A.3-17 is

$$\{\sigma \cdot \tau\} = \sum_i \sum_l \delta_i \delta_l \left( \sum_j \sigma_{ij} \tau_{jl} \right)$$

Then, equating the coefficients of  $\delta_i \delta_l$  in these two expressions, we get

$$\{\sigma \cdot \tau\}_{il} = \sum_j \sigma_{ij} \tau_{jl}$$

Appendix A: p. 819, Ex. 5

The total angular momentum of the rigid structure is

$$\mathbf{L} = \sum_{\nu} m_{\nu} [\mathbf{R}_{\nu} \times \mathbf{v}_{\nu}]$$

and the velocity of an individual particle is  $\mathbf{v}_{\nu} = [\mathbf{W} \times \mathbf{R}_{\nu}]$ . Hence the angular momentum is

$$\mathbf{L} = \sum_{\nu} m_{\nu} [\mathbf{R}_{\nu} \times [\mathbf{W} \times \mathbf{R}_{\nu}]] \equiv [\Phi \cdot \mathbf{W}]$$

in which  $\Phi$  is the second-order "moment of inertia" tensor. This form is chosen in order to be parallel to the linear-momentum expression  $\mathbf{p} = m\mathbf{v}$ .

We start by considering the  $i$ th component of the angular momentum, making use of the comment just after Eq. A.2-21 to write out the cross products explicitly:

$$\begin{aligned} L_i &= \sum_{\nu} \sum_j \sum_k \sum_m \sum_n m_{\nu} \epsilon_{ijk} R_{\nu j} \epsilon_{kmn} W_m R_{\nu n} \\ &= \sum_{\nu} \sum_j \sum_m \sum_n m_{\nu} (\delta_{im} \delta_{jn} - \delta_{jm} \delta_{in}) R_{\nu j} W_m R_{\nu n} \end{aligned}$$

To get the second line we have summed on  $k$  using Eq. A.2-7. Next we perform the summations on  $m$  and  $n$  to get

$$\begin{aligned} L_i &= \sum_{\nu} \sum_j m_{\nu} (R_{\nu j} W_i R_{\nu j} - R_{\nu j} W_j R_{\nu i}) = \sum_{\nu} m_{\nu} \sum_j (R_{\nu j} R_{\nu j} W_i - R_{\nu i} R_{\nu j} W_j) \\ &= \sum_{\nu} m_{\nu} (\mathbf{R}_{\nu} \cdot \mathbf{R}_{\nu}) W_i - \sum_{\nu} m_{\nu} [\mathbf{R}_{\nu} \mathbf{R}_{\nu} \cdot \mathbf{W}]_i \end{aligned}$$

The second form is a rearrangement of the first form, enabling us to use the rule that a dot indicates a sum on adjacent indices (see top of p. 823). Then in the third form we have introduced the dot-product notations of Eqs. A.2-20 and A.3-18.

Finally we write the last result as a vector equation

$$\mathbf{L} = \sum_{\nu} m_{\nu} (\mathbf{R}_{\nu} \cdot \mathbf{R}_{\nu}) \mathbf{W} - \sum_{\nu} m_{\nu} [\mathbf{R}_{\nu} \mathbf{R}_{\nu} \cdot \mathbf{W}]$$

This is very close to the form that we are seeking, but the first term on the right will have to be written as a tensor dotted into a vector, in order to match up with the second term. We do this by making use of Eq. A.3-20 to write

$$\begin{aligned} \mathbf{L} &= \sum_v m_v (\mathbf{R}_v \cdot \mathbf{R}_v) [\boldsymbol{\delta} \cdot \mathbf{W}] - \sum_v m_v [\mathbf{R}_v \mathbf{R}_v \cdot \mathbf{W}] \\ &= \sum_v m_v \left[ \{ (\mathbf{R}_v \cdot \mathbf{R}_v) \boldsymbol{\delta} - \mathbf{R}_v \mathbf{R}_v \} \cdot \mathbf{W} \right] \end{aligned}$$

This equation gives the relation between the angular momentum and the moment-of-inertia tensor. Since the moment-of-inertia tensor is not isotropic, the angular momentum and the angular velocity are not pointing in the same direction.

We finally get for the moment-of-inertia tensor:

$$\Phi = \sum_v m_v \{ (\mathbf{R}_v \cdot \mathbf{R}_v) \boldsymbol{\delta} - \mathbf{R}_v \mathbf{R}_v \}$$

This is a good illustration of how the operator tensor-dot-vector arises naturally in a mechanics problem.



**Appendix A: p. 819, Ex. 6**

The expression for the kinetic energy can be written as follows:

$$K = \sum_{\nu} \frac{1}{2} m_{\nu} (\dot{\mathbf{R}}_{\nu} \cdot \dot{\mathbf{R}}_{\nu}) = \sum_{\nu} \frac{1}{2} m_{\nu} ([\mathbf{W} \times \mathbf{R}_{\nu}] \cdot [\mathbf{W} \times \mathbf{R}_{\nu}])$$

$$= \sum_{\nu} \frac{1}{2} m_{\nu} \sum_i [\mathbf{W} \times \mathbf{R}_{\nu}]_i [\mathbf{W} \times \mathbf{R}_{\nu}]_i$$

Next we expand the cross products using the statement just after Eq. A.2-21 to get

$$K = \sum_{\nu} \frac{1}{2} m_{\nu} \sum_i \left[ \sum_j \sum_k \epsilon_{ijk} W_j R_{\nu k} \right] \left[ \sum_m \sum_n \epsilon_{imn} W_m R_{\nu n} \right]$$

$$= \sum_{\nu} \frac{1}{2} m_{\nu} \sum_j \sum_k \sum_m \sum_n \left( \sum_i \epsilon_{ijk} \epsilon_{imn} \right) R_{\nu k} R_{\nu n} W_j W_m$$

Application of Eq. A.2-7 then gives

$$K = \sum_{\nu} \frac{1}{2} m_{\nu} \sum_j \sum_k \sum_m \sum_n (\delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}) R_{\nu k} R_{\nu n} W_j W_m$$

$$= \sum_{\nu} \frac{1}{2} m_{\nu} \sum_j \sum_k (R_{\nu k} R_{\nu k} W_j W_j - R_{\nu k} R_{\nu j} W_j W_k)$$

$$= \sum_{\nu} \frac{1}{2} m_{\nu} [(\mathbf{R}_{\nu} \cdot \mathbf{R}_{\nu})(\mathbf{W} \cdot \mathbf{W}) - (\mathbf{R}_{\nu} \mathbf{R}_{\nu} : \mathbf{W} \mathbf{W})]$$

Here we have used the rule that a dot indicates the sum on adjacent indices. Next we note that  $(\mathbf{W} \cdot \mathbf{W}) = (\boldsymbol{\delta} : \mathbf{W} \mathbf{W})$ , so that

$$K = \sum_{\nu} \frac{1}{2} m_{\nu} \left( \{(\mathbf{R}_{\nu} \cdot \mathbf{R}_{\nu}) \boldsymbol{\delta} - (\mathbf{R}_{\nu} \mathbf{R}_{\nu})\} : \mathbf{W} \mathbf{W} \right) = \frac{1}{2} (\boldsymbol{\Phi} : \mathbf{W} \mathbf{W})$$

Thus the result has been written in terms of the moment-of-inertia tensor. This is the rigid-body analog of  $K = \frac{1}{2} m v^2$  for a single particle of mass  $m$ .

This exercise has shown how a double-dot product arises naturally in a mechanics problem.

Appendix A: p. 823, Ex. 1

First we expand the del operator and the vector  $\mathbf{v}$  in terms of their components to get

$$\nabla = \left( \delta_x \frac{\partial}{\partial x} + \delta_y \frac{\partial}{\partial y} + \delta_z \frac{\partial}{\partial z} \right) \quad \mathbf{v} = v_x \delta_x + v_y \delta_y + v_z \delta_z$$

Then we multiply these two polynomial expressions (in the sense of taking the dot products term by term) to get

$$\begin{aligned} (\nabla \cdot \mathbf{v}) &= (\delta_x \cdot \delta_x) \frac{\partial v_x}{\partial x} + (\delta_x \cdot \delta_y) \frac{\partial v_y}{\partial x} + (\delta_x \cdot \delta_z) \frac{\partial v_z}{\partial x} \\ &\quad + (\delta_y \cdot \delta_x) \frac{\partial v_x}{\partial y} + (\delta_y \cdot \delta_y) \frac{\partial v_y}{\partial y} + (\delta_y \cdot \delta_z) \frac{\partial v_z}{\partial y} \\ &\quad + (\delta_z \cdot \delta_x) \frac{\partial v_x}{\partial z} + (\delta_z \cdot \delta_y) \frac{\partial v_y}{\partial z} + (\delta_z \cdot \delta_z) \frac{\partial v_z}{\partial z} \end{aligned}$$

Next we evaluate the dot products of the unit vectors, using Eqs. A.2-9 and 10

$$\begin{aligned} (\nabla \cdot \mathbf{v}) &= (1) \frac{\partial v_x}{\partial x} + (0) \frac{\partial v_y}{\partial x} + (0) \frac{\partial v_z}{\partial x} \\ &\quad + (0) \frac{\partial v_x}{\partial y} + (1) \frac{\partial v_y}{\partial y} + (0) \frac{\partial v_z}{\partial y} \\ &\quad + (0) \frac{\partial v_x}{\partial z} + (0) \frac{\partial v_y}{\partial z} + (1) \frac{\partial v_z}{\partial z} \end{aligned}$$

**Appendix A: p. 823, Ex. 2**

$$\begin{aligned} a. \quad [\nabla \times \mathbf{v}]_x &= 0 \\ [\nabla \times \mathbf{v}]_y &= 0 \\ [\nabla \times \mathbf{v}]_z &= -b \end{aligned}$$

Rotational

$$\begin{aligned} b \quad [\nabla \times \mathbf{v}]_x &= 0 \\ [\nabla \times \mathbf{v}]_y &= 0 \\ [\nabla \times \mathbf{v}]_z &= 0 \end{aligned}$$

Irrotational

$$\begin{aligned} c. \quad [\nabla \times \mathbf{v}]_x &= 0 \\ [\nabla \times \mathbf{v}]_y &= 0 \\ [\nabla \times \mathbf{v}]_z &= b - b = 0 \end{aligned}$$

Irrotational

$$\begin{aligned} c. \quad [\nabla \times \mathbf{v}]_x &= 0 \\ [\nabla \times \mathbf{v}]_y &= 0 \\ [\nabla \times \mathbf{v}]_z &= b + b = 2b \end{aligned}$$

Rotational

Appendix A: p. 823, Ex. 3

a.  $(\nabla \cdot \mathbf{v}) = 0$

$(\nabla \mathbf{v})_{xy} = b$  and all other component are zero

$$[\nabla \cdot \mathbf{vv}]_x = \frac{\partial}{\partial x} v_x v_x + \frac{\partial}{\partial y} v_y v_x + \frac{\partial}{\partial z} v_z v_x = 0$$

$$[\nabla \cdot \mathbf{vv}]_y = \frac{\partial}{\partial x} v_x v_y + \frac{\partial}{\partial y} v_y v_y + \frac{\partial}{\partial z} v_z v_y = 0$$

$$[\nabla \cdot \mathbf{vv}]_z = \frac{\partial}{\partial x} v_x v_z + \frac{\partial}{\partial y} v_y v_z + \frac{\partial}{\partial z} v_z v_z = 0$$

b.  $(\nabla \cdot \mathbf{v}) = b$

$(\nabla \mathbf{v})_{xx} = b$  and all other components are zero

$$[\nabla \cdot \mathbf{vv}]_x = \frac{\partial}{\partial x} v_x v_x + \frac{\partial}{\partial y} v_y v_x + \frac{\partial}{\partial z} v_z v_x = 2b^2 x$$

$$[\nabla \cdot \mathbf{vv}]_y = \frac{\partial}{\partial x} v_x v_y + \frac{\partial}{\partial y} v_y v_y + \frac{\partial}{\partial z} v_z v_y = 0$$

$$[\nabla \cdot \mathbf{vv}]_z = \frac{\partial}{\partial x} v_x v_z + \frac{\partial}{\partial y} v_y v_z + \frac{\partial}{\partial z} v_z v_z = 0$$

c.  $(\nabla \cdot \mathbf{v}) = 0$

$(\nabla \mathbf{v})_{xy} = b, (\nabla \mathbf{v})_{yx} = b$  and all others are zero

$$[\nabla \cdot \mathbf{vv}]_x = \frac{\partial}{\partial x} v_x v_x + \frac{\partial}{\partial y} v_y v_x + \frac{\partial}{\partial z} v_z v_x = b^2 x$$

$$[\nabla \cdot \mathbf{vv}]_y = \frac{\partial}{\partial x} v_x v_y + \frac{\partial}{\partial y} v_y v_y + \frac{\partial}{\partial z} v_z v_y = b^2 y$$

$$[\nabla \cdot \mathbf{vv}]_z = \frac{\partial}{\partial x} v_x v_z + \frac{\partial}{\partial y} v_y v_z + \frac{\partial}{\partial z} v_z v_z = 0$$

$$d. (\nabla \cdot \mathbf{v}) = 0$$

$$(\nabla \mathbf{v})_{xy} = -b, (\nabla \mathbf{v})_{yx} = b \quad \text{and all others are zero}$$

$$[\nabla \cdot \mathbf{v}\mathbf{v}]_x = \frac{\partial}{\partial x} v_x v_x + \frac{\partial}{\partial y} v_y v_x + \frac{\partial}{\partial z} v_z v_x = -b^2 x$$

$$[\nabla \cdot \mathbf{v}\mathbf{v}]_y = \frac{\partial}{\partial x} v_x v_y + \frac{\partial}{\partial y} v_y v_y + \frac{\partial}{\partial z} v_z v_y = -b^2 y$$

$$[\nabla \cdot \mathbf{v}\mathbf{v}]_z = \frac{\partial}{\partial x} v_x v_z + \frac{\partial}{\partial y} v_y v_z + \frac{\partial}{\partial z} v_z v_z = 0$$

Appendix A: p. 523, Ex. 4

$$a. \quad (\nabla \cdot [\boldsymbol{\alpha} \cdot \mathbf{r}]) = \sum_i \sum_j \frac{\partial}{\partial x_i} (\alpha_{ij} x_j) = \sum_i \sum_j \alpha_{ij} \delta_{ij} = \sum_i \alpha_{ii} = 0$$

$$b. \quad [\nabla \times [\boldsymbol{\alpha} \cdot \mathbf{r}]]_n = \sum_p \sum_q \varepsilon_{npq} \frac{\partial}{\partial x_p} \left( \sum_m \alpha_{qm} x_m \right) \\ = \sum_p \sum_q \sum_m \varepsilon_{npq} \alpha_{qm} \delta_{pm} = \sum_p \sum_q \varepsilon_{npq} \alpha_{qp} = 0$$

or  $[\nabla \times [\boldsymbol{\alpha} \cdot \mathbf{r}]] = 0$

$$c. \quad \{\nabla[\boldsymbol{\alpha} \cdot \mathbf{r}]\}_{pq} = \sum_n \frac{\partial}{\partial x_p} (\alpha_{qn} x_n) = \sum_n \alpha_{qn} \delta_{pn} = \alpha_{qp} = \alpha_{pq}$$

or  $\nabla[\boldsymbol{\alpha} \cdot \mathbf{r}] = \boldsymbol{\alpha}$

$$d. \quad \{\nabla[\boldsymbol{\alpha} \cdot \mathbf{r}]\}_{pq}^\dagger = \{\nabla[\boldsymbol{\alpha} \cdot \mathbf{r}]\}_{qp} = \alpha_{pq} = \alpha_{qp}$$

$$e. \quad [\nabla \cdot [\boldsymbol{\alpha} \cdot \mathbf{r}][\boldsymbol{\alpha} \cdot \mathbf{r}]]_n = \sum_p \sum_q \sum_m \frac{\partial}{\partial x_p} (\alpha_{pq} x_q \alpha_{nm} x_m) \\ = \sum_p \sum_q \sum_m \alpha_{nm} \alpha_{pq} (\delta_{pq} x_m + \delta_{pm} x_q) \\ = \sum_q \sum_m \alpha_{nm} \alpha_{qq} x_m + \sum_q \sum_m \alpha_{nm} \alpha_{mq} x_q \\ = 0 + [\{\boldsymbol{\alpha} \cdot \boldsymbol{\alpha}\} \cdot \mathbf{r}]_n$$

or  $[\nabla \cdot [\boldsymbol{\alpha} \cdot \mathbf{r}][\boldsymbol{\alpha} \cdot \mathbf{r}]] = [\{\boldsymbol{\alpha} \cdot \boldsymbol{\alpha}\} \cdot \mathbf{r}]$

**Appendix A: p. 823, Ex. 5**

a. First we write the expression on the left in component form:

$$\nabla^2(\nabla \cdot \mathbf{v}) = \sum_i \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_i} \left( \sum_j \frac{\partial}{\partial x_j} v_j \right) = \sum_i \sum_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} v_j$$

Then we interchange the order of differentiation to get

$$\nabla^2(\nabla \cdot \mathbf{v}) = \sum_i \sum_j \frac{\partial}{\partial x_j} \left( \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_i} v_j \right) = \sum_j \frac{\partial}{\partial x_j} (\nabla^2 \mathbf{v})_j = (\nabla \cdot \nabla^2 \mathbf{v})$$

b. We write the left side in component form, making use of the definition of the transpose given in Eq. A.3-8:

$$[\nabla \cdot (\nabla \mathbf{v})^\dagger] = \sum_i \sum_j \delta_j \frac{\partial}{\partial x_i} (\nabla \mathbf{v})_{ij}^\dagger = \sum_i \sum_j \delta_j \frac{\partial}{\partial x_i} (\nabla \mathbf{v})_{ji} = \sum_i \sum_j \delta_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} v_i$$

Then we change the order of differentiation to get

$$[\nabla \cdot (\nabla \mathbf{v})^\dagger] = \sum_i \sum_j \delta_j \frac{\partial}{\partial x_j} \left( \frac{\partial}{\partial x_i} v_i \right) = \sum_j \delta_j \frac{\partial}{\partial x_j} (\nabla \cdot \mathbf{v}) = \nabla(\nabla \cdot \mathbf{v})$$

where use has been made of Eq. A.4-6.

Appendix A: p. 823, Ex. 6

a. Proof that  $\text{div curl } \mathbf{v} = 0$

$$\begin{aligned}(\nabla \cdot [\nabla \times \mathbf{v}]) &= \sum_m \frac{\partial}{\partial x_m} [\nabla \times \mathbf{v}]_m \\ &= \sum_m \frac{\partial}{\partial x_m} \sum_p \sum_q \varepsilon_{mpq} \frac{\partial}{\partial x_p} v_q \\ &= \sum_m \sum_p \sum_q \varepsilon_{mpq} \frac{\partial^2 v_q}{\partial x_m \partial x_p} = 0\end{aligned}$$

Here we have the double sum on  $m$  and  $p$ , and in the summand we have the product of the permutation symbol (which is antisymmetric in the indices  $m$  and  $p$ ) and the second derivative operator (which is symmetric in the indices  $m$  and  $p$ ). We know that this sum will be zero (see Exercise 5 on p. 815).

b. Proof that  $\text{curl grad } s = 0$

$$[\nabla \times \nabla s]_m = \sum_n \sum_p \varepsilon_{mnp} \frac{\partial}{\partial x_n} \frac{\partial}{\partial x_p} s = 0$$

Here again we have a sum on two indices of a product of a quantity that is symmetric with respect to the same two indices and a quantity that is antisymmetric on these same two indices.



Appendix A: p. 823, Ex. 7

$$\begin{aligned}
 a. (\nabla \cdot \mathbf{r}) &= \left( \left\{ \sum_i \delta_i \frac{\partial}{\partial x_i} \right\} \cdot \left\{ \sum_j \delta_j x_j \right\} \right) = \sum_i \sum_j (\delta_i \cdot \delta_j) \frac{\partial}{\partial x_i} x_j \\
 &= \sum_i \sum_j (\delta_i \cdot \delta_j) \delta_{ij} = \sum_i (\delta_i \cdot \delta_i) = \sum_i 1 = 3
 \end{aligned}$$

$$\begin{aligned}
 b. [\nabla \times \mathbf{r}]_k &= \left[ \left\{ \sum_i \delta_i \frac{\partial}{\partial x_i} \right\} \times \left\{ \sum_j \delta_j x_j \right\} \right]_k \\
 &= \sum_i \sum_j [\delta_i \times \delta_j]_k \frac{\partial}{\partial x_i} x_j = \sum_i \sum_j \varepsilon_{kij} \frac{\partial}{\partial x_i} x_j = \sum_i \sum_j \varepsilon_{kij} \delta_{ij} = 0
 \end{aligned}$$

since the double sum on two indices (here  $i$  and  $j$ ) over the product of a quantity that is symmetrical in the two indices ( $\delta_{ij}$ ) and one that is antisymmetric in the same two indices ( $\varepsilon_{kij}$ ) is zero.

$$\begin{aligned}
 c. [\mathbf{r} \times [\nabla \cdot \mathbf{v}\mathbf{v}]]_i &= \sum_j \sum_k \varepsilon_{ijk} x_j [\nabla \cdot \mathbf{v}\mathbf{v}]_k = \sum_j \sum_k \varepsilon_{ijk} x_j \sum_n \frac{\partial}{\partial x_n} (v_n v_k) \\
 &= \sum_j \sum_k \varepsilon_{ijk} \left[ \sum_n \frac{\partial}{\partial x_n} (x_j v_n v_k) - \sum_n v_n v_k \frac{\partial}{\partial x_n} x_j \right] \\
 &= \sum_j \sum_k \sum_n \varepsilon_{ijk} \frac{\partial}{\partial x_n} (x_j v_n v_k) - \sum_j \sum_k \varepsilon_{ijk} v_j v_k \\
 &= \sum_n \frac{\partial}{\partial x_n} \left( v_n \sum_j \sum_k \varepsilon_{ijk} x_j v_k \right) = \sum_n \frac{\partial}{\partial x_n} (v_n [\mathbf{r} \times \mathbf{v}]_i) \\
 &= (\nabla \cdot \mathbf{v} [\mathbf{r} \times \mathbf{v}])_i = [\nabla \cdot \mathbf{v} [\mathbf{r} \times \mathbf{v}]]_i
 \end{aligned}$$

Therefore, since the component  $i$  was selected arbitrarily, the relation is true for all three components. As a consequence

$$[\mathbf{r} \times [\nabla \cdot \mathbf{v}\mathbf{v}]] = [\nabla \cdot \mathbf{v} [\mathbf{r} \times \mathbf{v}]]$$

**Appendix A: p. 823, Ex. 8**

First, we let  $\mathbf{sv} = \mathbf{w}$ , and then we write the  $i$ th component in expanded form:

$$\begin{aligned} [\nabla \times [\nabla \cdot \mathbf{vw}]]_i &= \sum_j \sum_k \epsilon_{ijk} \frac{\partial}{\partial x_j} [\nabla \cdot \mathbf{vw}]_k \\ &= \sum_j \sum_k \epsilon_{ijk} \frac{\partial}{\partial x_j} \left( \sum_n \frac{\partial}{\partial x_n} v_n w_k \right) \\ &= \sum_n \frac{\partial}{\partial x_n} \sum_j \sum_k \epsilon_{ijk} \frac{\partial}{\partial x_j} (w_k v_n) \\ &= \sum_n \frac{\partial}{\partial x_n} \{ \nabla \times \mathbf{vw} \}_{in} \\ &= \sum_n \frac{\partial}{\partial x_n} \{ \nabla \times \mathbf{vw} \}_{ni}^\dagger \\ &= \left[ \nabla \cdot \{ \nabla \times \mathbf{vw} \}^\dagger \right]_i \end{aligned}$$

The derivation was performed for the  $i$ th component only. Since the choice of  $i$  was arbitrary, the same result holds for all components. Therefore

$$[\nabla \times [\nabla \cdot \mathbf{svv}]] = \left[ \nabla \cdot \{ \nabla \times \mathbf{svv} \}^\dagger \right]$$

In this development we have made use of the statement after Eq A.3-19 about the components of  $\{\mathbf{v} \times \boldsymbol{\tau}\}$ .

**Appendix A: p. 823, Ex. 9**

a. First we write the left side of the equation in terms of the components and then differentiate term by term

$$\nabla \frac{1}{r} = \sum_i \delta_i \frac{\partial}{\partial x_i} \frac{1}{(\sum_k x_k^2)^{1/2}} = \sum_i \delta_i \left( -\frac{1}{2} \frac{2x_i}{(\sum_k x_k^2)^{3/2}} \right)$$

Then put the result back into the original notation to get

$$\nabla \frac{1}{r} = -\sum_i \delta_i \left( \frac{x_i}{r^3} \right) = -\frac{1}{r^3} \sum_i \delta_i x_i = -\frac{1}{r^3} \mathbf{r}$$

b. Write out the gradient operator, and then perform the differentiation

$$\begin{aligned} \nabla f(r) &= \sum_i \delta_i \frac{df(r)}{dx_i} = \sum_i \delta_i \frac{df}{dr} \left( \frac{\partial r}{\partial x_i} \right) \\ &= \sum_i \delta_i \frac{df}{dr} \left( \frac{\partial}{\partial x_i} (\sum_j x_j^2)^{1/2} \right) = \frac{df}{dr} \sum_i \delta_i \left( \frac{1}{2} \frac{2x_i}{(\sum_j x_j^2)^{1/2}} \right) \end{aligned}$$

Next we rewrite the result in the original notation

$$\nabla f(r) = \frac{df}{dr} \frac{\sum_i \delta_i x_i}{(\sum_j x_j^2)^{1/2}} = \frac{df}{dr} \frac{\mathbf{r}}{r}$$

c. We write the expression in component form and then perform the differentiation

$$\nabla(\mathbf{a} \cdot \mathbf{r}) = \sum_i \delta_i \frac{\partial}{\partial x_i} \left( \sum_j a_j x_j \right) = \sum_i \sum_j \delta_i a_j \frac{\partial x_j}{\partial x_i} = \sum_i \sum_j \delta_i a_j \delta_{ij} = \sum_i \delta_i a_i = \mathbf{a}$$

Appendix A: p. 824, Ex. 10

$$a. \quad \frac{\partial}{\partial t} \rho v_x = - \left( \frac{\partial}{\partial x} \rho v_x v_x + \frac{\partial}{\partial y} \rho v_y v_x + \frac{\partial}{\partial z} \rho v_z v_x \right) - \frac{\partial p}{\partial x} - \left( \frac{\partial}{\partial x} \tau_{xx} + \frac{\partial}{\partial y} \tau_{yx} + \frac{\partial}{\partial z} \tau_{zx} \right) + \rho g_x$$

$$\frac{\partial}{\partial t} \rho v_y = - \left( \frac{\partial}{\partial x} \rho v_x v_y + \frac{\partial}{\partial y} \rho v_y v_y + \frac{\partial}{\partial z} \rho v_z v_y \right) - \frac{\partial p}{\partial y} - \left( \frac{\partial}{\partial x} \tau_{xy} + \frac{\partial}{\partial y} \tau_{yy} + \frac{\partial}{\partial z} \tau_{zy} \right) + \rho g_y$$

$$\frac{\partial}{\partial t} \rho v_z = - \left( \frac{\partial}{\partial x} \rho v_x v_z + \frac{\partial}{\partial y} \rho v_y v_z + \frac{\partial}{\partial z} \rho v_z v_z \right) - \frac{\partial p}{\partial z} - \left( \frac{\partial}{\partial x} \tau_{xz} + \frac{\partial}{\partial y} \tau_{yz} + \frac{\partial}{\partial z} \tau_{zz} \right) + \rho g_z$$

b. The components are written out in full in Eqs. B.1-1 through B.1-7 on p. 843.

**Appendix A: p. 825, Ex. 1**

a The divergence of  $\mathbf{v}$  is given by

$$(\nabla \cdot \mathbf{v}) = \frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3} = \frac{\partial x_1}{\partial x_1} + \frac{\partial v_3}{\partial x_2} + \frac{\partial v_2}{\partial x_3} = 1$$

Then the integral of the divergence over the volume is

$$\int_0^4 \int_0^2 \int_0^1 (\nabla \cdot \mathbf{v}) dx dy dz = 8$$

b. There will be six surface integrals,  $I_k^\pm$ : the subscript  $k$  (= 1,2,3) gives the coordinate direction perpendicular to the face, and the superscript indicates the direction (positive or negative) in which the face is "looking."

$$I_1^- = \int_0^4 \int_0^2 (-\delta_x \cdot \mathbf{v})|_{x=0} dy dz = \int_0^4 \int_0^2 (-\delta_x \cdot \delta_x x)|_{x=0} dy dz = 0$$

$$I_1^+ = \int_0^4 \int_0^2 (\delta_x \cdot \mathbf{v})|_{x=1} dy dz = \int_0^4 \int_0^2 v_x|_{x=1} dy dz = 8$$

$$I_2^- = \int_0^1 \int_0^4 (-\delta_y \cdot \mathbf{v})|_{y=0} dz dx = -\int_0^1 \int_0^4 z dz dx = -8$$

$$I_2^+ = \int_0^1 \int_0^4 (\delta_y \cdot \mathbf{v})|_{y=2} dz dx = \int_0^1 \int_0^4 z dz dx = 8$$

$$I_3^- = \int_0^2 \int_0^1 (-\delta_z \cdot \mathbf{v})|_{z=0} dx dy = -\int_0^2 \int_0^1 y dx dy = -2$$

$$I_3^+ = \int_0^2 \int_0^1 (\delta_z \cdot \mathbf{v})|_{z=4} dx dy = \int_0^2 \int_0^1 y dx dy = 2$$

When we add up the individual surface integrals we get +8.

**Appendix A: p. 825, Ex. 2**

The surface integral on the left side is evaluated as follows:

$$\begin{aligned}\int (\mathbf{n} \cdot [\nabla \times \mathbf{v}]) dS &= \int_0^2 \int_0^4 (\boldsymbol{\delta}_x \cdot [\nabla \times \mathbf{v}]) dy dz \\ &= \int_0^2 \int_0^4 [\nabla \times \mathbf{v}]_x dy dz = \int_0^2 \int_0^4 \left( \frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z} \right) dy dz \\ &= \int_0^2 \int_0^4 \left( \frac{\partial y}{\partial y} - \frac{\partial z}{\partial z} \right) dy dz = \int_0^2 \int_0^4 (1 - 1) dy dz = 0\end{aligned}$$

The line integral has to be broken up into a sum of 4 integrals:

$$\begin{aligned}\oint (\mathbf{t} \cdot \mathbf{v}) dC &= \int_0^2 (\boldsymbol{\delta}_y \cdot \mathbf{v}) \Big|_{z=0}^{x=1} dy + \int_0^4 (\boldsymbol{\delta}_z \cdot \mathbf{v}) \Big|_{y=2}^{x=1} dz \\ &\quad + \int_0^2 (-\boldsymbol{\delta}_y \cdot \mathbf{v}) \Big|_{z=4}^{x=1} dy' + \int_0^4 (-\boldsymbol{\delta}_z \cdot \mathbf{v}) \Big|_{y=0}^{x=1} dz'\end{aligned}$$

The primes on  $y$  and  $z$  in the last two integrals are added to indicate that these are variables in the  $y$  and  $z$  directions, but taken in the positive direction on the curve  $C$ . The dot products with the unit vectors select the desired component of the vector  $\mathbf{v}$ . Therefore we get:

$$\begin{aligned}\oint (\mathbf{t} \cdot \mathbf{v}) dC &= \int_0^2 (z) \Big|_{z=0}^{x=1} dy + \int_0^4 (y) \Big|_{y=2}^{x=1} dz + \int_0^2 (-z) \Big|_{z=4}^{x=1} dy' + \int_0^4 (-y) \Big|_{y=0}^{x=1} dz' \\ &= 0 + 2 \int_0^4 dz - 4 \int_0^2 dy' + 0 = 0\end{aligned}$$

Thus, Stokes' theorem is satisfied.

**Appendix A: p. 825, Ex. 3**

We begin by evaluating the integral on the left side of Eq. A.5-5:

$$\begin{aligned}\int_V s dV &= \int_0^{4t} \int_0^{2t} \int_0^t (x + y + zt) dx dy dz \\ &= \frac{1}{2} x^2 \Big|_0^t \cdot 8t^2 + \frac{1}{2} y^2 \Big|_0^{2t} \cdot 4t^2 + t \cdot \frac{1}{2} z^2 \Big|_0^{4t} \cdot 2t^2 \\ &= 4t^4 + 8t^4 + 16t^5 = 12t^4 + 16t^5\end{aligned}$$

Then the left side of Eq. A.5-5 is:

$$\frac{d}{dt} \int_V s dV = 48t^3 + 80t^4$$

The volume integral on the right side of Eq. A.5-5 is:

$$\int_V \frac{\partial s}{\partial t} dV = \int_0^{4t} \int_0^{2t} \int_0^t z dx dy dz = (t)(2t) \left( \frac{1}{2} z^2 \Big|_0^{2t} \right) = 16t^4$$

The surface integral on the right side of Eq. A.5-5 has to be written as the sum of 6 integrals, over the six faces of the expanding solid. However, since three of the surfaces ( $x = 0$ ,  $y = 0$ , and  $z = 0$ ) are not moving, those faces do not need to be considered. The three surface integrals are then evaluated one by one:

$$\begin{aligned}\int_{S_x} s(\mathbf{v}_s \cdot \mathbf{n}) dS &= \int_0^{4t} \int_0^{2t} (x + y + zt) \Big|_{x=t} dy dz \\ &= (t)(2t)(4t) + \left( \frac{1}{2} (2t)^2 \right) (4t) + (t)(2t) \left( \frac{1}{2} (4t)^2 \right) \\ &= 16t^3 + 16t^4\end{aligned}$$

$$\begin{aligned}\int_{S_y} s(\mathbf{v}_s \cdot \mathbf{n}) dS &= 2 \int_0^{4t} \int_0^t (x + y + zt) \Big|_{y=2t} dx dz \\ &= 2 \left[ \left( \frac{1}{2} t^2 \right) (4t) + (2t)(t)(4t) + (t) \left( \frac{1}{2} (4t)^2 \right) (t) \right] \\ &= 20t^3 + 16t^4\end{aligned}$$

$$\begin{aligned}
 \int_{S_z} s(\mathbf{v}_s \cdot \mathbf{n}) dS &= 4 \int_0^{2t} \int_0^t (x + y + zt) \Big|_{z=4t} dx dy \\
 &= 4 \left[ \left( \frac{1}{2} t^2 \right) (2t) + \left( \frac{1}{2} (2t)^2 \right) (t) + (4t^2) (t) (2t) \right] \\
 &= 12t^3 + 32t^4
 \end{aligned}$$

When these surface integrals are summed we get

$$\int_S s(\mathbf{v}_s \cdot \mathbf{n}) dS = 48t^3 + 64t^4$$

Then the complete right side of Eq. A.5-5 becomes

$$\int_V \frac{\partial s}{\partial t} dV + \int_S s(\mathbf{v}_s \cdot \mathbf{n}) dS = (16t^4) + (48t^3 + 64t^4) = 48t^3 + 80t^4$$

in agreement with the expression obtained from the left side.



**Appendix A: p. 825, Ex. 4**

The tensor analog of Eq. A.5-4 is

$$\int_S [\mathbf{n} \cdot \{\nabla \times \boldsymbol{\tau}\}] dS = \oint_C [\mathbf{t} \cdot \boldsymbol{\tau}] dC$$

We now simplify the integrand in the surface integral on the left side, for the particular choice of  $\boldsymbol{\tau}$  indicated:

$$\begin{aligned} [\mathbf{n} \cdot \{\nabla \times \boldsymbol{\tau}\}]_k &= \sum_l \sum_i \sum_j n_l \epsilon_{ijl} \frac{\partial}{\partial x_i} \tau_{jk} \\ &= \sum_l \sum_i \sum_j n_l \epsilon_{ijl} \frac{\partial}{\partial x_i} \left( \sum_m \epsilon_{kmj} x_m \right) \\ &= \sum_l \sum_i \sum_j \sum_m n_l \epsilon_{ijl} \epsilon_{kmj} \delta_{im} \\ &= \sum_l \sum_i \sum_j n_l \epsilon_{ijl} \epsilon_{kij} \\ &= \sum_l n_l (2\delta_{kl}) = 2n_k \end{aligned}$$

In going from the 4th line to the 5th line we have made use of Eq. A.2-6--one of the properties of the permutation symbols.

Now we simplify, for the specific choice of  $\boldsymbol{\tau}$  indicated, the integrand on the right side:

$$[\mathbf{t} \cdot \boldsymbol{\tau}]_k = \sum_j t_j \tau_{jk} = \sum_j \sum_m t_j \epsilon_{kmj} x_m = \sum_j \sum_m \epsilon_{kmj} x_m t_j = \sum_j \sum_m \epsilon_{kmj} x_m t_j = [\mathbf{r} \times \mathbf{t}]_k$$

Therefore

$$2 \int_S \mathbf{n} dS = \oint_C [\mathbf{r} \times \mathbf{t}] dC$$

which is the desired result.

**Appendix A: p. 825, Ex. 5**

First we evaluate the volume integral ( $I$ ) on the left side of Eq. A.5-2:

$$I = \int_{-2}^{+2} \int_0^1 \int_0^{3-3y} (2x\delta_x + 2y\delta_y + 2z\delta_z) dz dy dx$$

The integral over the first term ( $I_x$ ) will be zero, since the integrand is odd in  $x$  and the interval over which the integration occurs is even. The integrals ( $I_y$  and  $I_z$ ) over the second and third terms are obtained as follows:

$$\begin{aligned} I_y &= 2\delta_y \int_{-2}^{+2} \int_0^1 \int_0^{3-3y} y dz dy dx = 8\delta_y \int_0^1 \int_0^{3-3y} y dz dy = 8\delta_y \int_0^1 y(3-3y) dy \\ &= 24\delta_y \left( \frac{1}{2}y^2 - \frac{1}{3}y^3 \right) \Big|_0^1 = 4\delta_y \end{aligned}$$

$$\begin{aligned} I_z &= 2\delta_z \int_{-2}^{+2} \int_0^1 \int_0^{3-3y} z dz dy dx = 4\delta_z \int_0^1 (z^2) \Big|_0^{3-3y} dy \\ &= 36\delta_z \int_0^1 (1-2y+y^2) dy = 12\delta_z \end{aligned}$$

Hence the volume integral is

$$I = 4\delta_y + 12\delta_z.$$

Next we evaluate the surface integral ( $J$ ) on the right side of Eq. A.5-2. First we evaluate the integral ( $J_x$ ) over the triangular surfaces at the ends:

$$J_x = \delta_x \int_0^1 \int_0^{3-3y} s \Big|_{x=+2} dz dy - \delta_x \int_0^1 \int_0^{3-3y} s \Big|_{x=-2} dz dy = 0$$

since  $s \Big|_{x=+2} = s \Big|_{x=-2}$ . Next we evaluate the integrals  $J_y$  and  $J_z$ , over the surfaces at  $y=0$  and  $z=0$ :

$$\begin{aligned} J_y &= -\delta_y \int_{-2}^{+2} \int_0^3 s \Big|_{y=0} dz dx = -\delta_y \int_{-2}^{+2} \int_0^3 (x^2 + z^2) dz dx = -\delta_y \int_{-2}^{+2} \left( x^2 z + \frac{1}{3} z^3 \right) \Big|_0^3 dx \\ &= -\delta_y \int_{-2}^{+2} (3x^2 + 9) dx = -\delta_y (16 + 36) = -52\delta_y \end{aligned}$$

$$\begin{aligned}
 J_z &= -\delta_z \int_{-2}^{+2} \int_0^1 s|_{z=0} dy dx = -\delta_z \int_{-2}^{+2} \int_0^1 (x^2 + y^2) dy dx = -\delta_z \int_{-2}^{+2} \left( x^2 y + \frac{1}{3} y^3 \right) \Big|_0^1 dx \\
 &= -\delta_z \int_{-2}^{+2} \left( x^2 + \frac{1}{3} \right) dx = -\frac{20}{3} \delta_z
 \end{aligned}$$

Finally we get the contribution  $J_s$  of the "slanting surface," which is described by the equation  $F(x, y, z) = 3 - 3y - z = 0$ . The outwardly directed normal unit vector is then

$$\mathbf{n} = \pm \frac{\nabla F}{|\nabla F|} = \pm \frac{-3\delta_y - \delta_z}{\sqrt{9+1}} = \frac{3\delta_y + \delta_z}{\sqrt{10}}$$

and

$$\begin{aligned}
 \mathbf{n} s|_{\text{surface}} &= \frac{3\delta_y + \delta_z}{\sqrt{10}} (x^2 + y^2 + z^2) \Big|_{z=3-3y} \\
 &= \frac{3\delta_y + \delta_z}{\sqrt{10}} (x^2 + 10y^2 - 18y + 9)
 \end{aligned}$$

The contribution of the slanting surface to the surface integral is then obtained by integrating over the slanting surface (or equivalently over the projection of the slanting surface onto the  $xy$ -plane and then multiplying by the appropriate factor) to get

$$\begin{aligned}
 J_s &= \int_S \mathbf{n} s dS = \sqrt{10} \int_{-2}^{+2} \int_0^1 \left( \frac{3\delta_y + \delta_z}{\sqrt{10}} \right) (x^2 + 10y^2 - 18y + 9) dy dx \\
 &= (3\delta_y + \delta_z) \int_{-2}^{+2} \left( x^2 y + \frac{10}{3} y^3 - 9y^2 + 9y \right) \Big|_0^1 dx \\
 &= \int_{-2}^{+2} \left( x^2 + \frac{10}{3} \right) dx = (3\delta_y + \delta_z) \left( \frac{1}{3} x^3 + \frac{10}{3} x \right) \Big|_{-2}^{+2} \\
 &= 56\delta_y + \frac{56}{3} \delta_z
 \end{aligned}$$

Thus the surface integral is

$$J = J_x + J_y + J_z + J_s = 0\delta_x - 52\delta_y - \frac{20}{3}\delta_z + 56\delta_y + \frac{56}{3}\delta_z = 4\delta_y + 12\delta_z$$

in agreement with the expression for the volume integral.

**Appendix A: p. 828, Ex. 1**

a. We rewrite the integral by using Eq. A.6-10

$$\begin{aligned} \int_0^{2\pi} \int_0^\pi \delta_r \sin \theta d\theta d\phi &= \int_0^{2\pi} \int_0^\pi (\delta_x \sin \theta \cos \phi + \delta_y \sin \theta \sin \phi + \delta_z \cos \theta) \sin \theta d\theta d\phi \\ &= \delta_x \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi + \delta_y \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \sin \phi d\phi \\ &\quad + \delta_z \int_0^\pi \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The  $\phi$ -integrals in the first two terms are zero, and the  $\theta$ -integral in the last term is zero. Note that the unit vectors in Cartesian coordinates can be taken out of the integrals, since they do not depend on the position in space.

The problem may also be solved by noting that for every value of  $\theta$  and  $\phi$ , there is another pair of  $\theta$  and  $\phi$  values for which  $\delta_r$  points in the opposite direction. Therefore the integral over the top half of the sphere will just cancel the integral over the bottom half of the sphere.

b. This problem may be solved by the same method used in (a), that is, by writing out the expression for  $\delta_r$  and evaluating all the integrals that appear. This is very tedious.

We can do the problem by another method that is much easier. One has to realize in advance that the integral will be isotropic, inasmuch as there is nothing in the integral that depends on the orientation in space. Recognizing this we may state then that

$$\int_0^{2\pi} \int_0^\pi \delta_r \delta_r \sin \theta d\theta d\phi = A\delta$$

That is, the integral will be some scalar constant  $A$  multiplied by the unit tensor. Now we take the trace of the above expression to get

$$\int_0^{2\pi} \int_0^\pi (\delta_r \cdot \delta_r) \sin \theta d\theta d\phi = 3A \quad \text{or} \quad \int_0^{2\pi} \int_0^\pi \sin \theta d\theta d\phi = 3A$$

The left side is then  $4\pi$ , and  $A = \frac{4}{3}\pi$ .

**Appendix A: p. 828, Ex. 2**

The unit tensor is defined in Eq. A.3-10. If we perform one of the summations we get:

$$\delta = \sum_i \delta_i \delta_i = \delta_x \delta_x + \delta_y \delta_y + \delta_z \delta_z$$

To convert this expression to spherical coordinates, we use Eqs. A.6-31 to 33. It is convenient to use the following abbreviations:  $S = \sin \theta$ ,  $C = \cos \theta$ ,  $s = \sin \phi$ , and  $c = \cos \phi$ .

$$\begin{aligned} \delta = & (Sc\delta_r + Cc\delta_\theta - s\delta_\phi)(Sc\delta_r + Cc\delta_\theta - s\delta_\phi) \\ & + (Ss\delta_r + Cs\delta_\theta + c\delta_\phi)(Ss\delta_r + Cs\delta_\theta + c\delta_\phi) \\ & + (C\delta_r - S\delta_\theta)(C\delta_r - S\delta_\theta) \end{aligned}$$

Next we collect the terms with the same dyadic coefficients:

$$\begin{aligned} \delta = & \delta_r \delta_r (S^2 c^2 + S^2 s^2 + C^2) + \delta_\theta \delta_\theta (C^2 c^2 + C^2 s^2 + S^2) + \delta_\phi \delta_\phi (s^2 + c^2) \\ & + (\delta_r \delta_\theta + \delta_\theta \delta_r)(SCc^2 + SCs^2 - SC) \\ & + (\delta_\theta \delta_\phi + \delta_\phi \delta_\theta)(-Csc + Csc) \\ & + (\delta_\phi \delta_r + \delta_r \delta_\phi)(-Ssc + Ssc) \end{aligned}$$

Then standard trigonometric formulas can be used to get the final result:

$$\delta = \delta_r \delta_r + \delta_\theta \delta_\theta + \delta_\phi \delta_\phi$$

**Appendix A: p. 839, Ex. 1**

a. We start with the expression for the position vector in cylindrical coordinates (see the caption of Fig. A.6-1):

$$\mathbf{r} = r\boldsymbol{\delta}_r + z\boldsymbol{\delta}_z$$

As the particle moves,  $r$ ,  $z$ , and  $\boldsymbol{\delta}_r$  change with time, but  $\boldsymbol{\delta}_z$  does not. Hence, from Eqs. A.6-10 to 12 we can obtain the time derivative as follows:

$$\begin{aligned} \frac{d}{dt}\boldsymbol{\delta}_r &= \frac{d}{dt}(\boldsymbol{\delta}_x \cos \theta + \boldsymbol{\delta}_y \sin \theta) \\ &= \boldsymbol{\delta}_x \left( \frac{d}{d\theta} \cos \theta \right) \left( \frac{d\theta}{dt} \right) + \boldsymbol{\delta}_y \left( \frac{d}{d\theta} \sin \theta \right) \left( \frac{d\theta}{dt} \right) \\ &= \boldsymbol{\delta}_x (-\sin \theta) \dot{\theta} + \boldsymbol{\delta}_y (\cos \theta) \dot{\theta} = \boldsymbol{\delta}_\theta \dot{\theta} \end{aligned}$$

In the last step, Eq. A.6-11 has been used. Then the time derivative of the position vector--that is, the velocity of the particle--is

$$\mathbf{v} = \frac{d}{dt}\mathbf{r} = \dot{r}\boldsymbol{\delta}_r + r\dot{\boldsymbol{\delta}}_r + \dot{z}\boldsymbol{\delta}_z = \boldsymbol{\delta}_r \dot{r} + \boldsymbol{\delta}_\theta r\dot{\theta} + \boldsymbol{\delta}_z \dot{z}$$

b. To get the particle acceleration, we have to differentiate the velocity with respect to the time. But  $\boldsymbol{\delta}_\theta$  has to be differentiated with respect to time, thus:

$$\frac{d}{dt}\boldsymbol{\delta}_\theta = \frac{d}{dt}(-\boldsymbol{\delta}_x \sin \theta + \boldsymbol{\delta}_y \cos \theta) = -\boldsymbol{\delta}_x (\cos \theta) \dot{\theta} - \boldsymbol{\delta}_y (\sin \theta) \dot{\theta} = -\boldsymbol{\delta}_r \dot{\theta}$$

In the last step, Eq. A.6-10 has been used.

The particle acceleration can now be obtained:

$$\begin{aligned} \mathbf{a} &= \frac{d}{dt}\mathbf{v} = \dot{\boldsymbol{\delta}}_r \dot{r} + \boldsymbol{\delta}_r \ddot{r} + \dot{\boldsymbol{\delta}}_\theta r\dot{\theta} + \boldsymbol{\delta}_\theta \dot{r}\dot{\theta} + \boldsymbol{\delta}_\theta r\ddot{\theta} + \boldsymbol{\delta}_z \ddot{z} \\ &= (\boldsymbol{\delta}_\theta \dot{\theta}) \dot{r} + \boldsymbol{\delta}_r \ddot{r} + (-\boldsymbol{\delta}_r \dot{\theta}) r\dot{\theta} + \boldsymbol{\delta}_\theta \dot{r}\dot{\theta} + \boldsymbol{\delta}_\theta r\ddot{\theta} + \boldsymbol{\delta}_z \ddot{z} \\ &= \boldsymbol{\delta}_r (\ddot{r} - r\dot{\theta}^2) + \boldsymbol{\delta}_\theta (r\ddot{\theta} + 2\dot{r}\dot{\theta}) + \boldsymbol{\delta}_z \ddot{z} \end{aligned}$$

Appendix A: p. 839, Ex. 2

a.  $(\nabla \cdot \mathbf{v})$  in spherical coordinates

$$\begin{aligned}
 (\nabla \cdot \mathbf{v}) &= \left( \left\{ \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right\} \cdot \{ \delta_r v_r + \delta_\theta v_\theta + \delta_\phi v_\phi \} \right) \\
 &= \left( \delta_r \frac{\partial}{\partial r} \cdot \delta_r v_r \right) + \left( \delta_r \frac{\partial}{\partial r} \cdot \delta_\theta v_\theta \right) + \left( \delta_r \frac{\partial}{\partial r} \cdot \delta_\phi v_\phi \right) \\
 &+ \left( \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \delta_r v_r \right) + \left( \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \delta_\theta v_\theta \right) + \left( \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \delta_\phi v_\phi \right) \\
 &+ \left( \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \cdot \delta_r v_r \right) + \left( \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \cdot \delta_\theta v_\theta \right) + \left( \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \cdot \delta_\phi v_\phi \right) \\
 &= (\delta_r \cdot \delta_r) \frac{\partial v_r}{\partial r} + (\delta_r \cdot \delta_\theta) \frac{\partial v_\theta}{\partial r} + (\delta_r \cdot \delta_\phi) \frac{\partial v_\phi}{\partial r} \\
 &+ (\delta_\theta \cdot \delta_r) \frac{1}{r} \frac{\partial v_r}{\partial \theta} + (\delta_\theta \cdot \delta_\theta) \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + (\delta_\theta \cdot \delta_\phi) \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} \\
 &\quad + (\delta_\theta \cdot \delta_\theta) \frac{v_r}{r} - (\delta_\theta \cdot \delta_r) \frac{v_\theta}{r} \\
 &+ (\delta_\phi \cdot \delta_r) \frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} + (\delta_\phi \cdot \delta_\theta) \frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} + (\delta_\phi \cdot \delta_\phi) \frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} \\
 &\quad + (\delta_\phi \cdot \delta_\phi) \frac{v_r}{r} + (\delta_\phi \cdot \delta_\phi) \frac{v_\theta \cos \theta}{r \sin \theta} \\
 &\quad + (\delta_\phi \cdot (-\delta_r \sin \theta + \delta_\theta \cos \theta)) \frac{v_\phi}{r \sin \theta} \\
 &= \frac{\partial v_r}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} + \frac{v_r}{r} + \frac{v_\theta \cos \theta}{r \sin \theta}
 \end{aligned}$$

This can easily be shown to be the same as Eq. (A) of Table A.7-3, which is more suitable for use in solving many problems.

b.  $(\nabla \times \mathbf{v})$  in spherical coordinates

$$[\nabla \times \mathbf{v}] = \left[ \left\{ \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right\} \times \{ \delta_r v_r + \delta_\theta v_\theta + \delta_\phi v_\phi \} \right]$$

$$\begin{aligned}
&= \left[ \delta_r \frac{\partial}{\partial r} \times \delta_r v_r \right] + \left[ \delta_r \frac{\partial}{\partial r} \times \delta_\theta v_\theta \right] + \left[ \delta_r \frac{\partial}{\partial r} \times \delta_\phi v_\phi \right] \\
&+ \left[ \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \times \delta_r v_r \right] + \left[ \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \times \delta_\theta v_\theta \right] + \left[ \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \times \delta_\phi v_\phi \right] \\
&+ \left[ \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \times \delta_r v_r \right] + \left[ \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \times \delta_\theta v_\theta \right] + \left[ \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \times \delta_\phi v_\phi \right] \\
&= \delta_\phi \frac{\partial v_\theta}{\partial r} - \delta_\theta \frac{\partial v_\phi}{\partial r} - \delta_\phi \frac{1}{r} \frac{\partial v_r}{\partial \theta} + \delta_r \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} + \delta_\theta \frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \delta_r \frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} \\
&\quad + \delta_\phi \frac{v_\theta}{r} - \delta_\theta \frac{v_\phi}{r} + \delta_r \frac{v_\theta \cos \theta}{r \sin \theta} \\
&= \delta_r \left( \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} - \frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} + \frac{v_\phi \cos \theta}{r \sin \theta} \right) + \delta_\theta \left( \frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} \right) \\
&\quad + \delta_\phi \left( \frac{\partial v_\theta}{\partial r} - \frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_\theta}{r} \right)
\end{aligned}$$

The components of this expression can be rearranged to give Eqs. (G), (H), and (I) of Table A.7-3.

c.  $\nabla \mathbf{v}$  in spherical coordinates

$$\begin{aligned}
\nabla \mathbf{v} &= \left\{ \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right\} \left\{ \delta_r v_r + \delta_\theta v_\theta + \delta_\phi v_\phi \right\} \\
&= \delta_r \frac{\partial}{\partial r} (\delta_r v_r) + \delta_r \frac{\partial}{\partial r} (\delta_\theta v_\theta) + \delta_r \frac{\partial}{\partial r} (\delta_\phi v_\phi) \\
&+ \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} (\delta_r v_r) + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} (\delta_\theta v_\theta) + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} (\delta_\phi v_\phi) \\
&+ \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (\delta_r v_r) + \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (\delta_\theta v_\theta) + \delta_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (\delta_\phi v_\phi) \\
&= \delta_r \delta_r \frac{\partial v_r}{\partial r} + \delta_r \delta_\theta \frac{\partial v_\theta}{\partial r} + \delta_r \delta_\phi \frac{\partial v_\phi}{\partial r} \\
&+ \delta_\theta \delta_r \frac{1}{r} \frac{\partial v_r}{\partial \theta} + \delta_\theta \delta_\theta \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \delta_\theta \delta_\phi \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} + \delta_\theta \delta_\theta \frac{v_r}{r} - \delta_\theta \delta_r \frac{v_\theta}{r}
\end{aligned}$$



$$\begin{aligned}
& +\delta_\phi\delta_r\frac{1}{r\sin\theta}\frac{\partial v_r}{\partial\phi} + \delta_\phi\delta_\theta\frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial\phi} + \delta_\phi\delta_\phi\frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial\phi} \\
& \quad + \delta_\phi\delta_\phi\frac{v_r}{r} + \delta_\phi\delta_\phi\frac{v_\theta}{r} - \delta_\phi\delta_r\frac{v_\phi}{r} - \delta_\phi\delta_\theta\frac{v_\phi\cos\theta}{r\sin\theta} \\
& = \delta_r\delta_r\frac{\partial v_r}{\partial r} + \delta_r\delta_\theta\frac{\partial v_\theta}{\partial r} + \delta_r\delta_\phi\frac{\partial v_\phi}{\partial r} \\
& + \delta_\theta\delta_r\left(\frac{1}{r}\frac{\partial v_r}{\partial\theta} - \frac{v_\theta}{r}\right) + \delta_\theta\delta_\theta\left(\frac{1}{r}\frac{\partial v_\theta}{\partial\theta} + \frac{v_\theta}{r}\right) + \delta_\theta\delta_\phi\frac{1}{r}\frac{\partial v_\phi}{\partial\theta} \\
& + \delta_\phi\delta_r\left(\frac{1}{r\sin\theta}\frac{\partial v_r}{\partial\phi} - \frac{v_\phi}{r}\right) + \delta_\phi\delta_\theta\left(\frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial\phi} - \frac{v_\phi\cos\theta}{r\sin\theta}\right) \\
& \quad + \delta_\phi\delta_\phi\left(\frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial\phi} + \frac{v_r}{r} + \frac{v_\theta\cos\theta}{r\sin\theta}\right)
\end{aligned}$$

The components of this expression agree with Eqs. (S) to (AA) in Table A.7-3.

d.  $[\nabla \cdot \boldsymbol{\tau}]$  in cylindrical coordinates

$$\begin{aligned}
[\nabla \cdot \boldsymbol{\tau}] &= \left[ \left\{ \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_z \frac{\partial}{\partial z} \right\} \cdot \left\{ \delta_r \delta_r \tau_{rr} + \delta_r \delta_\theta \tau_{r\theta} + \dots \right\} \right] \\
&= \delta_r \left( \frac{\partial \tau_{rr}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta r}}{\partial \theta} + \frac{\partial \tau_{zr}}{\partial z} \right) \\
&+ \delta_\theta \left( \frac{\partial \tau_{r\theta}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{z\theta}}{\partial z} \right) \\
&+ \delta_z \left( \frac{\partial \tau_{rz}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right) \\
&\quad + \frac{\tau_{rr}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_r \delta_r \right] + \frac{\tau_{r\theta}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_r \delta_\theta \right] + \frac{\tau_{rz}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_r \delta_z \right] \\
&\quad + \frac{\tau_{\theta r}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_\theta \delta_r \right] + \frac{\tau_{\theta\theta}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_\theta \delta_\theta \right] + \frac{\tau_{\theta z}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_\theta \delta_z \right] \\
&\quad + \frac{\tau_{zr}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_z \delta_r \right] + \frac{\tau_{z\theta}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_z \delta_\theta \right] + \frac{\tau_{zz}}{r} \left[ \delta_\theta \frac{\partial}{\partial \theta} \cdot \delta_z \delta_z \right]
\end{aligned}$$

That is, we first differentiate the components of the tensor, and then we indicate the differentiation of the unit dyads. Next we actually perform the differentiation of the unit dyads:

$$\begin{aligned}
 [\nabla \cdot \boldsymbol{\tau}] = & \delta_r \left( \frac{\partial \tau_{rr}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta r}}{\partial \theta} + \frac{\partial \tau_{zr}}{\partial z} \right) \\
 & + \delta_\theta \left( \frac{\partial \tau_{r\theta}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{z\theta}}{\partial z} \right) \\
 & + \delta_z \left( \frac{\partial \tau_{rz}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right) \\
 & + \delta_r \frac{\tau_{rr}}{r} + \delta_\theta \frac{\tau_{r\theta}}{r} + \delta_z \frac{\tau_{rz}}{r} + \delta_\theta \frac{\tau_{\theta r}}{r}
 \end{aligned}$$

Next we collect the terms that belong to each unit vector to get:

$$\begin{aligned}
 [\nabla \cdot \boldsymbol{\tau}] = & \delta_r \left( \frac{\partial \tau_{rr}}{\partial r} + \frac{\tau_{rr}}{r} + \frac{1}{r} \frac{\partial \tau_{\theta r}}{\partial \theta} + \frac{\partial \tau_{zr}}{\partial z} \right) \\
 & + \delta_\theta \left( \frac{\partial \tau_{r\theta}}{\partial r} + \frac{\tau_{r\theta}}{r} + \frac{\tau_{\theta r}}{r} + \frac{1}{r} \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{z\theta}}{\partial z} \right) \\
 & + \delta_z \left( \frac{\partial \tau_{rz}}{\partial r} + \frac{\tau_{rz}}{r} + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right)
 \end{aligned}$$

The components of this vector can now be put into the form shown in Eqs. (J), (K), and (L) of Table A.7-2.

Appendix A: p. 839, Ex. 3

a. From Eq. (A) with  $\mathbf{v}$  replaced by  $\rho\mathbf{v}$

$$(\nabla \cdot \rho\mathbf{v}) = \frac{1}{r} \frac{\partial}{\partial r} (r\rho v_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho v_\theta) + \frac{\partial}{\partial z} (\rho v_z)$$

b. From Eq. (J) with  $\boldsymbol{\tau}$  replaced by  $\rho\mathbf{v}\mathbf{v}$

$$[\nabla \cdot \rho\mathbf{v}\mathbf{v}]_r = \frac{1}{r} \frac{\partial}{\partial r} (r\rho v_r^2) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho v_\theta v_r) + \frac{\partial}{\partial z} (\rho v_z v_r) - \frac{\rho v_\theta^2}{r}$$

c. From Eq. (J) with  $\boldsymbol{\tau}$  replaced by  $p\boldsymbol{\delta}$

$$[\nabla \cdot p\boldsymbol{\delta}]_r = \frac{1}{r} \frac{\partial}{\partial r} (rp) - \frac{1}{r} = \frac{\partial p}{\partial r} \quad (\text{see also Eq. A.4-26})$$

d. From Eq (A) with  $\mathbf{v}$  replaced by  $[\boldsymbol{\tau} \cdot \mathbf{v}]$

$$\begin{aligned} (\nabla \cdot [\boldsymbol{\tau} \cdot \mathbf{v}]) &= \frac{1}{r} \frac{\partial}{\partial r} (r[\tau_{rr}v_r + \tau_{r\theta}v_\theta + \tau_{rz}v_z]) \\ &\quad + \frac{1}{r} \frac{\partial}{\partial \theta} [\tau_{\theta r}v_r + \tau_{\theta\theta}v_\theta + \tau_{\theta z}v_z] \\ &\quad + \frac{\partial}{\partial z} [\tau_{zr}v_r + \tau_{z\theta}v_\theta + \tau_{zz}v_z] \end{aligned}$$

e. From Eq. (Q) with  $\mathbf{w}$  replaced by  $\mathbf{v}$

$$[\mathbf{v} \cdot \nabla \mathbf{v}]_\theta = v_r \left( \frac{\partial v_\theta}{\partial r} \right) + v_\theta \left( \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) + v_z \left( \frac{\partial v_\theta}{\partial z} \right)$$

f. From Eqs. (S) to (AA)

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{rr} = 2 \left( \frac{\partial v_r}{\partial r} \right)$$

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{\theta\theta} = 2 \left( \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right)$$

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{zz} = 2 \left( \frac{\partial v_z}{\partial z} \right)$$

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{r\theta} = [\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{\theta r} = \left( \frac{\partial v_\theta}{\partial r} + \frac{1}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_r}{r} \right)$$

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{\theta z} = [\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{z\theta} = \left( \frac{1}{r} \frac{\partial v_z}{\partial \theta} + \frac{\partial v_\theta}{\partial z} \right)$$

$$[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{zr} = [\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger]_{rz} = \left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right)$$

**Appendix A: p. 839, Ex. 4**

a. We develop the Laplace operator from the definition of the del-operator as follows:

$$\begin{aligned}
 (\nabla \cdot \nabla) &= \left( \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_z \frac{\partial}{\partial z} \right) \cdot \left( \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_z \frac{\partial}{\partial z} \right) \\
 &= \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \\
 &= \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}
 \end{aligned}$$

The second term in the second line arises from differentiating  $\delta_r$  with respect to  $\theta$ . The result agrees with Eq. A.7-36.

Next we apply this operator to the vector  $\mathbf{v}$  thus:

$$\nabla^2 \mathbf{v} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \mathbf{v} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \mathbf{v} + \frac{\partial^2}{\partial z^2} \mathbf{v}$$

To do this, we operate on the three terms seriatim:

$$\begin{aligned}
 &\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} [\delta_r v_r + \delta_\theta v_\theta + \delta_z v_z] \right) \\
 &= \delta_r \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_r}{\partial r} \right) + \delta_\theta \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_\theta}{\partial r} \right) + \delta_z \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) \\
 &\frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} [\delta_r v_r + \delta_\theta v_\theta + \delta_z v_z] \\
 &= \frac{1}{r^2} \frac{\partial}{\partial \theta} \left[ \delta_\theta v_r + \delta_r \frac{\partial v_r}{\partial \theta} - \delta_r v_\theta + \delta_\theta \frac{\partial v_\theta}{\partial \theta} + \delta_z \frac{\partial v_z}{\partial \theta} \right] \\
 &= \frac{1}{r^2} \left[ -\delta_r v_r + \delta_\theta \frac{\partial v_r}{\partial \theta} + \delta_\theta \frac{\partial v_r}{\partial \theta} + \delta_r \frac{\partial^2 v_r}{\partial \theta^2} - \delta_\theta v_\theta - \delta_r \frac{\partial v_\theta}{\partial \theta} \right. \\
 &\quad \left. - \delta_r \frac{\partial v_\theta}{\partial \theta} + \delta_\theta \frac{\partial^2 v_\theta}{\partial \theta^2} + \delta_z \frac{\partial^2 v_z}{\partial \theta^2} \right] \\
 &\left[ \delta_r \left( -v_r + \frac{\partial^2 v_r}{\partial \theta^2} - 2 \frac{\partial v_\theta}{\partial \theta} \right) + \delta_\theta \left( -v_\theta + 2 \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial \theta^2} \right) \right]
 \end{aligned}$$

$$\left. + \delta_z \frac{\partial^2 v_z}{\partial \theta^2} \right]$$

$$\frac{\partial^2}{\partial z^2} [\delta_r v_r + \delta_\theta v_\theta + \delta_z v_z] = \delta_r \frac{\partial^2 v_r}{\partial z^2} + \delta_\theta \frac{\partial^2 v_\theta}{\partial z^2} + \delta_z \frac{\partial^2 v_z}{\partial z^2}$$

Next we collect all the terms of the three components of  $\nabla^2 \mathbf{v}$ :

$$\begin{aligned} [\nabla^2 \mathbf{v}]_r &= \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_r}{\partial r} \right) + \frac{1}{r^2} \left( -v_r + \frac{\partial^2 v_r}{\partial \theta^2} - 2 \frac{\partial v_\theta}{\partial \theta} \right) + \frac{\partial^2 v_r}{\partial z^2} \\ &= \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (r v_r) \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial^2 v_r}{\partial z^2} \end{aligned}$$

$$\begin{aligned} [\nabla^2 \mathbf{v}]_\theta &= \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_\theta}{\partial r} \right) + \frac{1}{r^2} \left( -v_\theta + 2 \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial \theta^2} \right) + \frac{\partial^2 v_\theta}{\partial z^2} \\ &= \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right) + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2} \end{aligned}$$

$$[\nabla^2 \mathbf{v}]_z = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2}$$

These results should be compared with Eqs. (M), (N), and (O) of Table A.7-2.

b. Use Eqs. (J), (K), and (L) together with Eqs. (S) to (AA) for the components of the velocity gradient tensor to get the same results as given above in (a).

c. Use gradient operations of Eqs. (D), (E), and (F), the divergence operation of Eq. (A), and the curl operations of Eqs. (G), (H), and (I) together with Eq. A.7-37 to get the results in (a).