
A HEAT TRANSFER TEXTBOOK

SIXTH EDITION

SOLUTIONS MANUAL FOR CHAPTER 11

by

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PROBLEM 11.1 Derive eqns. (11.9).

SOLUTION Using eqns. (11.2,4,6,8):

$$m_i = \frac{\rho_i}{\rho} = \frac{c_i M_i}{c M} = \frac{x_i M_i}{\sum_k x_k M_k}$$
$$x_i = \frac{c_i}{c} = \frac{\rho_i M}{\rho M_i} = \frac{m_i/M_i}{\sum_k m_k/M_k}$$

PROBLEM 11.2 A 1000 liter cylinder at 300 K contains a gaseous mixture composed of 0.10 kmol of NH_3 , 0.04 kmol of CO_2 , and 0.06 kmol of He. (a) Find the mass fraction for each species and the pressure in the cylinder. (b) After the cylinder is heated to 600 K, what are the new mole fractions, mass fractions, and molar concentrations? (c) The cylinder is now compressed isothermally to a volume of 600 liters. What are the molar concentrations, mass fractions, and partial densities? (d) If 0.40 kg of N_2 is injected into the cylinder while the temperature remains at 600 K, find the mole fractions, mass fractions, and molar concentrations.

SOLUTION

a) By eqn. (11.6), noting that the total number of moles is $0.1 + 0.04 + 0.06 = 0.2$ kmol,

$$x_{\text{NH}_3} = 0.1/0.2 = 0.5$$
$$x_{\text{CO}_2} = 0.04/0.2 = 0.2$$
$$x_{\text{He}} = 0.06/0.2 = 0.3$$

and with eqn. (11.8)

$$M = (0.5)(17.03) + (0.2)(44.01) + (0.3)(4.003) = 18.52 \text{ kg/kmol}$$

Thus, from eqn. (11.9)

$$m_{\text{NH}_3} = (0.5)(17.03)/(18.52) = 0.460$$
$$m_{\text{CO}_2} = (0.2)(44.01)/(18.52) = 0.475$$
$$m_{\text{He}} = (0.3)(4.003)/(18.52) = 0.0648$$

The pressure, from eqn. (11.13), is

$$p = cR^\circ T = (0.2 \text{ kmol/m}^3)(8314.5 \text{ J/kmol}\cdot\text{K})(300 \text{ K})$$
$$= 4.99 \times 10^5 \text{ Pa}$$

b) The mass fractions are unchanged. The total pressure, like the temperature, is doubled, $p = 2(4.99 \times 10^5) = 9.98 \times 10^5 \text{ Pa}$. Then, with eqn. (11.15),

$$p_{\text{NH}_3} = (0.5)(9.98 \times 10^5) = 4.99 \times 10^5 \text{ Pa}$$
$$p_{\text{CO}_2} = (0.2)(9.98 \times 10^5) = 2.00 \times 10^5 \text{ Pa}$$
$$p_{\text{He}} = (0.3)(9.98 \times 10^5) = 2.99 \times 10^5 \text{ Pa}$$

c) The mass fractions are still unchanged. The molar concentrations are

$$\begin{aligned}c_{\text{NH}_3} &= 0.1 \text{ kmol}/0.6 \text{ m}^3 = 0.167 \text{ kmol/m}^3 \\c_{\text{CO}_2} &= 0.04 \text{ kmol}/0.6 \text{ m}^3 = 0.0667 \text{ kmol/m}^3 \\c_{\text{He}} &= 0.06 \text{ kmol}/0.6 \text{ m}^3 = 0.100 \text{ kmol/m}^3\end{aligned}$$

From eqn. (11.4), the partial densities are

$$\begin{aligned}\rho_{\text{NH}_3} &= (0.167)(17.03) = 2.84 \text{ kg/m}^3 \\ \rho_{\text{CO}_2} &= (0.0667)(44.01) = 2.94 \text{ kg/m}^3 \\ \rho_{\text{He}} &= (0.100)(4.003) = 0.400 \text{ kg/m}^3\end{aligned}$$

d) We have added $(0.4 \text{ kg})/(28.01 \text{ kg/kmol}) = 0.0143 \text{ kmol N}_2$.

$$\begin{aligned}x_{\text{NH}_3} &= 0.1/0.2143 = 0.467 \\ x_{\text{CO}_2} &= 0.04/0.2143 = 0.187 \\ x_{\text{He}} &= 0.06/0.2143 = 0.280 \\ x_{\text{N}_2} &= 0.0143/0.2143 = 0.0667\end{aligned}$$

The molar mass of the mixture is

$$\begin{aligned}M &= (0.467)(17.03) + (0.187)(44.01) + (0.280)(4.003) + (0.0667)(28.01) \\ &= 19.17 \text{ kg/kmol}\end{aligned}$$

Thus,

$$\begin{aligned}m_{\text{NH}_3} &= (0.467)(17.03)/(19.17) = 0.415 \\ m_{\text{CO}_2} &= (0.187)(44.01)/(19.17) = 0.429 \\ m_{\text{He}} &= (0.280)(4.003)/(19.17) = 0.0585 \\ m_{\text{N}_2} &= (0.0667)(28.01)/(19.17) = 0.0975\end{aligned}$$

The molar concentrations calculated in part (c) are unchanged. For N_2 :

$$c_{\text{He}} = 0.0143 \text{ kmol}/0.6 \text{ m}^3 = 0.0238 \text{ kmol/m}^3$$

PROBLEM 11.3 The pressure of Jupiter's atmosphere increases with depth. The famous clouds of Jupiter are in a layer called the troposphere, in which the pressure rises from 0.1 bar to 10 bar. The top of the troposphere, called the tropopause, is about 50 km above the clouds and is at 0.1 bar and 110 K. The atmospheric mole fractions of hydrogen, helium, and methane are $x_{\text{H}_2} = 0.86$, $x_{\text{He}} = 0.136$, and $x_{\text{CH}_4} = 0.0018$. Other species have small but localized concentrations, e.g., in the troposphere's clouds of ammonia ice. (a) Calculate the molar concentrations and the partial densities of H_2 , He , and CH_4 at the tropopause. (b) Find the number of hydrogen atoms per unit volume (number density), \mathcal{N}_{H_2} at the tropopause.

(c) Estimate \mathcal{N}_{H_2} at the base of the Jovian troposphere, where the pressure is 10 bar and the temperature is 340 K.

SOLUTION

(a) From eqn. (11.13)

$$c = \frac{p}{R^\circ T} = \frac{0.1 \times 10^5 \text{ Pa}}{(8314.5 \text{ J/kmol}\cdot\text{K})(110 \text{ K})} = 0.01093 \text{ kmol/m}^3$$

and with $x_i = c_i/c$,

$$c_{\text{H}_2} = (0.86)(0.01093) = 0.00940 \text{ kmol/m}^3 = 9.40 \text{ mol/m}^3$$

$$c_{\text{He}} = (0.136)(0.01093) = 0.00149 \text{ kmol/m}^3 = 1.49 \text{ mol/m}^3$$

$$c_{\text{CH}_4} = (0.0018)(0.01093) = 0.0000197 \text{ kmol/m}^3 = 0.0197 \text{ mol/m}^3$$

With eqn. (11.4),

$$\rho_i = M_i c_i$$

and molar concentrations in kmol/m³

$$\rho_{\text{H}_2} = (2.016)(0.00940) = 0.0190 \text{ kg/m}^3$$

$$\rho_{\text{He}} = (4.003)(0.00149) = 0.00596 \text{ kg/m}^3$$

$$\rho_{\text{CH}_4} = (16.04)(0.0000197) = 0.000316 \text{ kg/m}^3$$

where the molar masses, in kg/kmol, can be taken from Table 11.3 or elsewhere.

(b) The number of molecules of species i per unit volume is $N_A c_i$ where N_A is Avogadro's number. So, working in mol,

$$\begin{aligned} \mathcal{N}_{\text{H}_2} &= (6.0221 \times 10^{23} \text{ molecules/mol})(9.40 \text{ mol/m}^3) \\ &= 5.66 \times 10^{24} \text{ molecules/m}^3 \end{aligned}$$

(c) From eqn. (11.13),

$$c = \frac{p}{R^\circ T} = \frac{10 \times 10^5}{(8314.5)(340)} = 0.354 \text{ kmol/m}^3$$

If we estimate the mole fraction to be the same as for the upper atmosphere, and now working in kmol

$$\begin{aligned} \mathcal{N}_{\text{H}_2} &= N_A x_{\text{H}_2} c \\ &= (6.0221 \times 10^{26} \text{ molecules/kmol})(0.86)(0.354 \text{ kmol/m}^3) \\ &= 1.83 \times 10^{26} \text{ molecules/m}^3 \end{aligned}$$

Misc. facts about Jupiter's atmosphere: The atmosphere of Jupiter continues smoothly from the gas phase to a supercritical fluid phase as the pressure rises. Ammonia is present in the troposphere, and condenses to form clouds. Water is present deeper in the troposphere. Neon is dissolved into liquid helium and transported downward by helium rain. Photochemistry in the upper atmosphere can produce ethane and ethyne. Elements present in the upper atmosphere are fully reduced by combination with hydrogen. Convection in the troposphere transports some molecules vertically, giving rise to geographic patterns of molecular abundance.

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PROBLEM 11.4 In Example (11.2), suppose that the only gases at the s -surface are CO, O₂, and N₂. As before, assume that $m_{\text{O}_2,s}$ is very small. Find $j_{\text{N}_2,s}$, $n_{\text{N}_2,s}$, and $m_{\text{N}_2,s}$.

SOLUTION From eqn. (11.21)

$$\sum_i \vec{j}_i = 0 = j_{\text{CO},s} + j_{\text{O}_2,s} + j_{\text{N}_2,s}$$

$$j_{\text{N}_2,s} = -j_{\text{CO},s} - j_{\text{O}_2,s} = -45.7 + 26.7 = -19.0 \text{ g/m}^2\text{s} \quad \leftarrow \text{Answer}$$

No N₂ flows through the s -surface or reacts there, so $n_{\text{N}_2,s} = 0$. ← Answer

The diffusion flux of N₂ toward the wall simply opposes the mass-average velocity away from the wall. Therefore, with eqn. (11.20)

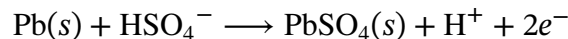
$$n_{\text{N}_2,s} = 0 = m_{\text{N}_2,s} n_s + j_{\text{N}_2,s}$$

$$m_{\text{N}_2,s} = -\frac{j_{\text{N}_2,s}}{n_s} = \frac{19.0}{20.0} = 0.95$$

Another way to get the same answer is with eqn. (11.3):

$$m_{\text{N}_2,s} = 1 - m_{\text{CO},s} - m_{\text{O}_2,s} = 1 - 0.05 - 0 = 0.95 \quad \leftarrow \text{Answer}$$

PROBLEM 11.5 Small automobile batteries commonly contain an aqueous solution of sulfuric acid (H₂SO₄) with lead and lead oxide plates as electrodes. Current is generated by the reaction of the electrolyte with the electrode material. The reaction at the lead electrode (the anode) is



where the (s) denotes a solid phase component. If the current density at such an electrode is $i = 5 \text{ mA/cm}^2$, what is the mole flux of HSO₄[−] (bisulfate) to the electrode? Recall that the

charge of an electron is -1.609×10^{-19} C and that $1 \text{ A} = 1 \text{ C/s}$. What is the mass flux of HSO_4^- ? At what mass rate is PbSO_4 produced? At what rate does H^+ flow away from the electrode?

SOLUTION Two electrons are released for each mole of bisulfate reaching the electrode, so we may write the current in terms of the mole flux of HSO_4^- through an s -surface just over the electrode:

$$i = 5 \text{ mA/cm}^2 = 2(1.609 \times 10^{-19} \text{ C})(6.0221 \times 10^{26} \text{ kmol/kg})(N_{\text{HSO}_4^-,s} \text{ kmol/m}^2\text{s})$$

Solving

$$\begin{aligned} N_{\text{HSO}_4^-,s} &= \frac{(5 \times 10^{-3}/10^{-4}) \text{ A/m}^2}{2(1.609 \times 10^{-19})(6.0221 \times 10^{26})} \\ &= 2.580 \times 10^{-7} \text{ kmol/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

The mass flux is just

$$\begin{aligned} n_{\text{HSO}_4^-,s} &= M_{\text{HSO}_4^-} N_{\text{HSO}_4^-,s} = (97.06 \text{ kg/kmol})(2.580 \times 10^{-7} \text{ kmol/m}^2\text{s}) \\ &= 2.504 \times 10^{-5} \text{ kg/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

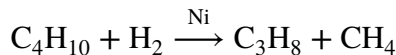
The electrode reaction creates one mole of PbSO_4 for each mole of HSO_4^- reaching the electrode, so

$$\begin{aligned} \dot{r}_{\text{PbSO}_4}'' &= M_{\text{PbSO}_4} N_{\text{HSO}_4^-,s} \\ &= (303.3 \text{ kg/kmol})(2.580 \times 10^{-7} \text{ kmol/m}^2\text{s}) \\ &= 7.825 \times 10^{-5} \text{ kg/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

H^+ ions flow away at the rate of one mole per mole of HSO_4^- , so

$$N_{\text{H}^+,s} = -N_{\text{HSO}_4^-,s} = -2.580 \times 10^{-7} \text{ kmol/m}^2\text{s} \quad \leftarrow \text{Answer}$$

PROBLEM 11.6 In catalysis, one gaseous species reacts with another on the surface of a catalyst to form a gaseous product. For example, butane (C_4H_{10}) reacts with hydrogen on the surface of a nickel catalyst to form propane (C_3H_8) and methane (CH_4). This heterogeneous reaction, referred to as hydrogenolysis, is



The molar rate of consumption of C_4H_{10} per unit area in the reaction is

$$\dot{R}_{\text{C}_4\text{H}_{10}} = A(e^{-\Delta E/R^\circ T}) p_{\text{C}_4\text{H}_{10}} p_{\text{H}_2}^{-2.4}$$

where $A = 2.9 \times 10^9 \text{ kmol/m}^2\text{s}$, $\Delta E = 1.9 \times 10^8 \text{ J/kmol}$, and p_i is in atm.

- If $p_{\text{C}_4\text{H}_{10},s} = p_{\text{C}_3\text{H}_8,s} = 0.2 \text{ atm}$, $p_{\text{CH}_4,s} = 0.17 \text{ atm}$, and $p_{\text{H}_2,s} = 0.3 \text{ atm}$ at a nickel surface with conditions of 440°C and 0.87 atm total pressure, what is the rate of consumption of butane?
- What are the mole fluxes of butane and hydrogen to the surface? What are the mass fluxes of propane and methane away from the surface?

- (c) What is $v_{C_4H_{10},s}$? What are v_s and v_s^* ?
 (d) What is the diffusional mole flux of butane? What is the diffusional mass flux of propane? What is the flux of Ni?

SOLUTION

(a)

$$\begin{aligned} \dot{R}_{C_4H_{10}} &= (2.9 \times 10^9) \exp\left[-\frac{1.9 \times 10^8}{(8314.5)(440 + 273.15)}\right] (0.2)(0.3)^{-2.4} \\ &= 1.27 \times 10^{-4} \text{ kmol/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

- (b) Let a negative flux be toward the surface and a positive flux be away from the surface. Then, from stoichiometry:

$$\dot{R}_{C_4H_{10}} = -N_{C_4H_{10}} = -N_{H_2,s} = +N_{C_3H_8,s} = +N_{CH_4,s} \quad \leftarrow \text{Answer}$$

The mass fluxes are $n_i = M_i N_i$. With $M_{C_3H_8} = 44.09 \text{ kg/kmol}$ and $M_{CH_4} = 16.04 \text{ kg/kmol}$, we find

$$\begin{aligned} n_{C_3H_8,s} &= (44.09)(1.27 \times 10^{-4}) = 5.58 \times 10^{-3} \text{ kg/m}^2\text{s} \\ &= 5.58 \text{ g/m}^2\text{s} \quad \leftarrow \text{Answer} \\ n_{CH_4,s} &= (16.04)(1.27 \times 10^{-4}) = 2.03 \times 10^{-3} \text{ kg/m}^2\text{s} \\ &= 2.03 \text{ g/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

- (c) With eqns. (11.17) and (11.4)

$$v_{C_4H_{10},s} = n_{C_4H_{10},s} / \rho_{C_4H_{10},s} = N_{C_4H_{10},s} / c_{C_4H_{10},s}$$

With eqn. (11.12)

$$c_{C_4H_{10},s} = \frac{p_{C_4H_{10},s}}{R^\circ T} = \frac{(0.2)(101325)}{(8314.5)(440 + 273.15)} = 3.418 \times 10^{-3} \text{ kmol/m}^3$$

so the species average speed, which is negative because it is toward the surface, is

$$v_{C_4H_{10},s} = \frac{-1.27 \times 10^{-4}}{3.418 \times 10^{-3}} = -0.00372 \text{ m/s} \quad \leftarrow \text{Answer}$$

No net mass flux occurs at the surface of the catalyst, so $v = v^* = 0$. $\leftarrow \text{Answer}$

- (d) Because $v = v^* = 0$, $n = N = 0$ and eqns. (11.20) and (11.24) show that the total and diffusional mass and mole fluxes are equal. Nickel is a catalyst and has no flux.

COMMENT: In these experiments, the catalyst material contained 5 wt% Ni and had a BET area of 240 m^2 per gram of catalyst. The reported reaction rates were given in $\text{mol h}^{-1} \text{ g}_{Ni}^{-1}$.

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PROBLEM 11.7 Show that $\mathcal{D}_{12} = \mathcal{D}_{21}$ in a binary mixture.

SOLUTION From eqn. (11.21), $\vec{j}_1 + \vec{j}_2 = 0$, and so, with eqn. (11.26)

$$\begin{aligned}\vec{j}_1 &= -\vec{j}_2 \\ -\rho\mathcal{D}_{12}\nabla m_1 &= +\rho\mathcal{D}_{21}\nabla m_2 \\ -\mathcal{D}_{12}\nabla m_1 &= \mathcal{D}_{21}\nabla m_2\end{aligned}$$

But with eqn. (11.3)

$$\nabla(m_1 + m_2) = \nabla(1) = 0$$

so $-\nabla m_1 = -\nabla m_2$. Substituting into the previous equation

$$\begin{aligned}-\mathcal{D}_{12}\nabla m_1 &= -\mathcal{D}_{21}\nabla m_1 \\ \mathcal{D}_{12} &= \mathcal{D}_{21} \quad \longleftarrow \text{Answer}\end{aligned}$$

PROBLEM 11.8 Using the definitions of the fluxes, velocities, and concentrations, derive eqn. (11.30) from eqn. (11.26) for binary diffusion.

SOLUTION From eqns. (11.26), (11.19), (11.30) and (11.23)

$$\begin{aligned}\vec{j}_1 &= -\rho\mathcal{D}_{12}\nabla m_1 = \rho_1(\vec{v}_1 - \vec{v}) & (*) \\ \vec{J}_1 &= -c\mathcal{D}_{12}\nabla x_1 = c_1(\vec{v}_1 - \vec{v}^*)\end{aligned}$$

With eqns. (11.16), (11.3), (11.22), and (11.7)

$$\begin{aligned}\vec{v}_1 - \vec{v} &= \vec{v}_1 - (m_1\vec{v}_1 + m_2\vec{v}_2) = m_2(\vec{v}_1 - \vec{v}_2) \\ \vec{v}_1 - \vec{v}^* &= \vec{v}_1 - (x_1\vec{v}_1 + x_2\vec{v}_2) = x_2(\vec{v}_1 - \vec{v}_2)\end{aligned}$$

Thus

$$\vec{J}_1 = c_1x_2(\vec{v}_1 - \vec{v}_2) = c_1(m_1M/M_2)(\vec{v}_1 - \vec{v}_2) = \frac{M}{M_1M_2}\vec{j}_1 \quad (\dagger)$$

where we also use eqn. (11.9).

Next, we need to express \vec{j}_1 in terms of ∇x_1 . With eqn. (11.8)

$$\begin{aligned}\nabla m_1 &= \nabla\left(\frac{x_1M_1}{M}\right) = \frac{M_1}{M}\nabla x_1 - \frac{x_1M_1}{M^2}\nabla M \\ &= \frac{M_1}{M}\nabla x_1 - \frac{x_1M_1}{M^2}(M_1\nabla x_1 + M_2\nabla x_2)\end{aligned}$$

and with $\nabla x_2 = -\nabla x_1$, $M = x_1M_1 + x_2M_2$, and $x_1 + x_2 = 1$

$$= \frac{M_1}{M^2}(M - x_1M_1 + x_1M_2)\nabla x_1 = \frac{M_1M_2}{M^2}\nabla x_1 \quad (**)$$

Hence, upon substituting eqns. (*) and (**) into eqn. (†), we find our result:

$$\begin{aligned}\vec{J}_1 &= \frac{M}{M_1 M_2} (-\rho \mathcal{D}_{12} \nabla m_1) \\ &= -c \mathcal{D}_{12} \left(\frac{M^2}{M_1 M_2} \frac{M_1 M_2}{M^2} \nabla x_1 \right) \\ &= -c \mathcal{D}_{12} \nabla x_1 \quad \leftarrow \text{Answer}\end{aligned}$$

PROBLEM 11.9 Fill in the details involved in obtaining eqn. (11.33) from eqn. (11.32).

SOLUTION

$$j_A \Big|_{x_0} = \eta \rho \bar{C} \left(m_A \Big|_{x_0 - a\ell} - m_A \Big|_{x_0 + a\ell} \right) \quad (11.32)$$

We may use a Taylor expansion of $m_A(x)$ about $x = x_0$:

$$m_A \Big|_{x_0 + a\ell} = m_A \Big|_{x_0} + \frac{dm_A}{dx} \Big|_{x_0} (x_0 + a\ell - x_0) + \dots$$

Likewise

$$m_A \Big|_{x_0 - a\ell} = m_A \Big|_{x_0} + \frac{dm_A}{dx} \Big|_{x_0} (x_0 - a\ell - x_0) + \dots$$

Substituting these into eqn. (11.32)

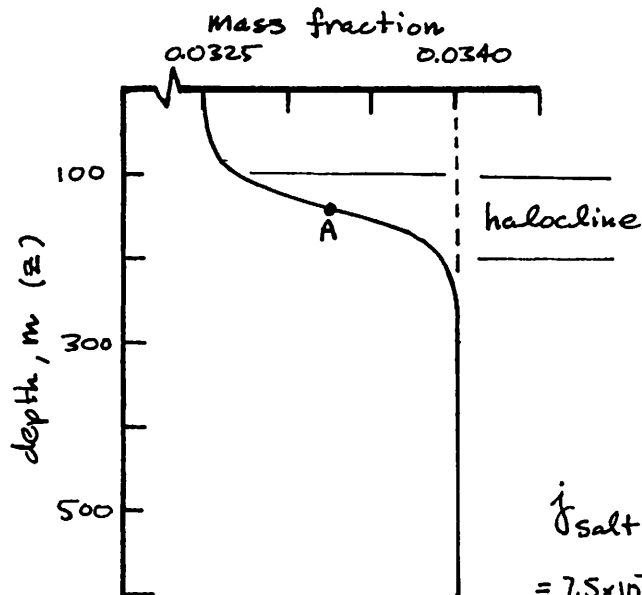
$$j_A \Big|_{x_0} = \eta \rho \bar{C} \left(-2 \frac{dm_A}{dx} \Big|_{x_0} (a\ell) \right)$$

which we can rearrange as

$$j_A \Big|_{x_0} = -\rho (2\eta a \bar{C} \ell) \frac{dm_A}{dx} \Big|_{x_0} \quad \leftarrow \text{Answer} \quad (11.33)$$

Comment: The second-order terms in the two Taylor series cancel out, so that the error in the expression for j_A is $\mathcal{O}(\ell^3)$.

- 11.10 The salt concentration in the ocean increases with increasing depth, z . A model for the concentration distribution in the upper ocean is $S = 33.25 + 0.75 \tanh(0.026z - 3.7)$ where S is the salinity in grams of salt per kg of ocean water and z is the distance below the surface in m. a.) Plot the mass fraction of salt as a function of z . (the region of rapid transition of $m_{\text{salt}}(z)$ is called the halocline.) b.) Ignoring the effects of oceanic motion, compute $j_{\text{salt}}(z)$. Use a value of $D_{\text{salt, water}} = 1.5 \times 10^{-5} \text{ cm}^2/\text{s}$. Indicate the position of maximum diffusion on your plot of the salt concentration. c.) The upper region of the ocean is well-mixed by wind-driven waves and turbulence while the lower region and halocline tend to be calmer. Using $j_{\text{salt}}(z)$ from b.), make a simple estimate of the amount of salt carried upward in one week in a 5 km^2 horizontal area of the sea.



(a) Salinity, $S = 1000 \times m_{\text{salt}}$

(b) Under this assumption, just differentiate $m_{\text{salt}}(z)$ and using Fick's Law, i.e. assume pure diffusion.

$$j_{\text{salt}}(z) = -\rho D_{12} \frac{d}{dz} m_{\text{salt}} = 7.5 \times 10^{-4} (0.026) \text{sech}^2(0.026z - 3.7) (-\rho D_{12})$$

The density of salt-water may be approximated as having a uniform value:

$$\rho = \rho + \rho_{\text{H}_2\text{O}} = \rho_{\text{H}_2\text{O}} \left(1 + \frac{m_{\text{salt}}}{1 + m_{\text{salt}}} \right) \approx \rho_{\text{H}_2\text{O}} (1 + m_{\text{salt}})$$

We make the additional approximation that the partial density, $\rho_{\text{H}_2\text{O}}$, is the same as the density of pure water $\approx 999 \text{ kg/m}^3$.

$$\text{so: } \rho \approx 999(1 + 0.03325) = \underline{1032 \text{ kg/m}^3}$$

$$\text{Then: } j_{\text{salt}}(z) = -3.02 \times 10 \frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \text{sech}^2(0.026z - 3.7)$$

The flux is vertically upward. The point of maximum j_{salt} is the maximum slope point of m_{salt} (pt. A): $0 = 0.026z_A - 3.7$

$$\underline{z_A = 142 \text{ m.}} \leftarrow$$

(c) The flat form of the salt concentration profile in the upper region may be attributed to turbulent mixing. (The fresher

water near the surface originates from rainfall and nearby land masses.) We may reason that salt diffuses slowly from lower water into the fresher water above at a rate given approximately by $j_{\text{salt, max}}$: transport is primarily diffusive at this level and the upward flux shouldn't exceed this value. Then:

$$\begin{aligned} \text{mass flow upward per 5 sq. km per week} &= j_{\text{max}} \cdot \text{sq. km} \cdot \text{1 wk} \\ &= (3.02 \times 10^{-11} \text{ kg/m}^2\text{s}) (1000 \text{ m})^2 (3600 \cdot 24 \cdot 7) 5 = \underline{91.3 \text{ kg}} \leftarrow \end{aligned}$$

This flux complicates oceanographic modeling.

- 11.11 Consider two chambers held at temperatures T_1 and T_2 , respectively, and joined by a small insulated tube. The chambers are filled with a binary gas mixture, with the tube open, and allowed to come to steady state. If the Soret effect is taken into account, what is the concentration difference between the two chambers? Assume an effective mean value of the thermal diffusion ratio is known.

In steady state, there is no mass flow between the chambers.

Assuming the tube is too small to allow convection (recirculation)

Eqn. (11.37) gives:

$$\bar{j}_1 = 0 = -\rho D_{12} \left[\frac{d}{dx} m_1 + \frac{M_1 M_2}{M^2} k_T \frac{d}{dx} \ln T \right]$$

so

$$\frac{dm_1}{dx} = -\frac{M_1 M_2}{M^2} k_T \frac{d}{dx} \ln T \quad \leftarrow \begin{array}{l} \text{integrate from } T_1 = T(x_1) \\ \text{to } T_2 = T(x_2) \end{array}$$

$$m_1(x_2) - m_1(x_1) = \frac{M_1 M_2}{M^2} \int_{x_1}^{x_2} k_T \frac{d \ln T}{dx} dx = \frac{M_1 M_2}{M^2} \bar{k}_T \ln \left(\frac{T_2}{T_1} \right)$$

for a mean value \bar{k}_T . The difference in concentration between the chambers is:

$$m_1(x_2) - m_1(x_1) = \frac{M_1 M_2}{M^2} \bar{k}_T \ln \left(\frac{T_2}{T_1} \right)$$

- 11.12 a.) Work Problem 6.36. b.) A fluid is said to be incompressible if the density of a fluid particle does not change as it moves about in the flow (i.e., if $D\rho/Dt = 0$). Show that an incompressible flow satisfies $\vec{\nabla} \cdot \vec{u} = 0$. c.) How does the condition of incompressibility differ from that of constant density? Describe a flow that is incompressible but which does not have "constant density."

(b) From Problem (6.36):

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = \left(\frac{\partial \rho}{\partial t} + \vec{u} \cdot \nabla \rho \right) + \rho \nabla \cdot \vec{u} = 0$$

or

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \vec{u} \quad \left\{ \begin{array}{l} \text{For an incompressible fluid, we clearly} \\ \text{have } \underline{\nabla \cdot \vec{u} = 0} \end{array} \right. \longleftarrow$$

(c) "Constant density" is generally taken to mean that ρ is spatially uniform and constant in time. Thus, all fluid particles would have the same density. In an incompressible flow each particle may have a different, but unchanging, density. Thus, the flow may have spatial gradients of density, i.e. it may be stratified. The most significant example of an incompressible, stratified fluid is the ocean, which is colder and saltier at greater depths and thus shows increasing density as one moves downward from the surface.

- 11.13 Carefully derive equation (11.44). Note that ρ is not assumed constant in (11.44).

Eqs. (11.40) and (11.42) give:

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla} \cdot \nabla \rho_i = -\nabla \cdot \vec{f}_i + \dot{r}_i \quad \left(\begin{array}{l} \text{2nd term in incompressible} \\ \text{form} \end{array} \right) \quad (*)$$

Introduce Fick's Law and assume ρD_{im} spatially uniform:

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla} \cdot \nabla \rho_i = -\nabla \cdot (-\rho D_{im} \nabla m_i) + \dot{r}_i = +\rho D_{im} \nabla^2 m_i + \dot{r}_i$$

Now: $\frac{D\rho_i}{Dt} = \rho \frac{Dm_i}{Dt} + m_i \frac{D\rho}{Dt} = \rho \frac{Dm_i}{Dt}$, for incompressible flow

Thus:

$$\boxed{\frac{Dm_i}{Dt} = D_{im} \nabla^2 m_i + \dot{r}_i / \rho_i} \quad \text{Eqn. (11.44)}$$

11.14 Derive the equation of species conservation on a molar basis, using c_i rather than p_i . Also obtain an equation in c_i alone, analogous to equation (11.44), but without introducing incompressibility. What assumptions must be made to obtain the latter result?

$$\begin{aligned} \frac{d}{dt} \int_R c_i dR &= - \int_S \vec{N}_i \cdot d\vec{S} + \int_R \dot{R}_i dR \quad (\dot{R}_i = \text{molar rate of} \\ &\quad \text{creation of species } i) \\ &\quad \text{kgmole/m}^3 \cdot \text{s} \\ &= - \int_S c_i \vec{v}^* \cdot d\vec{S} - \int_S \vec{J}_i^* \cdot d\vec{S} + \int_R \dot{R}_i dR \end{aligned}$$

using (11.24) and (11.22). On the first line, the first term is the rate of storage, the second is the rate of inflow, and the third the rate of creation of species i in the region R . By Gauss' theorem and the usual arguments, this leads to:

$$\boxed{\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \vec{v}^*) = -\nabla \cdot \vec{J}_i^* + \dot{R}_i} \quad \text{molar analog of}$$

Now use Fick's Law, $\vec{J}_i^* = -c_i D_{im} \nabla x_i$ and assume both c and D_{im} are independent of (x, y, z) . The boxed eqn becomes:

$$\boxed{\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \vec{v}^*) = D_{im} \nabla^2 c_i + \dot{R}_i} \quad \text{closest analog of}$$

The first two terms are not $\frac{D}{Dt}$. The eqn may be recast to give D/Dt , but the result is rather awkward.

- 11.15 Find the following concentrations: a) The mole fraction of air in solution with water at 50°C and 1 atm, exposed to air at the same conditions. $H = 4.88 \times 10^4$ atm. b.) The mole fraction of ammonia in air above an aqueous solution with $x_{\text{NH}_3} = 0.05$ at 0.9 atm. and 40°C, and $H = 1522$ mm Hg. c.) the mole fraction of SO_2 in an aqueous solution at 15°C and 1 atm., if $p_{\text{SO}_2} = 28.0$ mm Hg and $H = 1.42 \times 10^4$ mm Hg. d.) the partial pressure of ethylene over an aqueous solution at 25°C and 1 atm. with $x_{\text{C}_2\text{H}_4} = 1.75 \times 10^{-5}$ and $H = 11.4 \times 10^3$ atm.

(a) Under these conditions, the air is essentially dry and

$$p_{\text{air}} \approx 1 \text{ atm. Thus, } \chi_{\text{air}} = (1 \text{ atm}) / (4.88 \times 10^4 \text{ atm}) = \underline{2.05 \times 10^{-5}}$$

by Henry's Law, (11.46).

(b) From Henry's Law, $p_{\text{NH}_3} = (1522 \text{ mm Hg})(0.05) = 76.1 \text{ mm Hg.}$

The gas-side mole fraction is $\chi_{\text{NH}_3} = p_{\text{NH}_3} / 0.9 \text{ atm} = \underline{0.111}$

(c) Again use Henry's Law: $\chi_{\text{SO}_2} = p_{\text{SO}_2} / H = 28.0 / 1.42 \times 10^4 = \underline{1.97 \times 10^{-3}}$

(d) $p_{\text{C}_2\text{H}_4} = (11.4 \times 10^3 \text{ atm})(1.75 \times 10^{-5}) = \underline{0.200}$

- 11.16 Use a steam table to estimate: a.) The mass fraction of water vapor in air over water at 1 atm and 20°C, 50°C, 70°C, and 90°C. b.) The partial pressure of water over a 3 percent by weight aqueous solution of HCl at 50°C. c.) The boiling point at 1 atm of salt water with a mass fraction $m_{\text{NaCl}} = 0.18$.

(a) Using Raoult's law and the reasoning of example 11.3,

$p_{\text{H}_2\text{O},s} = p_{\text{sat},\text{H}_2\text{O}}(T_s)$. With a steam table, eqn. (11.15), (11.8), and (11.9), we have:

$T(^{\circ}\text{C})$	$p_{\text{sat}}(\text{kPa})$	$\chi_{\text{H}_2\text{O},s}$	$M_c \left(\frac{\text{kg}}{\text{kgmole}} \right)$	$M_{\text{H}_2\text{O},s}$
20	2.339	0.02308	28.71	0.01449
50	12.349	0.1219	27.63	0.07951
70	31.19	0.3078	25.59	0.2167
90	70.14	0.6922	21.39	0.5832

(b) $M_{\text{HCl}} = 36.46 \text{ kg/kgmole}$. By (11.8), with $m_{\text{HCl}} = 0.03$, $M_{\text{soln}} = 18.30$.

By (11.9), $\chi_{\text{H}_2\text{O},\text{soln}} = 0.0151$. Raoult's law then yields:

$$p_{\text{H}_2\text{O},s} = p_{\text{sat},\text{H}_2\text{O}} (1 - 0.0151) = (12.349 \text{ kPa})(0.9849) \\ = \underline{12.16 \text{ kPa}} \leftarrow$$

(c) $M_{\text{NaCl}} = 58.44 \text{ kg/kgmole}$. The molecular weight of the soln is 20.58 kg/kgmole , and $x_{\text{NaCl},\text{soln}} = 0.06340$. The solution's boiling point is the temperature at which $p_{\text{H}_2\text{O},s} = 1 \text{ atm}$:

$$101325 \text{ Pa} = p_{\text{sat},\text{H}_2\text{O}}(T_{\text{B.P.}})(1 - 0.06340)$$

or $p_{\text{sat},\text{H}_2\text{O}}(T_{\text{B.P.}}) = 108,184 \text{ Pa}$. From a steam table, we find $T_{\text{B.P.}} = \underline{101.8^\circ\text{C}} \leftarrow$

PROBLEM 11.17 Consider one-dimensional, binary diffusion in which isothermal ideal gases 1 and 2 travel in opposite directions along the z -axis of a tube. Assume that the flow has a zero mass-average velocity, so that mass transfer purely diffusive. (a) Show that the conservation equations for mass, species, and momentum are satisfied by $v = 0$, $j_1 = -j_2 = \text{constant}$, and $p = \text{constant}$. (b) Use Fick's law to solve for $m_1(z)$, if $m_1(0) = 0$ and $m_1(L) = 1$. (c) Find j_1 in terms of the molar masses of the gases. (*Hint: ρ is not constant; use $\rho = Mc$ and write M in terms of m_1 before integrating*). (d) Write the mole fluxes in terms of the mass fluxes and solve for the mole-average velocity, v^* . Under what condition is $v^* = 0$? (e) Suppose that gas 1 is helium and gas 2 is air at $T = 276 \text{ K}$ and $p = 1 \text{ atm}$, with $L = 1 \text{ m}$. Calculate v^* , and j_i and N_i for both gases. Are the molar diffusion rates equal and opposite?

SOLUTION

a) In steady, one-dimensional flow, the mass and species equations, (11.40) and (11.41), may be simplified to

$$\frac{d}{dz}(\rho v) = 0 \quad \text{eqn. (11.41)}$$

$$\frac{d}{dz}(\rho_i v + j_i) = \frac{d}{dz}(n_i) = 0 \quad \text{eqn. (11.40)}$$

When $v = 0$, the first equation is satisfied and $n = 0$. The second equation shows that $\rho_i v = n_i = \text{constant}$, and with eqns. (11.18) and (11.20)

$$n_i = \rho_i v + j_i = j_i = \text{constant}$$

Finally, eqn. (11.21) shows that $j_1 = -j_2$, as is always the case in binary diffusion.

The momentum equation will be familiar from past studies of fluid mechanics. If the fluid has zero velocity, and if gravitational pressure gradients are negligible over the height of the system, then $p = \text{constant}$. (If the fluid flowed through the tube, i.e. had a non-zero mass-average velocity, then viscous drag would produce an axial pressure gradient.)

b) With Fick's law,

$$j_i = -\rho \mathcal{D}_{12} \frac{dm_1}{dz} = \text{constant} = c_1$$

At this point, we need to think a little: the mass density will vary with the mass fractions, even though p and T are constant. On the other hand, the molar density, from eqn. (11.13) will be constant: $c = p/R^\circ T$. So, we need the molar mass of the mixture from eqn. (11.8):

$$\frac{1}{M} = \frac{m_1}{M_1} + \frac{m_2}{M_2} = m_1 \left(\frac{1}{M_1} - \frac{1}{M_2} \right) + \frac{1}{M_2} = \frac{m_1(M_2 - M_1) + M_1}{M_1 M_2} \quad (*)$$

Now returning to Fick's law and rearranging

$$-\frac{c \mathcal{D}_{12} M_1 M_2}{m_1(M_2 - M_1) + M_1} \frac{dm_1}{dz} = c_1$$

The integral we need, with $m_1(0) = 0$, is

$$\int_0^{m_1(z)} \frac{dm_1}{am_1 + b} = \frac{1}{a} \ln \left(\frac{am_1(z)}{b} + 1 \right)$$

where $a = (M_2 - M_1)$ and $b = M_1$. Collecting all this

$$\frac{1}{a} \ln \left(\frac{am_1(z)}{b} + 1 \right) = -\frac{c_1 z}{c\mathcal{D}_{12}M_1M_2}$$

and with $m_1(L) = 1$, we find

$$c_1 = -\frac{c\mathcal{D}_{12}M_1M_2}{L} \frac{1}{a} \ln \left(\frac{a}{b} + 1 \right)$$

so that

$$\ln \left(\frac{am_1(z)}{b} + 1 \right) = \frac{z}{L} \ln \left(\frac{a}{b} + 1 \right)$$

and a little more algebra gives

$$m_1(z) = \frac{1}{a} \left(\frac{a}{b} + 1 \right)^{z/L} - \frac{b}{a}$$

and finally substituting for a and b gives

$$m_1(z) = \frac{(M_2/M_1)^{z/L} - M_1}{M_2 - M_1} \quad \leftarrow \text{Answer}$$

c) With Fick's law

$$j_1 = -cM\mathcal{D}_{12} \frac{dm_1}{dz} = -\frac{cM\mathcal{D}_{12}}{L(M_2 - M_1)} \ln \left(\frac{M_2}{M_1} \right)$$

and using eqn. (*) to eliminate M

$$j_1 = -\frac{c\mathcal{D}_{12}M_1M_2}{L(M_2 - M_1)} \ln \left(\frac{M_2}{M_1} \right) \quad \leftarrow \text{Answer}$$

d) $N_i = n_i/M_i = j_i/M_i$ and $N = n/M = 0$. With eqn. (11.22)

$$v^* = c^{-1} (j_1/M_1 + j_2/M_2) = c^{-1} j_1 (1/M_1 - 1/M_2) = -\frac{\mathcal{D}_{12}}{L} \ln \left(\frac{M_2}{M_1} \right)$$

The mole-average velocity is only zero if $M_1 = M_2$.

e) From Table 11.1, $\mathcal{D}_{\text{He-air}} = 6.24 \times 10^{-5} \text{ m}^2/\text{s}$, and $M_{\text{He}} = 4.003$ and $M_{\text{air}} = 28.96$:

$$v^* = -\frac{(6.24 \times 10^{-5})}{1} \ln \left(\frac{28.96}{4.003} \right) = -1.235 \times 10^{-4} \text{ m/s} \quad \leftarrow \text{Answer}$$

With $c = (101325)/[(8314.5)(276)] = 0.0442 \text{ kmol/m}^2$,

$$\begin{aligned} j_1 = -j_2 &= -\frac{(0.0442)(6.24 \times 10^{-5})(4.003)(28.96)}{(1)(28.96 - 4.003)} \ln \left(\frac{28.96}{4.003} \right) \\ &= -2.54 \times 10^{-5} \text{ kg/m}^2\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

$$J_1 = \frac{n_1}{M_1} = \frac{j_1}{M_1} = -\frac{2.54 \times 10^{-5}}{4.003} = -6.34 \times 10^{-6} \text{ kmol/m}^2\text{s} \quad \leftarrow \text{Answer}$$

$$J_2 = \frac{n_2}{M_2} = \frac{j_2}{M_2} = \frac{2.54 \times 10^{-5}}{28.96} = 8.77 \times 10^{-7} \text{ kmol/m}^2\text{s} \quad \leftarrow \text{Answer}$$

COMMENT: What should be very clear is that the mole fluxes are entirely unequal. Even so, many textbooks call this problem “equimolar counterdiffusion” and begin with the *assumption* that $J_1 = -J_2$ if $p = \text{constant}$! Mills [1] discusses this common error in more detail.

REFERENCE:

[1] A.F Mills, On steady one-dimensional diffusion in binary ideal gas mixtures, *Int. J. Heat Mass Transfer*, **46**(13):2495–2497, 2003, [https://doi.org/10.1016/S0017-9310\(02\)00537-9](https://doi.org/10.1016/S0017-9310(02)00537-9).

PROBLEM 11.18 Suppose that a steel fitting with a carbon mass fraction of 0.2% is put into contact with carburizing gases at 910°C, and that these gases produce a steady mass fraction, $m_{C,u}$, of 1.0% carbon just within the surface of the metal. The diffusion coefficient of carbon in this steel is [1]

$$\mathcal{D}_{C,Fe} = (1.2 \times 10^{-5} \text{ m}^2/\text{s}) \exp[-(1.34 \times 10^8 \text{ J/kmol})/(R^\circ T)]$$

for T in kelvin. How long does it take to produce a carbon concentration of 0.6% by mass at a depth of 0.5 mm? How much less time would it take if the temperature were 950°C?

SOLUTION

We can refer to Example 11.9 and Fig. 11.12. As shown in the example, the solution for mass fraction of carbon in the iron is

$$\frac{m_C(x, t) - m_{C,u}}{m_{C,0} - m_{C,u}} = \text{erf}\left(\frac{x}{2\sqrt{\mathcal{D}_{C,Fe}t}}\right)$$

The boundary conditions are:

$$m_{C,u} = 0.010 \quad m_{C,0} = 0.002$$

To find the time for $m_C(x = 0.5 \text{ mm}, t) = 0.006$, we need the argument of erf to satisfy

$$\frac{m_C(x, t) - m_{C,u}}{m_{C,0} - m_{C,u}} = \frac{0.006 - 0.010}{0.002 - 0.010} = 0.500$$

From a table of the error function or an online error function calculator, we find $\text{erf}(0.47694) = 0.50000$. For each temperature, we must find the time that makes the argument equal 0.47694:

$$t = \frac{1}{\mathcal{D}_{C,Fe}} \left(\frac{0.0005}{2(0.47694)} \right)^2 = \frac{2.748 \times 10^{-7} \text{ m}^2}{\mathcal{D}_{C,Fe} \text{ m}^2/\text{s}} \quad (*)$$

We can evaluate the diffusion coefficient at the two temperatures given, 910°C = 1183 K and 950°C = 1223 K:

$$\begin{aligned} \mathcal{D}_{C,Fe} &= (1.2 \times 10^{-5} \text{ m}^2/\text{s}) \exp[-(1.34 \times 10^8)/(8314.5)T] \\ &= \begin{cases} 1.454 \times 10^{-11} \text{ m}^2/\text{s} & \text{at 1183 K} \\ 2.271 \times 10^{-11} \text{ m}^2/\text{s} & \text{at 1223 K} \end{cases} \end{aligned}$$

Putting these numbers into eqn. (*) we find

$$t = \begin{cases} 1.890 \times 10^4 \text{ s} = 5.250 \text{ h} = 5 \text{ h } 15 \text{ min} & \text{at 1183 K} = 910^\circ\text{C} \\ 1.210 \times 10^4 \text{ s} = 3.362 \text{ h} = 3 \text{ h } 22 \text{ min} & \text{at 1223 K} = 950^\circ\text{C} \end{cases} \quad \longleftarrow \text{Answer}$$

A 40 K increase of temperature reduces the carburization time by 1/3.

Comment: Carburization is widely used for hardening metal parts, and the process has been widely studied. Analyses have addressed additional factors including convection, the temperature dependence of physical properties, and base metal composition. Real processes may begin with carburization as described here, but then be followed by an “annealing period” during which the part is held at a somewhat lower temperature while the steep concentration profile in the metal diffuses to a more uniform carbon concentration in the zone just under the surface [1].

[1] Goldstein, J.I., Moren, A.E., “Diffusion modeling of the carburization process,” *Metallurgical Transactions A*, **9**:1515–1525, 1978. doi:10.1007/BF02661934

PROBLEM 11.19 (a) Derive eqn. (11.62) for the mole flux across a stagnant layer, working by analogy to the mass-based analysis of Section 11.5 that led to eqn. (11.58b). Assume that $c\mathcal{D}_{12}$ is constant, and use z as the coordinate across the layer. (b) Show that the molar concentration profile, analogous to eqn. (11.61), is

$$\frac{1 - x_2(z)}{1 - x_{2,0}} = \left(\frac{1 - x_{2,L}}{1 - x_{2,0}} \right)^{x/L}$$

SOLUTION

a) For one-dimensional steady mass transfer in the z -direction, the mole fluxes N_1 and N_2 satisfy eqn. (11.50), with $n_i = M_i N_i$,

$$\frac{dN_1}{dz} = \frac{dN_2}{dz} = 0$$

so that $N_2 = \text{constant}$ and $N_1 = 0$ throughout the layer.

With eqns. (11.24), (11.25), and (11.7)

$$N_1 = x_1 N + J_1 = (1 - x_2)N - J_2 = 0 \tag{*}$$

$$N_2 = x_2 N + J_2 = x_2 \frac{J_2}{(1 - x_2)} + J_2$$

and eliminating N with eqn. (*)

$$N_2 = J_2 \left(\frac{1}{1 - x_2} \right) = \text{constant in } z$$

Now substituting the molar form of Fick’s law, eqn. (11.30),

$$N_2 = \left(-c\mathcal{D}_{12} \frac{dx_2}{dz} \right) \left(\frac{1}{1 - x_2} \right) = \text{constant in } z$$

which is the molar analog of eqn. (11.58a).

The integration proceeds as in the mass-based case that gave eqn. (11.58b), but now assuming that $c\mathcal{D}_{12}$ is constant:

$$\frac{N_2}{c\mathcal{D}_{12}} \int_0^L dz = - \int_{x_{2,0}}^{x_{2,L}} \frac{dx_2}{1 - x_2} \tag{**}$$

from which

$$N_2 = \frac{c\mathcal{D}_{12}}{L} \ln \left(\frac{1 - x_{2,L}}{1 - x_{2,0}} \right) \longleftarrow \text{Answer}$$

which is eqn. (11.62).

b) Use the integral in eqn. (**), but set the upper limit to z rather than L :

$$\frac{N_2}{c\mathcal{D}_{12}} \int_0^z dz = - \int_{x_{2,0}}^{x_2(z)} \frac{dx_2}{1-x_2}$$

from which

$$\frac{N_2 z}{c\mathcal{D}_{12}} = \ln\left(\frac{1-x_2(z)}{1-x_{2,0}}\right)$$

Now eliminate N_2 with the result of part (a)

$$\ln\left(\frac{1-x_2(z)}{1-x_{2,0}}\right) = \frac{x}{L} \ln\left(\frac{1-x_{2,L}}{1-x_{2,0}}\right)$$

from which

$$\frac{1-x_2(z)}{1-x_{2,0}} = \left(\frac{1-x_{2,L}}{1-x_{2,0}}\right)^{x/L} \quad \leftarrow \text{Answer}$$

Comment: $c\mathcal{D}_{12}$ is independent of pressure, so the assumption of constant $c\mathcal{D}_{12}$ is appropriate for a constant temperature gas mixture. Further, c is independent of the mole fraction, so it will not change across the layer even though a concentration gradient is present. This fact makes the molar result more accurate than the mass-based result, which assumes that $\rho\mathcal{D}_{12}$ is constant: the variation in composition will affect ρ , since $\rho = Mc$.

PROBLEM 11.20 A Stefan tube 1 cm in diameter initially has a pool of liquid carbon tetrachloride 200.0 mm below the top. Pure argon flows over the tube. The system is held at 60°C and 8.0×10^4 Pa. During a 12 hr experiment, the pool level drops by 6.1 mm. What is the diffusivity of CCl_4 in Ar? The vapor pressure of CCl_4 is $\log_{10} p_v = 4.023 - 1222/(T - 45.74)$, where p_v is in bar and T in K. The specific gravity of liquid CCl_4 is 1.59.

SOLUTION We may use eqn. (11.64). The specific gravity tells us that

$$\rho_{\text{CCl}_4} = \text{SG}(\rho_{\text{H}_2\text{O}}) = (1.59)(982.9) = 1563 \text{ kg/m}^3$$

From Table 11.3, $M_{\text{CCl}_4} = 153.82$ kmol/kg. The total pressure is $p = 8 \times 10^4$ Pa, and the saturation pressure of CCl_4 , or vapor pressure, is

$$\log_{10} p_v = 4.023 - \frac{1222}{333.15 - 45.74} = -0.2288 \text{ so } p_v = 0.5905 \text{ bar}$$

Then

$$\begin{aligned} \mathcal{D}_{12} &= \frac{[L^2(t) - L_0^2]}{2(t - t_0)} \left(\frac{\rho_{\text{CCl}_4}}{M_{\text{CCl}_4}}\right) \left(\frac{R^\circ T}{p}\right) \left[\ln\left(\frac{p}{p - p_{\text{sat},2}}\right)\right]^{-1} & (11.64) \\ &= \frac{[(0.2061)^2 - (0.2000)^2]}{2(12)(3600)} \left(\frac{1563}{153.82}\right) \left(\frac{(8314.5)(333.15)}{8 \times 10^4}\right) \left[\ln\left(\frac{8 \times 10^4}{8 \times 10^4 - 59050}\right)\right]^{-1} \\ &= 7.53 \times 10^{-6} \text{ m}^2/\text{s} \quad \leftarrow \text{Answer} \end{aligned}$$

Comment: The Antoine equation used for vapor pressure is from the NIST Chemistry Webbook, <https://webbook.nist.gov>, accessed 17 January 2024.

PROBLEM 11.21 A Stefan tube at 60°C contains a pool of liquid ethanol 15 cm below the top. Pure nitrogen gas flows across the top. The total pressure is 1.2 bar. Plot the concentration profiles of ethanol and nitrogen in the tube, in terms of both mass fraction and mole fraction (see Problem 11.19b). The vapor pressure of ethanol (C₂H₅OH) is given by $\log_{10} p_v = 5.247 - 1599/(T - 46.42)$ for p_v is in bar and T in K.

SOLUTION At 60°C = 333.15 K,

$$\log_{10} p_v = 5.247 - \frac{1599}{333.15 - 46.42} = -0.3297 \text{ so } p_v = 0.4681 \text{ bar}$$

From eqn. (11.15),

$$x_{\text{C}_2\text{H}_5\text{OH},0} = \frac{0.4681}{1.2} = 0.3901$$

and at the top $x_{\text{C}_2\text{H}_5\text{OH},L} = 0$. With eqn. (11.8), molar mass above the liquid surface is

$$\begin{aligned} \frac{1}{M_0} &= \frac{x_{\text{C}_2\text{H}_5\text{OH},0}}{M_{\text{C}_2\text{H}_5\text{OH}}} + \frac{x_{\text{N}_2,0}}{M_{\text{N}_2}} \\ &= \frac{0.3901}{46.07} + \frac{1 - 0.3901}{28.01} \\ M_0 &= 33.07 \text{ kg/kmol} \end{aligned}$$

and with eqn. (11.9), the mass fractions are

$$m_{\text{C}_2\text{H}_5\text{OH},0} = \frac{(0.3901)(46.07)}{33.07} = 0.5435$$

and $m_{\text{C}_2\text{H}_5\text{OH},L} = 0$.

Now we can use the result of Problem 11.19b and eqn. (11.61)

$$\begin{aligned} \frac{1 - x_{\text{C}_2\text{H}_5\text{OH}}(z)}{1 - x_{\text{C}_2\text{H}_5\text{OH},0}} &= \left(\frac{1 - x_{\text{C}_2\text{H}_5\text{OH},L}}{1 - x_{\text{C}_2\text{H}_5\text{OH},0}} \right)^{z/L} \\ \frac{1 - m_{\text{C}_2\text{H}_5\text{OH}}(z)}{1 - m_{\text{C}_2\text{H}_5\text{OH},0}} &= \left(\frac{1 - m_{\text{C}_2\text{H}_5\text{OH},L}}{1 - m_{\text{C}_2\text{H}_5\text{OH},0}} \right)^{z/L} \end{aligned} \quad (11.61)$$

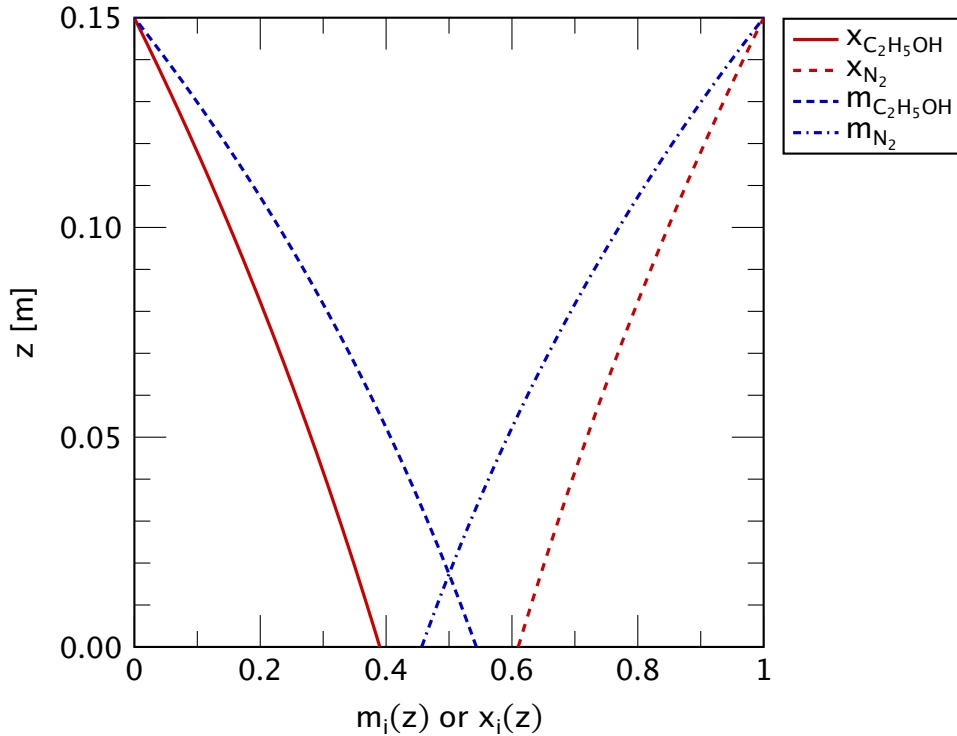
which rearrange to

$$\begin{aligned} x_{\text{C}_2\text{H}_5\text{OH}}(z) &= 1 - (1 - x_{\text{C}_2\text{H}_5\text{OH},0}) \left(\frac{1 - x_{\text{C}_2\text{H}_5\text{OH},L}}{1 - x_{\text{C}_2\text{H}_5\text{OH},0}} \right)^{z/L} \\ &= 1 - (0.6099)^{1-z/(0.15)} \end{aligned}$$

with $x_{\text{N}_2}(z) = 1 - x_{\text{C}_2\text{H}_5\text{OH}}(z)$, and

$$m_{\text{C}_2\text{H}_5\text{OH}}(z) = 1 - (0.4565)^{1-z/(0.015)}$$

with $m_{\text{N}_2}(z) = 1 - m_{\text{C}_2\text{H}_5\text{OH}}(z)$. The plots are below.



Comment: The Antoine equation used for vapor pressure is from the NIST Chemistry Webbook, <https://webbook.nist.gov>, accessed 19 January 2024.

PROBLEM 11.22 Consider mass convection in a binary mixture, in which only species 1 is transferred through the s -surface. Show that $g_{m,1} = g_{m,2}$. How does $j_{2,s}$ relate to $n_{1,s}$?

SOLUTION From eqns. (11.66), (11.3), and (11.21) we have

$$g_{m,1} = \frac{j_{1,s}}{m_{1,s} - m_{1,e}} = \frac{-j_{2,s}}{1 - m_{2,s} - 1 + m_{2,e}} = \frac{j_{2,s}}{m_{2,s} - m_{2,e}} = g_{m,2} \quad \leftarrow \text{Answer}$$

This applies for either low rate or high rate mass transfer.

Although $n_{2,s} = 0$, species 2 may have a non-zero diffusive flux at the wall

$$n_{2,s} = 0 = j_{2,s} + m_{2,s}n = j_{2,s} + m_{2,s}n_{1,s}$$

$$j_{2,s} = -m_{2,s}n_{1,s} \quad \leftarrow \text{Answer}$$

The reason that $j_{2,s}$ is not zero is that species 2 diffuses against the convective velocity caused by the transport of species 1 away from the wall.

PROBLEM 11.23 A small sphere in a gas at rest has a low vapor pressure of species 1, so that species 1 is dilute in the gas phase. When natural convection around the sphere is negligible, the steady mass flux of species 1 in the radial direction is $n_{1,r} \cong j_{1,r} = -\rho \mathcal{D}_{12} dm_1/dr$. Use a mass balance to obtain the s -surface mass flux in terms of the difference between the concentration

far from the sphere, $m_{1,\infty}$, and near the surface, $m_{1,s}$. Approximate $\rho\mathcal{D}_{12}$ as constant, which is accurate if species 1 is dilute. Then use eqns. (11.66) and (11.69) to show that $\text{Nu}_{m,D} = 2$. What condition must apply for convection to be negligible?

SOLUTION Let the small sphere have a radius R , and consider a control surface of radius $r > R$ outside the small sphere. In steady state, the mass flow leaving the small sphere must equal the mass leaving the outer sphere. Therefore

$$4\pi R^2 j_{1,r} \Big|_R = 4\pi r^2 j_{1,r} \Big|_r = \text{constant in } r = \mathbb{C}$$

$$-4\pi r^2 \rho \mathcal{D}_{12} \frac{dm_1}{dr} \Big|_r = \mathbb{C}$$

Rearrange and integrate

$$\underbrace{\int_{m_{1,s}}^{m_{1,\infty}} dm_1}_{=m_{1,\infty}-m_{1,s}} = -\frac{\mathbb{C}}{4\pi\rho\mathcal{D}_{12}} \underbrace{\int_R^\infty \frac{dr}{r^2}}_{=1/R}$$

Hence, with a bit of algebra,

$$j_{1,s} = j_{1,r} \Big|_R = \frac{\mathbb{C}}{4\pi R^2} = \frac{4\pi\rho\mathcal{D}_{12}R(m_{1,s} - m_{1,\infty})}{4\pi R^2} = \frac{\rho\mathcal{D}_{12}}{R}(m_{1,s} - m_{1,\infty}) \quad \leftarrow \text{Answer}$$

With eqns. (11.69) and (11.66), and putting $D = 2R$ for the diameter,

$$\text{Nu}_{m,D} = \frac{g_{m,1}D}{\rho\mathcal{D}_{12}} = \frac{j_{1,s}(2R)}{\rho\mathcal{D}_{12}(m_{1,s} - m_{1,\infty})} = 2 \quad \leftarrow \text{Answer}$$

This result can be compared to eqn. (8.33) for natural convection from a sphere

$$\text{Nu}_D = 2 + \frac{0.589 \text{Ra}_D^{1/4}}{[1 + (0.492/\text{Pr})^{9/16}]^{4/9}} \quad (8.33)$$

which limits to $\text{Nu}_D = 2$ when $\text{Ra}_D \ll 1$. From the analogy of heat and mass transfer, or eqn. (11.71), we must have

$$\text{Ra}_D = \text{Gr}_D \text{Sc} = \frac{g\Delta\rho D^3}{\mu\mathcal{D}_{12}} \ll 1 \quad \leftarrow \text{Answer}$$

- 11.24 Gases are sometimes absorbed into liquids through "film absorption." A thin film of liquid is run down the inside of a vertical tube, through which flows the gas to be absorbed. Analyze this process under the following assumptions: The film flow is laminar and of constant thickness, δ_0 , with a velocity profile given by eqn. (8.51). The gas is only slightly soluble in the liquid, so the liquid properties are unaffected by it and it does not penetrate far beyond the liquid surface. The gas concentration at the s and u-surfaces does not vary along the length of the tube. The inlet concentration of gas in the liquid is $m_{1,0}$. Show that the mass transfer is given by

$$Nu_{m,x} = (u_0 x / \kappa D_{12})^{1/2}, \quad u_0 = \frac{(\rho_f - \rho_g) g \delta_0^2}{2\mu_f}$$

The mass transfer coefficient here is based on the concentration difference between the u-surface and the bulk liquid at $m_{1,0}$. (Hint: The small penetration assumption can be used to reduce the species equation for the film to the diffusion equation.)

Because the liquid film is thin, we ignore the curvature of the tube. As in Chapter 8, we may apply boundary layer assumptions and the appropriate form of the species conservation equation (11.44) becomes:

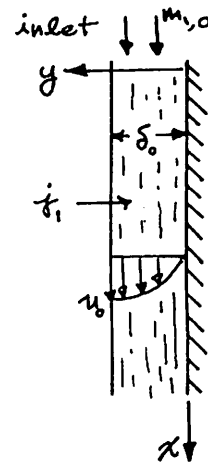
$$u \frac{\partial m_1}{\partial x} + v \frac{\partial m_1}{\partial y} = D_{1,m} \frac{\partial^2 m_1}{\partial y^2}$$

The velocity profile is (8.51):

$$u = \underbrace{\frac{(\rho_s - \rho_g) g \delta_0^2}{2\mu}}_{u_0} \left[2 \left(\frac{y}{\delta_0} \right) - \left(\frac{y}{\delta_0} \right)^2 \right], \quad v = 0$$

Because the gas does not penetrate far into the film, we may approximate u in the species eq'n by its surface value, u_0 . This is the important feature of the small penetration assumption. The species eq'n reduces to the diffusion eq'n:

$$u_0 \frac{\partial m_1}{\partial x} = D_{1,m} \frac{\partial^2 m_1}{\partial y^2} \quad ; \quad \frac{\partial m_1}{\partial x} = \left(\frac{D_{1,m}}{u_0} \right) \frac{\partial^2 m_1}{\partial y^2}$$



The boundary and initial conditions in the liquid film are:

$$m_1(y=\delta_0, x) = m_{1,u} ; m_1(x=0, y) = m_{1,o} ; m_1(y \rightarrow -\infty, x) = m_{1,o}$$

In the last condition, we use $y \rightarrow -\infty$ rather than $y=0$ because the small penetration approximation essentially removes all effects of the wall. We may cast this problem into the form eqn. (11.57) by transforming the y -coordinate to $\bar{y} = \delta_0 - y$; the d.e. is unaffected and the b.c.'s are

$$m_1(\bar{y}=0, x) = m_{1,u} ; m_1(x=0, \bar{y}) = m_{1,o} ; m_1(\bar{y} \rightarrow \infty, x) = m_{1,o}$$

From example 11.9, the solution is

$$\frac{m_1 - m_{1,u}}{m_{1,o} - m_{1,u}} = \operatorname{erf}\left(\frac{\bar{y}}{2\sqrt{D_{1,m}x/u_0}}\right)$$

To find the mass transfer coefficient, compute j_1 :

$$j_1 = -\rho D_{1,m} \left. \frac{\partial m_1}{\partial \bar{y}} \right|_{\bar{y}=0} = \rho D_{1,m} (m_{1,u} - m_{1,o}) \cdot \frac{2}{\sqrt{\pi}} \frac{1}{2} \left(\frac{u_0}{D_{1,m}x} \right)^{1/2}$$

(see eqn 5.54). The mass transfer coeff., $g_{m,1}^* = j_1 / (m_{1,u} - m_{1,o})$

is

$$g_{m,1}^* = \rho \left(\frac{u_0 D_{1,m}}{\pi x} \right)^{1/2} \quad \text{so} \quad \boxed{Nu_{m,x} = \left(\frac{u_0 x}{\pi D_{1,m}} \right)^{1/2}}$$

- 11.25 Benzene vapor flows through a 3 cm ID vertical tube. A thin film of initially pure water runs down the inside wall of the tube at a flow rate of 0.3 l/s. If the tube is 0.5 m long and 40°C, estimate the rate (in kg/s) at which benzene is absorbed into water over the entire length of the tube. The mass fraction of benzene at the u-surface is 0.206. (Hint: Use the result stated in Prob. . Obtain δ_0 from the results in Chapter 8.)

The properties of water at 40°C are: $\mu = 6.501 \times 10^{-4}$ kg/m·s, $\rho = 991.8$ kg/m³. The gas density will be small compared to ρ_{H_2O} .

The diffusion coefficient is calculated from eqn. (11.115):

$$D_{C_6H_6-H_2O} = \left(\frac{313.15}{6.501 \times 10^{-4}} \right) (4.4 \times 10^{-15}) \left(\frac{0.0187}{0.096} \right)^{1/6} \left(\frac{40.62}{30.76} \right)^{1/2}$$

$= 1.85 \times 10^{-9}$ m²/s. Next obtain the film thickness: the volume

flow rate = 0.3 l/s = 0.0003 m³/s = $\pi D \left(\frac{m}{\rho_f} \right) = \pi D \frac{(\rho_f - \rho_g)}{3\mu_f} g \delta_0^3$
by eqn (8.53). Thus:

$$\delta_0^3 = (0.0003)(3\mu_f) / [\pi D g (\rho_f - \rho_g)] ; \delta_0 = 0.861 \text{ mm}$$

Using the results of problem 11.40, $u_0 = (\rho_f - \rho_g) g \delta_0^2 / 2\mu_f = 5.545$ m/s, and $Num_{m,x} = (u_0 x / \pi D)^{1/2}$.

To get the overall rate of absorption, we need to integrate:

$$\begin{aligned} \text{rate of absorption} &= \pi D \int_0^L n_{C_6H_6,s} dx = \pi D (m_{C_6H_6,u} - m_{C_6H_6,0}) \int_0^L g_m dx \\ &= \rho_f (u_0 D / \pi)^{1/2} \cdot \pi D (m_u - m_0) \int_0^L x^{-1/2} dx \\ &= (991.8) ((5.545)(1.85 \times 10^{-9}) \pi)^{1/2} (0.03)(0.206) 2(0.5)^{1/2} \\ &= 1.556 \times 10^{-3} \text{ kg/s} = \underline{1.56 \text{ g/s}} \end{aligned}$$

We can check the small penetration assumption with eqn (5.51):

$$\text{penetration depth} = 3.65 \sqrt{D t} \approx 3.65 \sqrt{D L / u_0} = 13 \mu\text{m} \ll \delta_0.$$

- 11.26 a.) Write eqn. (11.44) and the b.c.'s in terms of a nondimensional mass fraction, ψ , analogous to the dimensionless temperature in eqn. (6.42). b.) For $\nu = D_{i,m}$, relate ψ to the Blasius function, f , for flow over a flat plate. c.) Note the similar roles of Pr and Sc in the two boundary layer transport processes. Infer the mass concentration analog of eqn. (6.55) and sketch the concentration and momentum b.l. profiles for $Sc \ll 1$, $Sc = 1$, and $Sc \gg 1$.

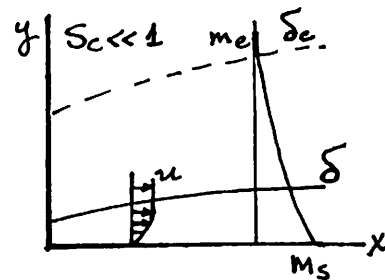
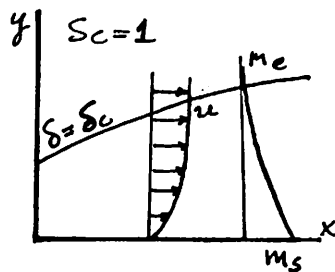
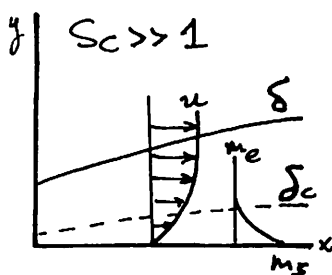
(a) The appropriate nondimensionalization is: $\psi = \frac{m_i - m_{i,s}}{m_{i,e} - m_{i,s}}$

The analog to (6.42) is then:

$$u \frac{\partial \psi}{\partial x} + v \frac{\partial \psi}{\partial y} = D_{i,m} \frac{\partial^2 \psi}{\partial y^2}; \quad \psi(y=0) = 0, \quad \psi(y \rightarrow \infty) = 1, \\ \frac{\partial \psi}{\partial y} \Big|_{y \rightarrow \infty} = 0$$

(b) Like (6.21), (6.41) & (6.43), when $\nu = D_{i,m}$, the distributions of concentration and velocity are identical: $\psi = f'$ ←

(c) The similarity of heat transfer and low-rate mass transfer shows that we need only replace δ_t by δ_c and α by $D_{i,m}$. Therefore: $\frac{\delta_c}{\delta} = Sc^{-1/3}$ for $0.6 \leq Sc \leq 50$ and low rates



11.27 When Sc is large, momentum diffuses more easily than mass, and the concentration b.l. thickness, δ_c , is much less than the momentum b.l. thickness, δ . On a flat plate, the small part of the velocity profile within the concentration b.l. is approximately $u/U_e = 3y/2\delta$. Compute $Nu_{m,x}$ based on this velocity profile, assuming a constant wall concentration. (Hint: Use the mass transfer analogs of eqn. (6.47) and (6.50) and note that $q_w/\rho c_p$ becomes $j_{i,s}/\rho$.)

The analog of (6.47) is: $\frac{d}{dx} \int_0^{\delta_c} u(m_i - m_{i,e}) dy = j_{i,s}/\rho$

and the analog of (6.50) is: $\left(\frac{m_i - m_{i,e}}{m_{i,s} - m_{i,e}}\right) = 1 - \frac{3}{2} \frac{y}{\delta_c} + \frac{1}{2} \left(\frac{y}{\delta_c}\right)^3$

Now, $j_{i,s}/\rho = -D_{i,m} \frac{\partial}{\partial y} (m_i - m_{i,e}) \Big|_{y=0} = (m_{i,s} - m_{i,e}) D_{i,m} \cdot \frac{3}{2} \frac{1}{\delta_c}$

And: $\frac{d}{dx} \int_0^{\delta_c} u(m_i - m_{i,e}) dy = U_e (m_{i,s} - m_{i,e}) \frac{d}{dx} \int_0^{\delta_c} \left(\frac{3}{2} \frac{y}{\delta_c}\right) \left(1 - \frac{3}{2} \frac{y}{\delta_c} + \frac{1}{2} \left(\frac{y}{\delta_c}\right)^3\right) dy$

$= U_e (m_{i,s} - m_{i,e}) \frac{d}{dx} \left(\frac{3}{20} \frac{\delta_c^2}{\delta}\right) = U_e (m_{i,s} - m_{i,e}) \cdot \frac{3}{20} \left(\frac{\delta_c}{\delta}\right) \frac{d\delta_c}{dx}$

since $\delta_c/\delta = f_n(Sc \text{ only})$ by analogy to eqn (6.46).

Combining the above equations, we obtain a d.e. for $\delta_c(x)$:

$$D_{i,m} \frac{3}{2} \frac{1}{\delta_c} = U_e \frac{3}{20} \left(\frac{\delta_c}{\delta}\right) \frac{d\delta_c}{dx} \quad \text{where } \frac{\delta_c}{\delta} = f_n(x)$$

$$\left(\frac{10 D_{i,m}}{U_e}\right) \left(\frac{\delta}{\delta_c}\right) = \frac{d}{dx} \left(\frac{\delta_c^2}{2}\right) \quad \leftarrow \text{integrate with } \delta_c = 0 \text{ at } x = 0$$

$$\delta_c = \sqrt{(20 D_{i,m}/U_e) (\delta/\delta_c) \cdot x} \quad \leftarrow$$

Next introduce eqn (6.2) for δ and rearrange to find

$$\left(\frac{\delta_c}{\delta}\right)^{3/2} = \sqrt{\frac{20 D_{i,m} \cdot x}{U_e}} \cdot \sqrt{Re_x} / (4.64x), \text{ or } \left(\frac{\delta_c}{\delta}\right) = \frac{1}{1.025 Sc^{1/3}} \quad \leftarrow$$

The mass transfer coefficient is:

$$g_{m,i} = \frac{j_{i,s}}{(m_{i,s} - m_{i,e})} = \rho D_{i,m} \cdot \frac{3}{2} \frac{1}{\delta_c}$$

and the Nusselt number for mass transfer is:

$$\begin{aligned} \text{Nu}_{m,x} &= g_{m,i}^* \cdot x / \rho D_{i,m} = \frac{3}{2} \frac{x}{\delta_c} = \frac{3}{2\sqrt{20}} \sqrt{\frac{U_0 x}{\nu}} \sqrt{\frac{\nu}{D_{i,m}} \cdot \frac{\delta_c^2}{\delta}} \\ &= \frac{3}{2\sqrt{20}} \text{Re}_x^{1/2} \cdot \frac{Sc^{1/3}}{(1.025)^{1/2}} \end{aligned} \quad \boxed{\text{Nu}_{m,x} = 0.331 \text{Re}_x^{1/2} Sc^{1/3}}$$

This may be compared to problem (6.21) and eq'n (6.59).

- 11.28 Nitrous oxide is bled through the surface of a porous 3/8 in. OD tube at 0.025 liter/s per meter of tube length. Air flows over the tube at 25 ft/s. Both the air and tube are at 18°C and the ambient pressure is 1 atm. Estimate the mean concentration of N₂O at the tube surface.

At 1 atm, 18°C eq'n (11.108) gives: $D_{air, N_2O} = 1.480 \times 10^{-5} \text{ m}^2/\text{s}$. As a first estimate, take all properties as those of pure air and assume low-rate mass transfer — both assumptions are motivated by the low flow rate of N₂O from the tube.

$$\text{At } 18^\circ\text{C}, 1 \text{ atm: } \rho_{air} = 1.212 \text{ kg/m}^3, \quad \nu_{air} = 1.488 \times 10^{-5} \text{ m}^2/\text{s}$$

$$Sc = \nu/D = 1.003$$

The velocity of air and tube diameter are $U = 7.62 \text{ m/s}$, $D = 0.009525 \text{ m}$, and $Re_D = 4878$. This is a uniform wall flux problem and eq'n (7.65) is appropriate:

$$\overline{Nu}_{m,0} = 0.3 + \frac{0.62 Re_D^{1/2} Sc^{1/3}}{[1 + (0.4/Sc)^{1/3}]^{1/4}} \left[1 + \left(\frac{Re_D}{282,000} \right)^{5/8} \right]^{4/5} = 41.64$$

$$\overline{q_{m,N_2O}^*} = \overline{Nu}_{m,0} \cdot \rho D_{air,N_2O} / D = (41.64)(1.212)(1.483 \times 10^{-5}) / 0.009525$$

$$= 0.07858 \text{ kg/m}^2\cdot\text{s}$$

The mass flow rate of N₂O is, with $\rho_{N_2O} = 1.842 \text{ kg/m}^3$ (ideal gas),

$$\dot{n}_{N_2O,s} = (0.025 \times 10^{-3} \text{ m}^3/\text{s}\cdot\text{m})(1.842 \text{ kg/m}^3) / \pi(0.009525 \text{ m})$$

$$= 1.539 \times 10^{-3} \text{ kg/m}^2\cdot\text{s}$$

At low rates, $\dot{n}_{N_2O,s} = \overline{q_{m,N_2O}^*} \cdot \overline{B}_{m,N_2O}$ from which $\overline{B}_{m,N_2O} = 0.01958$.

With $m_{N_2O,e} = 0$, $\overline{B}_{m,N_2O} = (0 - m_{N_2O,s}) / (m_{N_2O,s} - 1)$. Solving,

$$\overline{m}_{N_2O,s} = 0.0192 \longleftarrow$$

This result justifies the use of air properties and low-rates.

PROBLEM 11.29 Helium is bled through a porous vertical wall, 40 cm high, into surrounding air at a rate of $87.0 \text{ mg/m}^2\text{s}$. Both the helium and the air are at 300 K, the environment is at 1 atm, and $\mathcal{D}_{\text{He,air}} = 7.12 \times 10^{-5} \text{ m}^2/\text{s}$. What is the average concentration of helium in the air along the wall, $\overline{m}_{\text{He},s}$?

SOLUTION This is a uniform flux natural convection problem. Here $\overline{g_{m,\text{He}}}$ and $\overline{\Delta\rho}$ depend on $\overline{m}_{\text{He},s}$, so the calculation is not as straightforward as it was for thermally driven natural convection.

To begin, let us assume that the concentration of helium at the wall is very small. Since $m_{\text{He},e} = 0$, if $m_{\text{He},s} \ll 1$, then $\overline{m}_{\text{He},s} - \overline{m}_{\text{He},e} \ll 1$ as well. The mass transfer driving force will be small, and the analogy to heat transfer can be used.

The mass flux of helium at the wall, $n_{\text{He},s}$, is given; and because the mass transfer rate is low,

$$n_{\text{He},s} \approx j_{\text{He},s} = \overline{g_{m,\text{He}}} (\overline{m}_{\text{He},s} - \overline{m}_{\text{He},e})$$

Hence,

$$\overline{\text{Nu}}_{m,L} = \frac{\overline{g_{m,\text{He}}} L}{\rho \mathcal{D}_{\text{He,air}}} = \frac{n_{\text{He},s} L}{\rho \mathcal{D}_{\text{He,air}} (\overline{m}_{\text{He},s} - \overline{m}_{\text{He},e})}$$

The appropriate Nusselt number is obtained from the mass transfer analog of eqn. (8.44b) for a vertical plate with uniform flux

$$\overline{\text{Nu}}_{m,L} = \frac{6}{5} \left(\frac{\text{Ra}_L^* \text{Sc}}{4 + 9\sqrt{\text{Sc}} + 10 \text{Sc}} \right)^{1/5}$$

where

$$\text{Ra}_L^* = \text{Ra}_L \overline{\text{Nu}}_{m,L} = \frac{g \overline{\Delta\rho} n_{\text{He},s} L^4}{\mu \rho \mathcal{D}_{\text{He,air}}^2 (\overline{m}_{\text{He},s} - \overline{m}_{\text{He},e})}$$

The Rayleigh number cannot be evaluated without assuming a value of the mass fraction of helium at the wall. As a first guess, we pick $\overline{m}_{\text{He},s} = 0.010$. Then the film composition is

$$m_{\text{He},f} = (0.010 + 0)/2 = 0.005$$

From eqn. (12.8) and the ideal gas law, we obtain estimates for the film density (at the film composition) and the wall density

$$\rho_f = 1.141 \text{ kg/m}^3 \quad \text{and} \quad \overline{\rho}_s = 1.107 \text{ kg/m}^3$$

At this low concentration of helium, we expect the film viscosity to be close to that of pure air: $\mu_f \cong \mu_{\text{air}} = 1.857 \times 10^{-5} \text{ kg/m}\cdot\text{s}$. The corresponding Schmidt number is $\text{Sc} = (\mu_f/\rho_f)/\mathcal{D}_{\text{He,air}} = 0.2286$. Outside the boundary layer, we have pure air with density

$$\rho_e = \rho_{\text{air}} = 1.177 \text{ kg/m}^3$$

From these values,

$$\begin{aligned} \text{Ra}_L^* &= \frac{9.806(1.177 - 1.107)(87.0 \times 10^{-6})(0.40)^4}{(1.857 \times 10^{-5})(1.141)(7.119 \times 10^{-5})^2(0.010)} \\ &= 1.424 \times 10^9 \end{aligned}$$

We may now evaluate the mass transfer Nusselt number

$$\overline{\text{Nu}}_{m,L} = \frac{6[(1.424 \times 10^9)(0.2286)]^{1/5}}{5[4 + 9\sqrt{0.2286} + 10(0.2286)]^{1/5}} = 37.73$$

From this value, we calculate

$$\begin{aligned}(\overline{m_{\text{He},s} - m_{\text{He},e}}) &= \frac{n_{\text{He},s} L}{\rho \mathcal{D}_{\text{He,air}} \overline{\text{Nu}}_{m,L}} \\ &= \frac{(87.0 \times 10^{-6})(0.40)}{(1.141)(7.12 \times 10^{-5})(37.73)} \\ &= 0.01136\end{aligned}$$

But $(\overline{m_{\text{He},s} - m_{\text{He},e}}) = \overline{m_{\text{He},s}}$. This value of the average wall concentration is only 13.6% higher than our initial guess of 0.010.

Using $\overline{m_{\text{He},s}} = 0.01136$ as our second guess, we repeat the preceding calculations with revised values of the densities to obtain

$$\overline{m_{\text{He},s}} = 0.01142 \quad \longleftarrow \text{Answer}$$

This result is within 0.5% of our second guess, so no further iteration is needed.

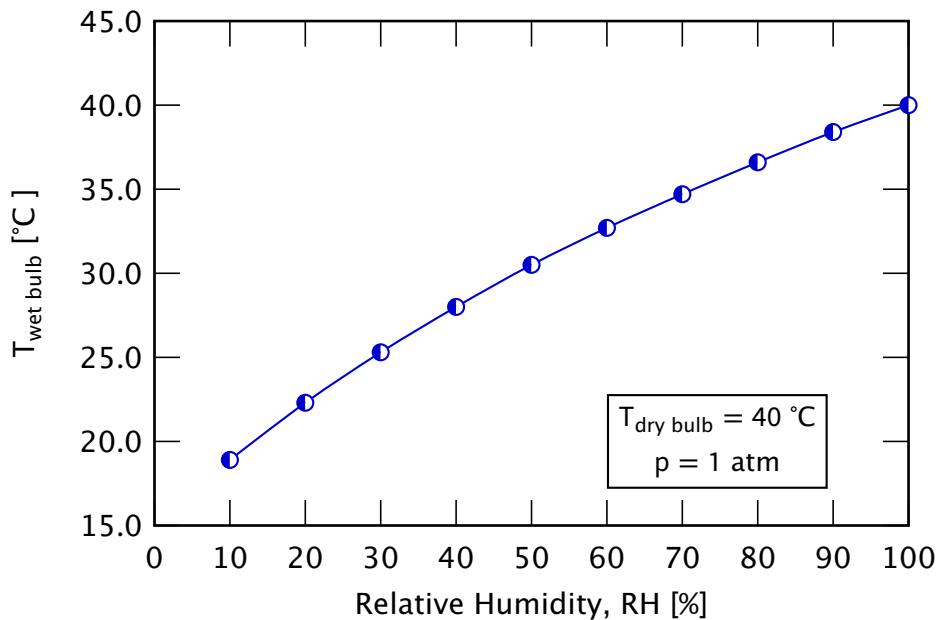
PROBLEM 11.30 We're off on a drive across West Texas. It's going to be hot today—40°C—but we're unsure of the humidity. We attach a “desert water bag” to the shaded side of our pickup truck. It's made of canvas, and it holds a liter and a half of drinking water. When we fill it, we make sure to saturate the canvas inside and out. Water will continue to permeate the fabric, but the weave is tight enough that no water drips from it. Plot the temperature of the water inside the bag as a function of the outdoor humidity. *Hint:* These bags were once widely used in the Western US, but they never found much use along the US Gulf coast.

SOLUTION

Water will evaporate from the wet canvas, cooling the water inside. In steady state, the bag should cool to the wet bulb temperature appropriate to the outdoor humidity, assuming that it is kept in the shade. This temperature can be found by solving eqn. (11.74), but a student familiar with psychrometry (from a thermodynamics class) can read the wet bulb temperature from a psychrometric chart as a function of RH. In addition, wet bulb temperature calculators are available online, e.g., www.weather.gov/epz/wxcalc_rh.

For $T_{\text{dry bulb}} = T_e = 40^\circ\text{C}$ and an atmospheric pressure of 1 atm = 1013.25 hPa = 1013.25 mbar, the results are as follow.

RH [%]	$T_{\text{wet bulb}} [^\circ\text{C}]$	RH [%]	$T_{\text{wet bulb}} [^\circ\text{C}]$
10	18.9	60	32.7
20	22.3	70	34.7
30	25.3	80	36.6
40	28.0	90	38.4
50	30.5	100	40.0



Comment: The water bag will be most effective in arid climates, such as the US Southwest. In humid areas, such as the US Gulf coast, the cooling effect is minimal.

PROBLEM 11.31 The following data were taken at a weather station over several months:

Date	$T_{\text{dry-bulb}}$	$T_{\text{wet-bulb}}$
3/15	15.5°C	11.0°C
4/21	22.0	16.8
5/13	27.3	25.8
5/31	32.7	20.0
7/4	39.0	31.2

Use eqn. (11.74) to find the mass fraction of water in the air at each date. Compare to values from a psychrometric chart.

SOLUTION By rearranging eqn. (11.74)

$$m_{\text{H}_2\text{O},e} = m_{\text{H}_2\text{O},s} - \left(\frac{c_{p,\text{air}} \text{Le}^{2/3} (T_e - T_{\text{wet-bulb}})}{h_{fg}|_{T_{\text{wet-bulb}}}} \right)$$

To solve, we take $\text{Le} = 0.847$, and note from Table A.6 that $c_{p,\text{air}} = 1006 \text{ J/kg}\cdot\text{K}$ in the range of interest, going up to 1007 for the hottest point. For better accuracy, optionally, we may replace $c_{p,\text{air}}$ by $c_p = \sum_i c_{p,i} m_{i,s}$ with $c_{p,\text{water vap.}} \cong 1920 \text{ J/kg}\cdot\text{K}$. The latent heat of vaporization is available in Table A.4 or any steam table. We may find $m_{\text{H}_2\text{O},s}$ as in Example 11.3 using a steam table.

$T_{\text{wet-bulb}}$ °C	h_{fg} kJ/kg·K	p_{sat} Pa	$m_{\text{H}_2\text{O},s}$ [-]	c_p J/kg·K	$m_{\text{H}_2\text{O},e}$ [-]
11.0	2475.4	1312	0.00810	1013	0.00645
16.8	2461.7	1914	0.01184	1017	0.00992
25.8	2440.3	3324	0.02067	1025	0.02061
20.0	2454.1	2339	0.01449	1019	0.00977
31.2	2558.5	4549	0.02842	1033	0.02560

Psychrometric charts provide moisture as γ in units of kg H₂O per kg dry air. To convert that to mass fraction, note that

$$m_{\text{H}_2\text{O}} = \rho_{\text{H}_2\text{O}}/\rho = 1/(1 + \rho_{\text{dry air}}/\rho_{\text{H}_2\text{O}}) = 1/(1 + 1/\gamma)$$

Values read from a chart are used in the table below.

Date	γ (chart)	$m_{\text{H}_2\text{O},e}$ (chart)	$m_{\text{H}_2\text{O},e}$ (computed)	%-difference
3/15	0.0064	0.00636	0.00645	1.4%
4/21	0.0098	0.00970	0.00992	2.2
5/13	0.0206	0.0202	0.02061	2.0
5/31	0.0095	0.00941	0.00977	3.8
7/4	0.0260	0.0253	0.02560	1.2

Comment 1: The values read from a psychrometric chart are within 1.2 to 0.5% values obtained from a reliable online calculator, with the largest difference found at the smallest γ . Not all such calculators give the same values, however—*Caveat emptor!*

Comment 2: The psychrometric chart is based on thermodynamic relationships, such as the adiabatic saturation temperature, rather than transport relationships, as for the wet-bulb temperature. As a result, we don't expect exact agreement between these different calculations.

PROBLEM 11.32 During a coating process, a thin film of ethanol is wiped onto a thick flat plate, 0.1 m by 0.1 m. The initial thickness of the liquid film is 0.1 mm, and the initial temperature of both the plate and the film is 303 K. The air above the film is at 303 K, flows at 10 m/s, and contains no ethanol. (a) Assume that the plate is a poor conductor, so that heat transfer from it is negligible. After a short initial transient, the liquid film reaches a steady temperature. Find this temperature and calculate the time required for the film to completely evaporate. (b) Discuss what happens when the plate is a very good conductor of heat, and calculate a lower bound on the time to evaporate. Properties of ethanol are as follow: $\log_{10}(p_v \text{ mmHg}) = 9.4432 - 2287.8/(T \text{ K})$; $h_{fg} = 9.3 \times 10^5 \text{ J/kg}$; liquid density, $\rho_{\text{eth}} = 789 \text{ kg/m}^3$; $Sc = 1.30$ for ethanol vapor in air; vapor specific heat capacity, $c_{p_{\text{eth}}} = 1420 \text{ J/kg}\cdot\text{K}$.

SOLUTION

a) When the plate is a poor conductor, the thin film will cool to the wet bulb temperature appropriate for ethanol evaporating into air.

We will use values for pure air, assuming that the ethanol concentration in the boundary layer remains low. The relevant properties at 300 K (from Table A.6) are

$$\nu = 1.575 \times 10^{-5} \text{ m}^2/\text{s} \quad \rho = 1.177 \text{ kg/m}^3 \quad c_p = 1006 \text{ J/kg}\cdot\text{K}$$

and the Lewis number is

$$Le = Sc / Pr = (1.30) / (0.707) = 1.84$$

The air away from the plate contains no ethanol, so $m_{\text{eth},e} = 0$. At the surface of the film, the mass fraction will depend on the vapor pressure, which depends on the liquid surface temperature (see Examples 11.3 and 11.6). The relevant equations are (with $p_{\text{atm}} = 760 \text{ mmHg}$ and $M_{\text{eth}} = 46.07 \text{ kg/kmol}$, since ethanol is $\text{C}_2\text{H}_5\text{OH}$, cf. Table 11.2):

$$\begin{aligned} \log_{10}(p_{v,s} \text{ mmHg}) &= 9.4432 - 2287.8/(T_s \text{ K}) & (*) \\ x_{\text{eth},s} &= p_{v,s} / p_{\text{atm}} = p_{v,s} / (760) \\ m_{\text{eth},s} &= \frac{(x_{\text{eth},s})(46.07)}{[(x_{\text{eth},s})(46.07) + (1 - x_{\text{eth},s})(28.96)]} \end{aligned}$$

We need to iterate this set of equations with the energy balance for the wet bulb temperature, T_s , which follows eqn. (11.74):

$$\begin{aligned} T_s &= T_e - \left(\frac{h_{sf}}{c_p Le^{2/3}} \right) (m_{\text{eth},s} - m_{\text{eth},e}) \\ T_s &= 303 - \left(\frac{9.3 \times 10^5}{(1006)(1.84)^{2/3}} \right) m_{\text{eth},s} \\ T_s &= [303 - 615.7 m_{\text{eth},s}] \text{ K} & (**) \end{aligned}$$

In the table that follows, we guess T_s in eqn. (*), and evaluate sequentially until we get a revised value from eqn. (**). Since the revised values are sensitive to the guessed values, we can guess a new value between the original and revised values (in numerical methods parlance, this approach is called “under-relaxation”).

Guess T_s [K]	$p_{v,s}$ [mmHg]	$x_{\text{eth},s}$	$m_{\text{eth},s}$	Get T_s [K]
303.0	78.11	0.1028	0.1542	208.7
280.0	18.73	0.02463	0.03864	279.2
279.7	18.35	0.02415	0.03788	279.68

The liquid film temperature is $T_s = 279.7 \text{ K}$ ← Answer

The final value of $m_{\text{eth},s}$ is low enough (3.8 wt%) that we may neglect the effect of ethanol vapor on c_p and T_s (the difference would be on the order of +0.1 K).

To find the evaporation time, we need the mass transfer coefficient for the air flowing over the plate. If we assume the air flows parallel to a 0.1 m dimension

$$\text{Re}_L = \frac{(10)(0.1)}{1.575 \times 10^{-5}} = 6.349 \times 10^4 \implies \text{laminar flow}$$

Then, with eqn. (6.68) and the analogy between heat transfer and low rate mass transfer (eqn. 11.69)

$$\overline{\text{Nu}}_L = 0.664 \text{Re}_L^{1/2} \text{Sc}^{1/3} = 182.6 \quad (6.68)$$

The diffusion coefficient is

$$\mathcal{D}_{\text{eth,air}} = \frac{\nu}{\text{Sc}} = \frac{1.575 \times 10^{-5}}{1.30} = 1.212 \times 10^{-5} \text{ m}^2/\text{s}$$

and, with eqn. (11.69), the mass transfer coefficient is

$$\overline{g}_m = \overline{\text{Nu}}_L \frac{\rho \mathcal{D}_{\text{eth,air}}}{L} = (182.6) \frac{(1.177)(1.212 \times 10^{-5})}{0.1} = 0.0260 \text{ kg/m}^2\text{s}$$

Since the conditions are steady, the time T to complete evaporation is found by a mass balance, per unit area, where t is the film thickness:

$$\rho_{\text{eth}} t = \overline{g}_m (m_{\text{eth},s} - m_{\text{eth},e}) T$$

$$(789)(0.0001) = (0.0260)(0.03788) T$$

from which

$$T = 80.1 \text{ sec} \quad \leftarrow \text{Answer}$$

The film will completely evaporate in less than a minute and half.

- b) In this case, the thick plate will conduct heat into the ethanol film, holding its base temperature at 303 K. The top of the film will be cooler as a result of heat conduction through the film and heat loss to evaporation, but the two temperatures will grow closer as the film thins with ongoing evaporation. A lower bound on the evaporation time would be obtained for $T_s = 303 \text{ K}$, which we can quickly calculate using $m_{\text{eth},s} = 0.1542$ from the first row of the table in Part (a):

$$\rho_{\text{eth}} t = \overline{g}_m (m_{\text{eth},s} - m_{\text{eth},e}) T$$

$$(789)(0.0001) = (0.0260)(0.1542) T$$

from which

$$T = 19.7 \text{ sec} \quad \leftarrow \text{Answer}$$

This time is 75% less than the wet-bulb time. The reason is that the vapor pressure rises exponentially with the liquid surface temperature.

Comment 1: For part (b), one might worry about the conduction temperature drop from the plate to the surface of the ethanol film. With $k = 0.17 \text{ W/m}\cdot\text{K}$ for ethanol, the thermal resistance of the film is $t/k = 5.9 \times 10^{-4} \text{ m}^2\text{K/W}$, initially. The heat flux at liquid surface $q = h_{fg}\bar{g}_m m_{\text{eth},s}$, and for a surface temperature of 303 K, our values show $q = 3729 \text{ W/m}^2$. Combining q with the thermal resistance gives an *initial* temperature drop through the film of 2.2 K. So, the film surface temperature is initially slightly less than 301 K and the evaporation rate is slightly lower. This difference diminishes to zero, however, as the film gets thinner with continuing evaporation.

Comment 2: Further, one might worry about the conductive plate's surface cooling down through a transient heat conduction process. Using eqn (5.56) and the flux given in Comment 1, a copper plate's surface can be estimated to cool by about 0.7 K. Between this effect and the effect in Comment 1, the time to complete evaporation is probably about 10% longer than our lower bound calculation.

PROBLEM 11.33 Ice cubes left in a freezer will slowly sublime into the air. Suppose that a tray of ice cubes is left in a freezer with air at -10°C and a relative humidity of 50%. The air in the freezer is circulated by a small fan, creating a heat transfer coefficient from the top of the ice cube tray of $5 \text{ W/m}^2\text{K}$. If a 20 g ice cube is rectangular and has an exposed top surface area of 8 cm^2 , find the temperature of the ice cube and estimate the time required for it to sublime completely. Assume that no heat is transferred through the ice cube tray. For ice, take $h_{\text{sg}} = 2.837 \text{ MJ/kg}$, and for water vapor in air, take $\text{Sc} = 0.63$. The vapor pressure of ice is given in Example 11.6.

SOLUTION

Sublimation absorbs the latent heat, and so heat must be convected from the air to the ice. As a result, the ice will become cooler than the surrounding air. Further, the ice will cool to a “wet-bulb” temperature that remains fixed while the ice cube sublimates away. In that condition, no heat is conducted into the ice. The calculation needed then follows Sect. 11.7.

As mentioned, Example 11.6 provides the saturation vapor pressure at -10°C

$$p_{\text{sat}}(-10^\circ\text{C}) = 0.260 \text{ kPa}$$

so that the partial pressure at 50% relative humidity is

$$p_v = (0.50)(0.260) = 0.130 \text{ kPa}$$

Using the method of Example 11.3:

$$x_{\text{H}_2\text{O},e} = p_v/p_{\text{atm}} = (0.130) / (101.325) = 1.283 \times 10^{-3}$$

and

$$\begin{aligned} m_{\text{H}_2\text{O},e} &= \frac{(x_{\text{H}_2\text{O},e})(18.02)}{[(x_{\text{H}_2\text{O},e})(18.02) + (1 - x_{\text{H}_2\text{O},e})(28.96)]} \\ &= 7.99 \times 10^{-4} \end{aligned} \quad (11.48)$$

The mole fraction of water vapor above the ice will be smaller than $p_{\text{sat}}(-10^\circ\text{C})/p_{\text{atm}} = 2.6 \times 10^{-3}$ and the mass fraction will be similarly small, so we can be certain that $B_{m,\text{H}_2\text{O}} \ll 1$ and that the mass transfer rate is very low.

We may apply eqn. (11.74) directly by replacing the wet-bulb temperature by the ice temperature and h_{fg} by h_{sf}

$$T_e - T_{\text{ice}} = \left(\frac{h_{sf}|_{T_{\text{ice}}}}{c_{p,\text{air}} \text{Le}^{2/3}} \right) (m_{\text{H}_2\text{O},s} - m_{\text{H}_2\text{O},e}) \quad (11.74)$$

From Table A.6, $c_p = 1006 \text{ J/kg-K}$ and $\text{Pr} = 0.713$, for air at $260 \text{ K} = -13^\circ\text{C}$. We are given $h_{\text{sg}} = 2.837 \text{ MJ/kg}$. The Lewis number is

$$\text{Le} = \frac{\text{Sc}}{\text{Pr}} = \frac{0.63}{0.713} = 0.884$$

The rest of the solution is an iteration on the following equation:

$$\begin{aligned} T_{\text{ice}} &= T_e - \left(\frac{h_{sf}}{c_{p,\text{air}} \text{Le}^{2/3}} \right) (m_{\text{H}_2\text{O},s} - m_{\text{H}_2\text{O},e}) \\ &= -10 - \left(\frac{2.837 \times 10^6}{(1006)(0.884)^{2/3}} \right) (m_{\text{H}_2\text{O},s} - 7.99 \times 10^{-4}) \end{aligned}$$

We may guess T_{ice} , use that value to compute $m_{\text{H}_2\text{O},s}$ (following Examples 11.3 and 11.6), and then get a new value of T_{ice} by evaluating the right-hand side of the equation.

Guess T_{ice} [$^{\circ}\text{C}$]	Guess T_{ice} [K]	$m_{\text{H}_2\text{O},s}$	Get T_s [$^{\circ}\text{C}$]
-14.0	259.15	0.00112	-10.98
-10.0	263.15	0.00160	-12.45
-12.0	261.15	0.00134	-11.66
-11.8	261.35	0.00136	-11.72
-11.7	261.45	0.00135	-11.75

So, the ice has a temperature of $T_{\text{ice}} \cong 11.7^{\circ}\text{C}$. $\xleftarrow{\text{Answer}}$

We find the mass transfer coefficient from eqn. (11.73)

$$\frac{\bar{h}}{\bar{g}_m c_p} \cong \text{Le}^{2/3} \quad (11.73)$$

so that

$$\bar{g}_m = \frac{\bar{h}}{c_p \text{Le}^{2/3}} = \frac{5}{(1006)(0.884)^{2/3}} = 5.40 \times 10^{-3} \text{ kg/m}^2\text{-s}$$

The mass transfer rate is steady, so the time t to sublime the entire ice cube is found by solving

$$20 \text{ g} = A \bar{g}_m (m_{\text{H}_2\text{O},s} - m_{\text{H}_2\text{O},e}) t$$

$$0.020 \text{ kg} = (8 \times 10^{-4})(5.40 \times 10^{-3})(0.00135 - 7.99 \times 10^{-4}) t$$

from which

$$t = 8.40 \times 10^6 \text{ sec} = 2334 \text{ h} = 97.2 \text{ days} \quad \xleftarrow{\text{Answer}}$$

The ice cube will fully sublime in about 3 months.

Comment: The rate of sublimation depends on the temperature, humidity, and heat transfer coefficient present in any specific freezer. Warmer, drier freezers will tend to reduce the ice cube's lifetime.

PROBLEM 11.34 Bikram Yoga was a strenuous style of yoga done in a room at 38 to 41°C with relative humidity from 20 to 50%. People doing this yoga will generate body heat \dot{Q}_b of 300 to 600 W, which must be removed to avoid heat stroke. Calculate the rate at which one's body can cool under these conditions and compare it to the rate of heat generation.

The body sweats more as its need to cool increases, but the amount of sweat evaporated on the skin depends on air temperature and humidity. Sweating cannot exceed about 2 liters per hour, of which only about half evaporates (the rest will simply drip).

Assume that sweating skin has a temperature of 36°C and an emittance of 0.95, and that an average body surface area is $A_b = 1.8 \text{ m}^2$. Assume that the walls in the yoga studio are at the air temperature. Assume that the lightweight yoga clothing has no thermal effect. Water's vapor pressure can be taken from a steam table or other database. Convection to a person active in still air can be estimated from the following equation, see [11.79]:

$$\bar{h} = (5.7 \text{ W/m}^2\text{K}) \left(\frac{\dot{Q}_b}{(58.1 \text{ W/m}^2) A_b} - 0.8 \right)^{0.39}$$

Note that at high humidity and temperature, some people become overheated and must stop exercising.

SOLUTION

The body exchanges heat with the room by convection, radiation, and evaporation. If the rate of internal generation by exercise, \dot{Q}_b , exceeds the rate of cooling, the body's temperature will rise and potentially cause heat stroke. The three modes of heat transfer may be calculated as

$$\begin{aligned} Q_{\text{conv}} &= A_b \bar{h} (T_{\text{skin}} - T_{\text{air}}) \\ Q_{\text{rad}} &= A_b \varepsilon_{\text{skin}} \sigma (T_b^4 - T_{\text{walls}}^4) \\ Q_{\text{evap}} &= A_b \bar{g}_m (m_{\text{H}_2\text{O,skin}} - m_{\text{H}_2\text{O,air}}) h_{fg} \end{aligned}$$

where

$$\begin{aligned} T_{\text{skin}} &= 36^\circ\text{C} = 309 \text{ K} & T_{\text{walls}} &= T_{\text{air}} \\ \varepsilon_{\text{skin}} &= 0.95 & \sigma &= 5.670 \times 10^{-8} \text{ W/m}^2\text{K}^4 \\ A_b &= 1.8 \text{ m}^2 & h_{fg} &= 2.414 \times 10^6 \text{ J/kg-K} \end{aligned}$$

The mass transfer coefficient can be estimated from the heat transfer coefficient using eqn. (11.73)

$$\bar{g}_m = \frac{\bar{h}}{c_{p,\text{air}} \text{Le}^{2/3}} \quad \text{for} \quad \begin{cases} \text{Le} = 0.847 & \text{see Sect. 11.7} \\ c_{p,\text{air}} = 1007 \text{ J/kg-K} & \text{at } 309 \text{ K} \end{cases}$$

For the two values of \dot{Q}_b , we calculate \bar{h} and \bar{g}_m from the given equation

$$\begin{aligned} \dot{Q}_b = 300 \text{ W} & \quad \begin{cases} \bar{h} = 7.57 \text{ W/m}^2\text{K} \\ \bar{g}_m = 0.008397 \text{ kg/m}^2\text{s} \end{cases} \\ \dot{Q}_b = 600 \text{ W} & \quad \begin{cases} \bar{h} = 10.6 \text{ W/m}^2\text{K} \\ \bar{g}_m = 0.01178 \text{ kg/m}^2\text{s} \end{cases} \end{aligned}$$

Assuming wet skin, we can find the saturation vapor pressure at the skin temperature (36°C) from a steam table or from the [NIST Webbook](#):

$$p_{\text{sat}} = 0.0059479 \text{ MPa} = 5948 \text{ Pa}$$

Then, by following Example 11.3, we find

$$m_{\text{H}_2\text{O,skin}} = 0.03736$$

For the mass fraction of water in the air at a relative humidity (RH) less than 1, the mole fraction is

$$x_{\text{H}_2\text{O,room}} = \frac{p_{\text{H}_2\text{O,room}}}{p_{\text{atm}}} = \frac{\text{RH} \cdot p_{\text{sat}}(T_{\text{room}})}{p_{\text{atm}}} \quad (*)$$

Referring to a steam table

$$p_{\text{sat}} = \begin{cases} 6633 \text{ Pa} & 38^\circ\text{C} \\ 7788 \text{ Pa} & 41^\circ\text{C} \end{cases}$$

and with eqn. (*) and Example 11.3

$$m_{\text{H}_2\text{O,room}} = \begin{cases} 0.00819 & \text{RH } 20\%, 38^\circ\text{C} \\ 0.0243 & \text{RH } 50\%, 41^\circ\text{C} \end{cases}$$

N.B.: The amount of water vapor in the air becomes much higher with seemingly small increases in the temperature and RH.

We must also consider the maximum rate of sweat evaporation, 1 L/h. The associated heat removal is

$$\begin{aligned} Q_{\text{evap,max}} &= \rho_{\text{water}} h_{fg} (1 \text{ L/h}) (0.001 \text{ m}^3/\text{L}) (1 \text{ h}/3600 \text{ s}) \\ &= (993.6)(2.414 \times 10^6)(0.001)(3600)^{-1} = 666.3 \text{ W} \end{aligned}$$

We may now calculate all heat transfers for each of the four conditions, as in the table below. When the evaporative heat transfer exceeded $Q_{\text{evap,max}}$, we replaced it by 666.3 W.

Mode	20%, 38°C		50%, 41°C	
	300 W	600 W	300 W	600 W
Q_{rad}	-23.1	-23.1	-58.7	-58.7
Q_{conv}	-27.3	-38.2	-68.1	-95.4
Q_{evap}	666.3	666.3	476.5	666.3
Q_{total}	616.0	604.9	350.9	512.0

Can one stay cool? Reading from left to right on the bottom row, in the first case a person generating 300 W has twice the needed cooling power available and will not overheat. In the second case, the person can barely stay cool enough (and note that these estimates have significant uncertainty!). In the third case, the person can stay cooling, but again only barely. In the fourth case, the person will not be able to remain cool and would likely need to stop and lie down.

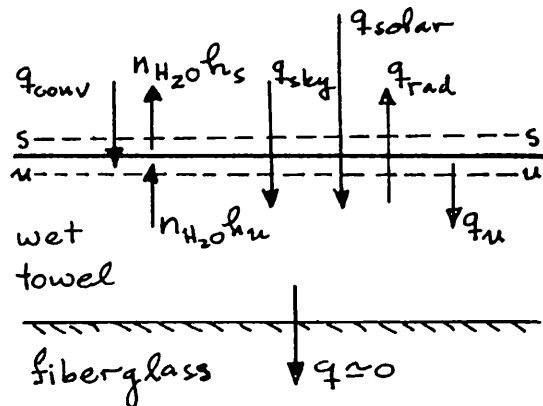
- 11.35 Biff Harwell has taken Deb sailing. Deb and Biff's towel fall into the harbor. Biff rescues them both from a passing dolphin, and then spreads his wet towel out to dry on the fiberglass foredeck of the boat. The incident solar radiation is 1050 W/m^2 ; the ambient air is at 31°C with $m_{\text{H}_2\text{O}} = 0.017$; the wind speed is 8 knots relative to the boat (1 knot = 1.151 mph); $\epsilon_{\text{towel}} = \alpha_{\text{towel}} = 1$; and the sky has the properties of a black body at 280 K. The towel is 3 ft in the windward direction and 2 ft wide. Help Biff to figure out how rapidly (in kg/s) water evaporates from the towel. (Help Biff to understand why Deb won't date him anymore.)

Construct an energy balance on the towel:

s-u surfaces: $q_{\text{conv}} = n_{\text{H}_2\text{O}} h_{fg}$
 $+ q_u$

u and below: $q_{\text{solar}} + q_{\text{sky}} + q_u$
 $= q_{\text{rad}}$

Fiberglass is a poor conductor, so the heat conducted from the bottom of the towel is ≈ 0 .



Combining the two balances, we have:

$$q_{\text{solar}} + q_{\text{sky}} - q_{\text{rad}} + q_{\text{conv}} = n_{\text{H}_2\text{O},s} h_{fg}$$

In this eq'n:

$$q_{\text{solar}} = 1050 \text{ W/m}^2, \quad q_{\text{sky}} = \sigma T_{\text{sky}}^4, \quad q_{\text{rad}} = \sigma T_s^4$$

and we have taken $\epsilon = \alpha = 1$ for the towel.

To begin the calculations, let's assume low-rates and properties of pure air at a film temperature $T_f = 36^\circ\text{C}$

(i.e. $T_s = 41^\circ\text{C}$): $\rho_f = 1.142 \text{ kg/m}^3$, $k_f = 0.02680 \text{ W/m}\cdot\text{K}$,

$$\mu_f = 1.895 \times 10^{-5} \text{ kg/m}\cdot\text{s}, \quad \text{Pr}_f = 0.710,$$

$$D_{\text{air-water}} = 2.697 \times 10^{-5} \text{ m}^2/\text{s}, \quad \text{Sc}_f = 0.615$$

The wind speed is $U = 8(1.151)(5280)(0.3048)/(3600) = 4.116 \text{ m/s}$.

The Reynolds number is $Re_L = 2.27 \times 10^5$ (laminar) so

$$\overline{Nu}_L = 0.664 Re_L^{1/2} \text{Pr}_f^{1/3}. \quad \text{From this, } \overline{Nu}_L = 282.2 \text{ and}$$

$$\overline{Nu}_{m,L} = 269.0; \quad \text{Solving, we have } \bar{h}^* = 8.271 \text{ W/m}^2\cdot\text{K} \text{ and}$$

$$\bar{q}_m^* = 0.009061 \text{ kg/m}^2\cdot\text{s}.$$

In terms of the unknown, T_s , the low rate energy balance is

$$(1398 \text{ W/m}^2) - \sigma T_s^4 + \bar{h}^*(T_e - T_s) = \bar{q}_m^* B_m h_{fg}$$

where $T_e = 304.2^\circ\text{K}$ and B_m and h_{fg} depend on T_s .

Solve by iteration on T_s :

$$\bar{h}^*(T_s - 304.2) = 1398 - \sigma T_s^4 - \bar{q}_m^* B_m h_{fg}$$

Guess T_s , evaluate the RHS with a steam table, and solve for the value of T_s implied on the LHS:

Guess T_s	$m_{\text{H}_2\text{O},s}$	h_{fg} (kJ/kg)	B_m	Implied T_s
314.2°K	0.04924	2404.3	0.03391	317.1°K
315.2	0.05200	2401.9	0.03692	308.5
314.7	0.05062	2403.1	0.03541	312.8

The surface temperature is slightly higher than 41.0°C and slightly less than 41.5°C . Evaluate the evaporation rate at 41.3°C : $m_{\text{H}_2\text{O},s} = 0.05007$, $h_{fg} = 2403.6 \text{ kJ/kg}$, $B_m = 0.03481$; implied $T_s = 41.3^\circ\text{C}$. $\dot{m}_{\text{H}_2\text{O},s} = (0.009061) \cdot (0.03481) = 0.0003154 \text{ kg/m}^2\cdot\text{s}$.

Check the assumptions: $\ln(1+B_m)/B_m = 0.983$, low rates do apply; $m_{\text{H}_2\text{O},f} = 0.0335$ - only changes will be for ρ , μ , Sc but since both μ and ρ decrease the effect on ν is small: the present property values are adequate for engineering purposes. The overall evaporation rate is $\dot{m} = 3(0.3048)(2)(0.3048)(\dot{m}_{\text{H}_2\text{O},s}) = \underline{1.76 \times 10^{-4} \text{ kg/s}}$ ←

PROBLEM 11.36 Small water droplets evaporate rapidly dry air. Suppose that a droplet is placed in a room at 30°C, 40% RH, and 1 atm. Calculate the lifetime of the droplet if its initial diameter is 0.2, 0.5, 1, 2, and 5 μm .

SOLUTION From Example 11.14, we know that the droplet cools rapidly to its wet bulb temperature and then evaporates until it vanishes, following the D^2 law, eqn. (11.75). In particular, $m_{\text{H}_2\text{O},s}$ is the mass fraction of water vapor adjacent to the droplet at the wet bulb temperature.

Therefore, the first step in this problem is to find $T_{\text{wet bulb}}$. We can do this the hard way, by solving eqn. (11.74), while calculating the mass fraction as in Example 11.3 for $\text{RH} = p_{\text{H}_2\text{O},e}/p_{\text{sat}}(T_e)$ —or we can do this the easy way, by using a psychrometric chart or psychrometric calculator. The author has written many problem solutions already, so he chooses the easy way:

$$T_{\text{wet bulb}} = 20.0^\circ\text{C} \text{ and } \gamma = 0.0106 \text{ kg H}_2\text{O/kg dry air}$$

Note that the moisture ratio on a psychrometric chart is for the dry bulb condition, not the wet bulb condition. Some algebra relates γ to $m_{\text{H}_2\text{O},e}$

$$m_{\text{H}_2\text{O},e} = \rho_{\text{H}_2\text{O}}/\rho = 1/(1 + \rho_{\text{dry air}}/\rho_{\text{H}_2\text{O}}) = 1/(1 + 1/\gamma) = 0.01049$$

We are not completely off the hook, however, as we still need to find $m_{\text{H}_2\text{O},s}$, which we do as in Example 11.3. With a steam table, $p_{\text{sat}}(20.0^\circ\text{C}) = 2339.3 \text{ Pa}$; then eqn. (11.47) gives $x_{\text{H}_2\text{O},s} = 0.02309$, and eqn. (11.48) gives $m_{\text{H}_2\text{O},s} = 0.01449$.

Now we may turn our attention to eqn. (11.75). Call the droplet's lifetime τ , so that $D(\tau) = 0$. Then, by rearranging eqn. (11.75):

$$\tau = \frac{\rho_l D_0^2}{8\rho \mathcal{D}_{\text{H}_2\text{O},\text{gas}}(m_{\text{H}_2\text{O},s} - m_{\text{H}_2\text{O},e})}$$

We need two densities and a diffusion coefficient. Liquid water at 20°C has $\rho_l = 998.2 \text{ kg/m}^3$. At water mass fractions near 1%, the density of air is close to that of dry air. We can easily be precise, however, by using eqn. (11.8) and the ideal gas law:

$$\begin{aligned} \rho &= \frac{p}{R^\circ T} M_{\text{mixture}} \\ &= \frac{(101325)}{(8314.5)(293.15)} [(0.02309)(18.02) + (1 - 0.02309)(28.96)] = 1.193 \text{ kg/m}^3 \end{aligned}$$

The diffusion coefficient may be computed from eqn. (11.36):

$$\mathcal{D}_{\text{H}_2\text{O},\text{air}} = 1.87 \times 10^{-10} \left(\frac{T^{2.072}}{p} \right) = 1.87 \times 10^{-10} \left(\frac{(293.15)^{2.072}}{1} \right) = 2.42 \times 10^{-5} \text{ m}^2/\text{s}$$

Putting all this together, for τ in seconds and D_0 in meters,

$$\begin{aligned} \tau &= \left[\frac{998.2}{8(1.193)(2.42 \times 10^{-5})(0.01449 - 0.01049)} \right] D_0^2 \\ &= 1.081 \times 10^9 D_0^2 \end{aligned}$$

which looks very large until we notice that $D_0^2 = \mathcal{O}(10^{-12} \text{ m}^2)$! The results are summarized below.

D_0 [μm]	0.2	0.5	1.0	2.0	5.0
τ [ms]	0.0432	0.270	1.08	4.32	27.0

Comment: Small droplets do not last very long! (Unless the air is quite humid!)

PROBLEM 11.37 A Couette flow (or stagnant film) model of a laminar boundary layer neglects streamwise derivatives locally, so that the velocity varies in y , but not x , from $u = 0$ at the wall to u_∞ at the edge of the b.l., $y = \delta$. The b.l. thickness δ is assumed increase only slowly with x . (a) Show that $u/u_\infty = y/\delta$ in laminar flow. (b) Calculate skin friction coefficient, C_f , the temperature profile, $T(y)$, and the Nusselt number, Nu_x , in terms of δ and δ_t . (c) Using eqns. (6.31b) and (6.55), show that the laminar Couette flow model results in estimates of $C_f(x)$ and Nu_x that differ from eqns. (6.33) and (6.58) by a constant on the order of one.

SOLUTION

a) We start with the continuity equation, eqn. (6.11a), neglecting the x -derivative:

$$u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = 0$$

This equation gives $v(y) = \text{constant} = 0$, since $v = 0$ at the wall. The momentum equation, eqn. (6.15), then becomes

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} = 0$$

which is easily solved for

$$u(y) = a + by = u_{\text{wall}} + (u_\infty - u_{\text{wall}}) \frac{y}{\delta} = u_\infty \frac{y}{\delta} \quad \leftarrow \text{Answer}$$

b) The wall shear stress is

$$\tau_w = \mu \left. \frac{\partial u}{\partial y} \right|_{y=0} = \frac{\mu u_\infty}{\delta}$$

so that

$$C_f(x) = \frac{\tau_w}{\rho u_\infty^2 / 2} = \frac{2x}{\delta Re_x} \quad \leftarrow \text{Answer}$$

The temperature profile satisfies eqn. (6.40), which simplifies like the momentum equation:

$$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} = 0$$

This equation can easily be solved for

$$T(y) = a + by = T_w + (T_\infty - T_w) \frac{y}{\delta_t}$$

in which δ_t the thermal boundary layer thickness. Then

$$h = \frac{-k \left. \frac{\partial T}{\partial y} \right|_{y=0}}{(T_w - T_\infty)} = \frac{k}{\delta_t}$$

and

$$Nu_x = \frac{hx}{k} = \frac{x}{\delta_t} \quad \leftarrow \text{Answer}$$

c) Now we can substitute the expressions for the boundary layer thicknesses from eqns. (6.31b) and (6.55):

$$C_f(x) = \frac{2x}{\delta \text{Re}_x} = \frac{2\sqrt{\text{Re}_x}}{4.64 \text{Re}_x} = \frac{0.431}{\sqrt{\text{Re}_x}} \quad \leftarrow \text{Answer}$$

$$\text{Nu}_x = \frac{x}{\delta_t} = \frac{x}{\delta} \frac{\delta}{\delta_t} = \frac{\sqrt{\text{Re}_x}}{4.64} \frac{\delta}{\delta_t} = 0.216 \text{Re}_x^{1/2} \text{Pr}^{1/3} \quad \leftarrow \text{Answer}$$

Comment: The coefficients are low by about 2/3 relative to eqns. (6.33) and (6.58) because the effective boundary thickness of the model is about 1/3 too large. In Section 11.8, this difference is accounted for by eqn. (11.80), which may be regarded as *defining* δ_c to provide the correct g_m^* for either laminar or turbulent flow.

PROBLEM 11.38 (a) What are the largest and smallest values of the mass transfer driving force, $B_{m,2}$? (b) Plot the blowing factor as a function of $B_{m,2}$. Indicate on your graph the regions of blowing, suction, and low-rate mass transfer.

SOLUTION

a) The mass transfer driving force, $B_{m,2}$, is

$$B_{m,2} = \frac{m_{2,s} - m_{2,e}}{1 - m_{2,s}}$$

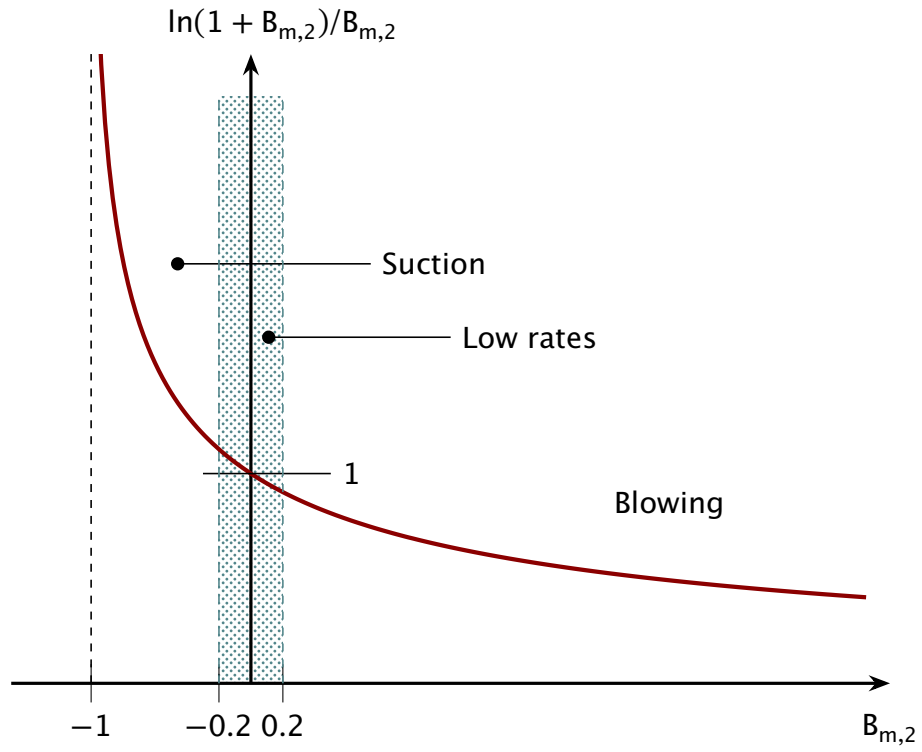
Let us first assume that $m_{2,s} \geq m_{2,e}$. Then, as $m_{2,s} \rightarrow 1$, $B_{m,2} \rightarrow \infty$. If $m_{2,s} \rightarrow m_{2,e}$, then $B_{m,2} \rightarrow 0$. Now assume that $m_{2,s} < m_{2,e}$. If $m_{2,s} \rightarrow 0$, $B_{m,2} \rightarrow -m_{2,e} \geq -1$. Therefore,

$$-1 \leq B_{m,2} \leq \infty \quad \leftarrow \text{Answer}$$

b) The blowing factor is $\text{BF} = \ln(1 + B_{m,2})/B_{m,2}$. As $B_{m,2} \rightarrow \infty$, $\text{BF} \rightarrow 0$. As $B_{m,2} \rightarrow -1^+$, $\text{BF} \rightarrow +\infty$. For $|B_{m,2}|$ small, $\ln(1 + B_{m,2}) \sim B_{m,2} - B_{m,2}^2/2 + \dots$, so $\text{BF} \sim 1 - B_{m,2}/2 + \dots$, or succinctly

$$\frac{\ln(1 + B_{m,2})}{B_{m,2}} \rightarrow \begin{cases} 0, & B_{m,2} \rightarrow \infty \\ 1 - B_{m,2}/2 + \dots, & |B_{m,2}| \rightarrow 0 \\ \infty, & B_{m,2} \rightarrow -1^+ \end{cases}$$

The plot is as shown below.



11.39 (a) Perform the integration to obtain eqn.(11.85). Then take the derivative and the limit needed to get eqns. (11.86) and (11.87).

(a) We have $\frac{d}{dy} \left(-k \frac{dT}{dy} + n_{i,s} c_{p,i} T \right) = 0$ which can be integrated once immediately:

$$-k \frac{dT}{dy} + n_{i,s} c_{p,i} T = C, \text{ an unknown constant}$$

Rearrange and integrate:

$$\int_0^y dy = y = \int_{T_s}^T \frac{(-k) dT}{C - n_{i,s} c_{p,i} T} = \frac{k}{n_{i,s} c_{p,i}} \ln \left(\frac{C - n_{i,s} c_{p,i} T}{C - n_{i,s} c_{p,i} T_s} \right)$$

or

$$(*) \quad \exp \left(\frac{y n_{i,s} c_{p,i}}{k} \right) = \frac{\mu - T}{\mu - T_s}, \quad \text{where the constant } \mu \text{ is } C/n_{i,s} c_{p,i} \text{ for convenience}$$

Now apply the b.c. $T(y = \delta_t) = T_e$:

$$\frac{\mu - T_e}{\mu - T_s} = \exp \left(\frac{\delta_t n_{i,s} c_{p,i}}{k} \right) = \eta, \quad \text{for convenience define } \eta \text{ as shown.}$$

Thus, $\mu = (T_e - T_s \eta) / (1 - \eta)$ and we have found the unknown constant μ (i.e. C). Substitute for μ in (*) and rearrange:

$$\begin{aligned} \frac{(T_e - T_s \eta) - T(1 - \eta)}{(T_e - T_s \eta) - T_s(1 - \eta)} &= \frac{(T - T_s)\eta - (T - T_e)}{(T_e - T_s)} \\ &= \frac{(T - T_s)(\eta - 1)}{(T_e - T_s)} + 1 = \exp \left(\frac{y n_{i,s} c_{p,i}}{k} \right) \end{aligned}$$

Now substitute for η and rearrange to obtain (11.85):

$$\boxed{\left(\frac{T - T_s}{T_e - T_s} \right) = \frac{\exp \left(\frac{y n_{i,s} c_{p,i}}{k} \right) - 1}{\exp \left(\frac{\delta_t n_{i,s} c_{p,i}}{k} \right) - 1}}$$

To get h , write:

$$h = +k \frac{d}{dy} \left(\frac{T - T_s}{T_e - T_s} \right) \Big|_{y=0} = \frac{n_{i,s} c_{p,i} \cdot \overset{1}{k/k}}{\exp\left(\frac{\delta_t n_{i,s} c_{p,i}}{k}\right) - 1}$$

Then use L'Hospital's rule to get h^* :

$$h^* = \lim_{n_{i,s} \rightarrow 0} h = \lim_{n_{i,s} \rightarrow 0} \frac{c_{p,i}}{(\delta_t c_{p,i})/k \cdot \exp(\delta_t n_{i,s} c_{p,i}/k)} = \frac{k}{\delta_t}$$

PROBLEM 11.40 (a) Derive eqn. (11.98) from eqn. (11.97). (b) In a test of a scramjet combustor, gas is injected through a porous section of the combustor wall [1]. The gas velocity is 980 m/s. As a result of viscous friction and gas compression, the temperature of an adiabatic section of the wall would be 1048 K: use this temperature as if it were the freestream temperature. The heat transfer coefficient without injection is $h^* = 720 \text{ W/m}^2\text{K}$. The injected gas is drawn from a reservoir at 350 K at a mass flux of $n_{i,s} = 0.3 \text{ kg/m}^2\text{s}$. What is the wall temperature T_s if the gas is He, Ar, or N_2 ? (c) Plot T_s for each gas if $0 \leq n_{i,s} \leq 1.5 \text{ kg/m}^2\text{s}$.

SOLUTION

a) Substitute for h in eqn. (11.98) with eqn. (11.88) and divide through by $n_{i,s}c_{p,i}$:

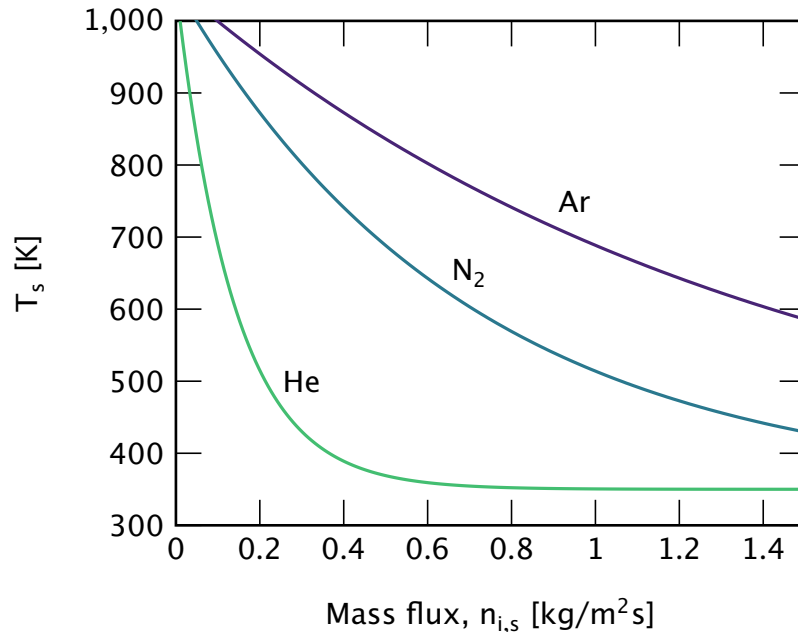
$$T_s = \frac{T_e + T_r[\exp(n_{i,s}c_{p,i}/h^*) - 1]}{1 + [\exp(n_{i,s}c_{p,i}/h^*) - 1]}$$

$$= T_r + (T_e - T_r) \exp(-n_{i,s}c_{p,i}/h^*) \quad \leftarrow \text{Answer}$$

b) The specific heat capacity does not depend strongly on either p or T , so we will overlook variations in the thermodynamic state, using 1 atm values from Table A.6 at 350 K:

$$c_{p,i} = \begin{cases} 521 \text{ J/kgK} & \text{Ar} \\ 1043 \text{ J/kgK} & \text{N}_2 \\ 5193 \text{ J/kgK} & \text{He} \end{cases} \quad \frac{n_{i,s}c_{p,i}}{h^*} = \begin{cases} 0.217 & \text{Ar} \\ 0.435 & \text{N}_2 \\ 2.164 & \text{He} \end{cases} \quad T_s = \begin{cases} 912 \text{ K} & \text{Ar} \\ 802 \text{ K} & \text{N}_2 \\ 430 \text{ K} & \text{He} \end{cases} \quad \leftarrow \text{Answer}$$

c)



REFERENCE:

[1] T. Langener, J. von Wolfersdorf, and J. Steelant, “Experimental Investigations on Transpiration Cooling for Scramjet Applications Using Different Coolants,” *AIAA J.*, **49**:7:1409–1419, 2011.

PROBLEM 11.41 Dry ice (solid CO₂) is used to cool medical supplies transported by a small plane to a remote village in Alaska. A roughly spherical chunk of dry ice, 5 cm in diameter, falls from the plane through air at 5°C. It reaches a terminal velocity of 40 m/s. What are the temperature and sublimation rate of the dry ice, assuming steady conditions? The latent heat of sublimation is about 590 kJ/kg and $\log_{10}(p_v \text{ bar}) = 6.81228 - 1301.679/(T \text{ K} - 3.494)$. The surface temperature will be well below the solid-vapor equilibrium temperature of CO₂ at 1 atm, which is -78.5°C. Use this correlation for forced convection over a sphere in air at room temperature

$$\overline{\text{Nu}}_D = 2 + 0.493 \text{Re}_D^{1/2} + 0.0011 \text{Re}_D$$

for $7800 \leq \text{Re}_D \leq 2.9 \times 10^5$ [1], and approximate the Prandtl number dependence. Neglect heat conduction into the ice. *Hint:* First use the properties of pure air, and then correct the properties if necessary.

SOLUTION This calculation is analogous to a wet-bulb temperature calculation if heat conduction, q_u , into the dry ice is neglected. Heat conduction would reduce the amount of energy available for sublimation at the surface, so that when we neglect conduction we obtain an upper bound on the sublimation rate and a lower bound on the surface temperature.

For a property reference state, we may first use the properties of pure air. We don't know the surface temperature, although it will be below -78.5°C. We can pick a film temperature that is easy to interpolate in Table A.6, say $T_f = 225 \text{ K}$ (which corresponds to $T_s = -101.3^\circ\text{C}$).

From Table A.6, for air: $k = 0.0206 \text{ W/m}\cdot\text{K}$, $\nu = 0.944 \times 10^{-5} \text{ m}^2/\text{s}$, $\text{Pr} = 0.721$, $\rho = 1.57 \text{ kg/m}^3$. We find the diffusivity from eqn. (11.108) with $\sigma_{AB} = 3.785 \text{ \AA}$, $\epsilon_{AB}/k_B = 129.4$, $\Omega_D(1.739) = 1.132$:

$$D_{\text{CO}_2, \text{air}} = 0.9254 \times 10^{-5} \text{ m}^2/\text{s} \quad \text{so} \quad \text{Sc} = 1.02$$

In the absence of conduction, the heat convected to the surface will balance the latent heat of sublimation. Our energy balance is

$$\begin{aligned} q_{\text{conv}} &= h_{sf, \text{CO}_2} n_{\text{CO}_2, s} \\ \bar{h}(T_{\text{air}} - T_s) &= h_{sf, \text{CO}_2} \bar{g}_m^* \ln(1 + B_{m, \text{CO}_2}) \end{aligned} \quad (*)$$

The Reynolds number is

$$\text{Re}_D = \frac{(40)(0.05)}{0.944 \times 10^{-5}} = 2.12 \times 10^5$$

and so $\overline{\text{Nu}}_D = 462$, from which

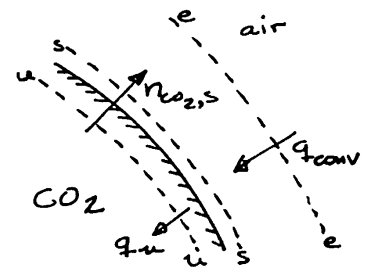
$$\bar{h}^* = (462)(0.0206)/(0.05) = 190.3 \text{ W/m}\cdot\text{K}$$

Now we face a minor problem: the correlation is for heat transfer in air at $\text{Pr} = 0.707$ or so. The Prandtl number dependence is likely to be $\text{Pr}^{1/3}$ or so. Thus, the difference for $\text{Pr} = 0.721$ is negligible. On the other hand, to use the analogy of heat and mass transfer, we must correct to $\text{Sc} = 1.02$, so we multiply the Nusselt number by $(1.02/0.707)^{1/3} = 1.13$ to find $\overline{\text{Nu}}_{m, D} = 522$ from which

$$\bar{g}_m^* = (522)(1.57)(0.9254 \times 10^{-5})/(0.05) = 0.1517 \text{ kg/m}^2\text{s}$$

Now, for the guessed surface temperature $T_s = -101.3^\circ\text{C} = 171.9 \text{ K}$, the vapor pressure is

$$\log_{10}(p_v \text{ bar}) = 6.81228 - 1301.679/(171.9 - 3.494) = -0.9171 \quad \text{or} \quad p_v = 0.1210 \text{ bar}$$



which gives $x_{\text{CO}_2,s} = 0.1194$, with eqn. (11.15) and then $m_{\text{CO}_2,s} = 0.1708$, with eqn. (11.9). The mass transfer driving force is

$$B_{m,\text{CO}_2} = \frac{0.1708 - 0}{1 - 0.1708} = 0.206$$

This value is at the edge of the low-rate mass transfer regime, but we can still apply the high rate equations. The right-hand side of eqn. (*) provides

$$n_{\text{CO}_2,s} = \bar{g}_m^* \ln(1 + B_{m,\text{CO}_2}) = 0.02842 \text{ kg/m}^2\text{s}$$

and eqn. (11.88) with $c_{p,\text{CO}_2} \cong 780 \text{ J/kgK}$ leads to $\bar{h} = 179.4 \text{ W/m}^2\text{K}$. Then we use eqn. (*) to find

$$T_s = T_{\text{air}} - \frac{h_{sf,\text{CO}_2} n_{\text{CO}_2,s}}{\bar{h}} = 5 + \frac{(5.90 \times 10^5)(0.02842)}{179.4} = -88.5^\circ\text{C}$$

(It would make sense to *put these equations into a spreadsheet to do the [tedious] iterations needs to find the solution.* However, as the author is old school, a hand iteration follows.)

Some caution is needed in making the next guess because the vapor pressure rises exponentially with temperature: a big temperature change will cause a massive increase in vapor pressure, but our two temperature estimates are close enough that a big change does not seem appropriate. Instead, we will repeat the calculation with $T_s = -97^\circ\text{C} = 176.2 \text{ K}$. Then

$$\log_{10}(p_v \text{ bar}) = 6.81228 - 1301.679/(176.2 - 3.494) = -0.7247 \quad \text{or} \quad p_v = 0.1885 \text{ bar}$$

which gives $x_{\text{CO}_2,s} = 0.1860$ and $m_{\text{CO}_2,s} = 0.2578$. The mass transfer driving force is

$$B_{m,\text{CO}_2} = \frac{0.2578 - 0}{1 - 0.2578} = 0.3473$$

Then, $n_{\text{CO}_2,s} = 0.04522 \text{ kg/m}^2\text{s}$, $\bar{h} = 173.2 \text{ W/m}^2\text{K}$, and we solve as before:

$$T_s = 5 + \frac{(5.90 \times 10^5)(0.04522)}{173.2} = -149.0^\circ\text{C}$$

The calculation is obviously *very unstable*. So we need to guess a lower value, say $T_s = -99^\circ\text{C}$. Proceeding as before, but with $T_s = -99^\circ\text{C}$, we find $x_{\text{CO}_2,s} = 0.1510$, $m_{\text{CO}_2,s} = 0.2128$, $B_{m,\text{CO}_2} = 0.2703$, $n_{\text{CO}_2,s} = 0.03630 \text{ kg/m}^2\text{s}$, $\bar{h} = 176.5 \text{ W/m}^2\text{K}$, and we solve as before:

$$T_s = 5 + \frac{(5.90 \times 10^5)(0.03630)}{176.5} = -116.3^\circ\text{C}$$

At this point, we may reasonably conclude that $-99^\circ\text{C} < T_s < -101.3^\circ\text{C}$. Further iteration does not make sense, given other approximations and uncertainties. We may estimate the sublimation rate as the average of the values computed at these two temperatures:

$$T_s \cong -100^\circ\text{C} \quad \longleftarrow \text{Answer}$$

$$n_{\text{CO}_2,s} = (0.02842 + 0.03630)/2 \cong 0.032 \text{ kg/m}^2\text{s} \quad \longleftarrow \text{Answer}$$

The final temperature is very close to our guessed film temperature. The film composition is about 10 wt% CO_2 . Given this low amount and the relative similar of many air and CO_2 properties, adjustment of the property reference will not significantly improve the accuracy of the solution.

Comment 1: The ambiguity in the Prandtl number dependence of the Nusselt number is a real-world problem. Available correlations that include the Prandtl number do not extend to such a high Reynolds number [1]; and those correlations, when extrapolated for air, give a value well below the

very accurate correlation for air from Ref. [1]. Extrapolating the Prandtl or Schmidt number from 0.7 to 1 is likely to provide better accuracy than extrapolating the Reynolds number.

Comment 2: The conduction heat flux at the surface of the ice may be small compared to the convective heat flux outside, as a result of the high temperature difference and the very high value of \bar{h} . We can calculate the conduction flux for $Fo > 0.2$ by differentiating eqn. (5.42) with respect to r (in f_1) for $Fo > 0.2$. Skipping the details, this calculation leads to

$$q_u = -k \left. \frac{dT}{dr} \right|_{r_o} = -\frac{k\Delta T A_1}{r_o} [\cos(\hat{\lambda}_1) - \sin(\hat{\lambda}_1)/\hat{\lambda}_1] \exp(-\hat{\lambda}_1^2 Fo)$$

We lack property data for dry ice, but can crudely approximate $k \approx 1$ W/m·K and $\alpha \approx 10^{-6}$ m²/s. This makes $Bi \approx 4.5$, so that $\hat{\lambda}_1 \approx 2.5$ and $A_1 \approx 1.75$. Hence,

$$q_u \approx 7315 \exp(-6.25 Fo) \text{ W/m}^2$$

Since the ice is falling fast, let's consider only $Fo = 0.2$. That's $t = (0.2)r_o^2/\alpha \approx 125$ s. The ice will have fallen 5000 m at terminal speed by then, so it's very likely to reach the ground within this time frame. In any case, the flux at this time is:

$$q_u \approx 2100 \text{ W/m}^2$$

The convective heat flux is $\bar{h}\Delta T = 178(5 + 100) = 18.7$ kW/m, which is almost 9 times larger. We conclude that conduction is negligible by the end of a long fall, but that it will be larger and perhaps significant in the early stages of the fall.

REFERENCES:

[1] J. B. Will, N. P. Kruyt, C. H. Venner, "An experimental study of forced convective heat transfer from smooth, solid spheres," *Int. J. Heat Mass Transfer*, **109**:1059–1067, 2017, doi:10.1016/j.ijheat-masstransfer.2017.02.018.

[2] Sublimation data are from NIST, <https://webbook.nist.gov>, accessed 9 February 2024.

- 11.42 Steam condenses on a 25-cm-high, cold vertical wall in a low-pressure condenser unit. The wall is isothermal at 25°C, and the ambient pressure is 8000 Pa. Air has leaked into the unit and reached a mass fraction of 0.04. The steam-air mixture is at 45°C and is blown downward past the wall at 8 m/s. (a) Estimate the rate of condensation on the wall. (b) Compare the result of part (a) to condensation without air in the steam. What do you conclude?

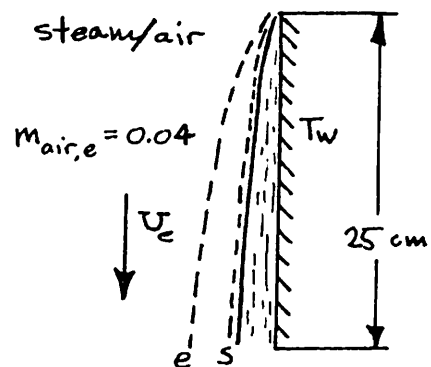
(a)

The energy balance for the wall is:

$$\bar{h}(T_e - T_s) - \bar{n}_{\text{H}_2\text{O},s} h_{fg} = \left(\frac{k}{\delta}\right)(T_s - T_w)$$

where $\bar{n}_{\text{H}_2\text{O},s} = \bar{q}_{m,\text{H}_2\text{O}} \cdot \bar{B}_{m,\text{H}_2\text{O}} < 0$

and $\left(\frac{k}{\delta}\right) = \bar{h}_{\text{Nusselt}}$ from eqn (8.62b)



This condensation problem will be characterized by high rates of suction which will tend to concentrate air near the liquid surface.

First evaluate \bar{h}_{Nusselt} . Guess a property reference temperature of 300 K for the liquid: $\rho_f = 996.6 \text{ kg/m}^3$, $k = 0.6084 \text{ W/m-K}$, $\mu = 8.23 \times 10^{-4} \text{ kg/m-s}$, $h_{fg} = 2438.0 \text{ kJ/kg}$.

Approximate: $\rho_f - \rho_g \approx \rho_f$, $h'_{fg} \approx h_{fg}$ since ρ_g and ΔT are small. Substitute into eqn (8.62b)

$$\text{Nu}_L = 4.919 \times 10^3 (T_s - T_w)^{-1/4}$$

or $\bar{h}_{\text{Nus.}} = 1.197 \times 10^4 (T_s - T_w)^{-1/4}$

Next evaluate \bar{h}^* for the vapor flow. Use a property reference temperature of 315 K and take the composition reference state as pure steam (close to saturation)

$$u_{\text{film}} \sim 0.03 \text{ m/s}$$

From Table A.5:

$$\rho = 0.05766 \text{ kg/m}^3$$

$$c_p = 1935 \text{ J/kg-K}$$

$$k = 0.01975 \text{ W/m-K}$$

$$\mu = 1.037 \times 10^{-5} \text{ kg/m-s}$$

$$\text{Pr} = 1.02$$

The Reynolds number is $Re_L = 11,126$: laminar.

Calculate \bar{h}^* from equation (6.68) : $\bar{h}^* = 5.570 \text{ W/m}^2\text{-K}$.

Finally, calculate \bar{g}_m^* . Use the same property ref. state.

From (11.36), $D_{\text{H}_2\text{O-air}} = 3.556 \times 10^{-4} \text{ m}^2/\text{s}$. Calculate $\text{Sc} = 0.506$.

Using (6.68) with the analogy of heat and mass transfer, Nu_m

= 121.6. Solving: $\bar{g}_m^* = 4.577 \times 10^{-3} \text{ kg/m}^2\text{-s}$.

The operating equations are:

$$\bar{h} (318.2 - \bar{T}_s) - \bar{n}_{\text{H}_2\text{O},s} (2.438 \times 10^6) = 1.197 \times 10^4 (\bar{T}_s - 298.2)^{3/4}$$

$$\bar{n}_{\text{H}_2\text{O},s} = (4.577 \times 10^{-3}) \ln(1 + B_m)$$

$$\bar{h} = (\bar{n}_{\text{H}_2\text{O},s} c_{p,\text{H}_2\text{O}}) / [\exp(\bar{n}_{\text{H}_2\text{O},s} c_{p,\text{H}_2\text{O}} / 5.570) - 1]$$

+ Steam table for $m_{\text{H}_2\text{O},s}(T_s)$. We solve iteratively for T_s : Use eqn. (11.48) for the mass fraction. The overall calculation is best done with a spreadsheet.

T_s (°C)	$m_{\text{H}_2\text{O},s}$	$B_{m,\text{H}_2\text{O}}$	$\bar{n}_{\text{H}_2\text{O},s}$ (kg/m ² -s)	\bar{h} (W/m ² -K)	\bar{T}_s (°C)
30.0	0.4131	-0.9318	-0.01229	24.13	28.45
28.5	0.3712	-0.9364	-0.01261	24.71	28.58
28.6	0.3775	-0.9357	-0.01256	24.62	28.56

It appears that T_s is about **28.5 degC**. This implies a film temperature of 310 K and film composition of 66.9 wt% H₂O, compared to 315 K and 100 wt% for our property ref. state.

An additional iteration on the property reference state increases g_m^* by about 5%, but has little effect on h^* . The net result is to raise T_s to 28.8 degC (negligible), but also to increase the mass flux to about $-0.0131 \text{ kg/m}^2\text{s}$.

$$\text{Condensation rate, } \underline{-n_{\text{H}_2\text{O},s}} = 0.013 \frac{\text{kg}}{\text{m}^2\text{-s}} \leftarrow$$

(b) Without air, the liquid surface will be at $T_{\text{set}} (8000 \text{ Pa}) = 41.51^\circ\text{C}$. The film temperature is $T_f = 306^\circ\text{K}$, close enough to our previous calculation:

$$\begin{aligned} \dot{m}'' &= (h_{fg})^{-1} \bar{h}_{\text{Nusselt}} (T_{\text{set}} - T_w) \\ &= (24380 \times 10^3)^{-1} (1.197 \times 10^4) (41.51 - 25.0)^{3/4} \\ &= \underline{0.04021 \text{ kg/m}^2\text{-s}} \leftarrow \end{aligned}$$

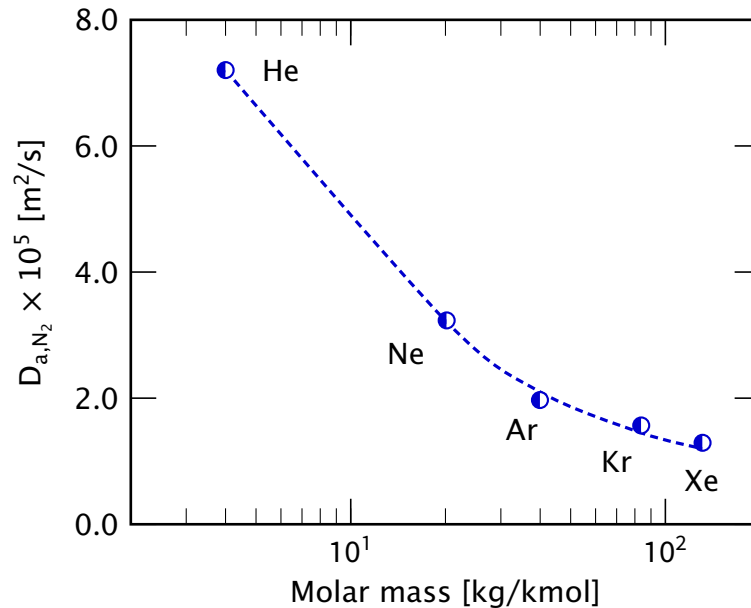
This small amount of air cuts condensation by 69 %!
Air leaks are a very serious problem for condensers.

PROBLEM 11.43 (a) Compute the binary diffusivity of each of the noble gases when they are individually mixed with nitrogen gas at 1 atm and 300 K. Plot the results as a function of the molar mass of the noble gas. What do you conclude? (b) Consider the addition of a small amount of helium, $x_{\text{He}} = 0.04$, to a mixture of nitrogen, $x_{\text{N}_2} = 0.48$, and argon, $x_{\text{Ar}} = 0.48$. Compute $\mathcal{D}_{\text{He},m}$ and compare it with $\mathcal{D}_{\text{Ar},m}$. Note that the increased concentration of argon does not raise its diffusivity in the mixture.

SOLUTION

a) We can make a table, with reference to Tables 11.3, 11.4, and eqn. (11.108):

	Ar	He	Kr	Ne	Xe
σ_{a,N_2} [Å]	3.516	3.115	3.608	3.253	3.804
$\varepsilon_{a,\text{N}_2}/k_B$ [K]	110.5	28.95	132.7	53.68	149.4
$k_B T/\varepsilon_{a,\text{N}_2}$	2.714	10.36	2.261	5.589	2.008
Ω_D	0.9769	0.7382	1.0331	0.8241	1.0746
M [kg/kmol]	39.95	4.003	83.80	20.18	131.29
$\mathcal{D}_{a,\text{N}_2} \times 10^5$ [m ² /s]	1.970	7.203	1.567	3.233	1.292



We see that the lighter species diffuse more readily than the heavier ones. ← Answer

b) Use Blanc's law, eqn. (11.109). With eqn. (11.108), we compute $\mathcal{D}_{\text{He},\text{Ar}} = 7.664 \times 10^5 \text{ m}^2/\text{s}$. Then

$$\mathcal{D}_{\text{He},m} = \left(\frac{x_{\text{Ar}}}{\mathcal{D}_{\text{He},\text{Ar}}} + \frac{x_{\text{N}_2}}{\mathcal{D}_{\text{He},\text{N}_2}} \right)^{-1} = \left(\frac{0.48}{7.664} + \frac{0.48}{7.203} \right)^{-1} \times 10^5 = 7.736 \times 10^5 \text{ m}^2/\text{s} \quad \leftarrow \text{Answer}$$

Since helium is a trace gas, it has little effect on the interaction of argon and nitrogen, so

$$\mathcal{D}_{\text{Ar},m} \cong \mathcal{D}_{\text{Ar},\text{N}_2} = 1.970 \times 10^5 \text{ m}^2/\text{s} \quad \leftarrow \text{Answer}$$

The helium diffuses more readily than the heavier argon.

PROBLEM 11.44 A mothball consists of a 2.5 cm diameter sphere of naphthalene ($C_{10}H_8$) that is hung by a wire in a closet. The solid naphthalene slowly sublimates to vapor, which drives off the moths. Estimate the lifetime of this mothball in a closet with a mean temperature of 20°C . Use the following data for naphthalene

$$\sigma = 6.18 \text{ \AA}, \quad \varepsilon/k_B = 561.5 \text{ K},$$

and, for the solid, $\rho_{C_{10}H_8} = 1145 \text{ kg/m}^3$ at 20°C . The vapor pressure of naphthalene near room temperature is approximated by

$$\log_{10}(p_v \text{ mmHg}) = 11.450 - 3729.3/(T \text{ K})$$

The integral you will obtain can be evaluated numerically. The latent heat of sublimation and evaporation rate are low enough that the wet-bulb temperature is essentially the ambient temperature.

SOLUTION

Natural convection is driven by a higher concentration of naphthalene near the mothball. At 20°C (293.15 K) for $1 \text{ atm} = 760 \text{ mmHg}$, with $M_{C_{10}H_8} = 128.17 \text{ kg/kmol}$,

$$p_v = 0.05352 \text{ mmHg} \quad (7.136 \text{ Pa})$$

$$x_{C_{10}H_8,s} = p_v / p_{\text{atm}} = 0.05352 / 760 = 7.042 \times 10^{-5}$$

$$m_{C_{10}H_8,s} = \frac{(x_{C_{10}H_8,s})(128.17)}{[(x_{C_{10}H_8,s})(128.17) + (1 - x_{C_{10}H_8,s})(28.96)]} = 3.116 \times 10^{-4}$$

The closet should maintain only a very low concentration of naphthalene, so $m_{C_{10}H_8,s} \cong 0$. Further, the concentration of naphthalene is low even close to the mothball, so we can use the properties of air for all properties *except for* the gas density near the mothball.

To find a mass transfer coefficient, we must estimate the diffusion coefficient with eqn. (11.108)

$$\mathcal{D}_{AB} = \frac{(1.8583 \times 10^{-7})T^{3/2}}{p\sigma_{AB}^2\Omega_D} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (11.108)$$

for p in atm, T in K, and \mathcal{D}_{AB} in m^2/s . We use eqns. (11.106) and (11.107) and Tables 11.3 and 11.4 to find the necessary constants at $T = 293.15 \text{ K}$:

$$\sigma_{AB} = (\sigma_{C_{10}H_8} + \sigma_{\text{air}})/2 = (6.18 + 3.711)/2 = 4.95 \text{ \AA}$$

$$\varepsilon_{AB} / k_B = \sqrt{(561.5)(78.6)} = 210 \text{ K}, \quad k_B T / \varepsilon_{AB} = 1.40$$

$$\Omega_D(1.40) = 1.2335$$

so that

$$\mathcal{D}_{C_{10}H_8,\text{air}} = \frac{(1.8583 \times 10^{-7})(293.15)^{3/2}}{(1)(4.95)^2(1.2335)} \sqrt{\frac{1}{128.17} + \frac{1}{28.96}} = 6.35 \times 10^{-6} \text{ m}^2/\text{s}$$

and with $\nu_{\text{air}} = 1.51 \times 10^{-5} \text{ m}^2/\text{s}$, the Schmidt number is

$$\text{Sc} = \nu / \mathcal{D}_{C_{10}H_8,\text{air}} = 1.51 \times 10^{-5} / 6.35 \times 10^{-6} = 2.38$$

Now, the naphthalene-containing air near the mothball will be denser than the fresh air farther away, so a natural convection boundary layer will form. For natural convection on a sphere, we use

eqn. (8.33) with the analogy between heat transfer and low rate mass transfer

$$\overline{\text{Nu}}_{m,D} = 2 + \frac{0.589 \text{ Ra}_D^{1/4}}{[1 + (0.492/\text{Sc})^{9/16}]^{4/9}} \quad (8.33)$$

$$\frac{\bar{g}_m D}{\rho \mathcal{D}_{\text{C}_{10}\text{H}_8,\text{air}}} = 2 + 0.5053 \text{ Ra}_D^{1/4} \quad (*)$$

$$\bar{g}_m = [2 + 0.5053 \text{ Ra}_D^{1/4}] \frac{\rho \mathcal{D}_{\text{C}_{10}\text{H}_8,\text{air}}}{D} \quad (**)$$

where the diameter of the mothball, D , decreases in time. The Rayleigh number is

$$\text{Ra}_D = \frac{g \Delta \rho D^3}{\rho \nu \mathcal{D}_{\text{C}_{10}\text{H}_8,\text{air}}}$$

We may find the densities using the ideal gas law. The mixture molar mass at the surface of the mothball is, with eqn. (11.8),

$$M_{\text{mix},s}^{-1} = \frac{3.116 \times 10^{-4}}{128.17} + \frac{1 - 3.116 \times 10^{-4}}{28.96} \implies M_{\text{mix},s} = 28.967 \text{ kg/kmol}$$

and

$$\rho_{\text{mix},s} = \frac{p M_{\text{mix},s}}{R^\circ T} = \frac{(101325)(28.967)}{(8314.46)(293.15)} = 1.20419 \text{ kg/m}^3$$

$$\rho_{\text{mix},e} = \frac{p M_{\text{air}}}{R^\circ T} = \frac{(101325)(28.96)}{(8314.46)(293.15)} = 1.20390 \text{ kg/m}^3$$

These densities differ by a very small amount, so a large number of digits must be carried. Then,

$$\text{Ra}_D = \frac{(9.806)(1.20419 - 1.20390)D^3}{(1.204)(1.51 \times 10^{-5})(6.35 \times 10^{-6})} = 2.49 \times 10^7 D^3$$

Because the density difference is very small, so is the Rayleigh number: the initial value (for $D = 2.5 \text{ cm}$) is only 388.5. However, from eqn. (*), we find that the Nusselt number varies between 2 and 4.24, so that both terms in eqn. (*) remain important.

A mass balance on the mothball gives us

$$\frac{d}{dt} \left(\rho_{\text{C}_{10}\text{H}_8,\text{solid}} \frac{\pi}{6} D^3 \right) = -\pi D^2 \bar{g}_m \Delta m_{\text{C}_{10}\text{H}_8} = \pi D^2 \bar{g}_m m_{\text{C}_{10}\text{H}_8,s}$$

$$\left(\rho_{\text{C}_{10}\text{H}_8,\text{solid}} \frac{\pi}{2} D^2 \right) \frac{dD}{dt} = -\pi D^2 \bar{g}_m m_{\text{C}_{10}\text{H}_8,s}$$

and with eqn. (**)

$$\frac{dD}{dt} = -\bar{g}_m \frac{2m_{\text{C}_{10}\text{H}_8,s}}{\rho_{\text{C}_{10}\text{H}_8,\text{solid}}} = [2 + 0.5053 (2.49 \times 10^7 D^3)^{1/4}] \frac{\rho \mathcal{D}_{\text{C}_{10}\text{H}_8,\text{air}}}{D} \frac{2m_{\text{C}_{10}\text{H}_8,s}}{\rho_{\text{C}_{10}\text{H}_8,\text{solid}}}$$

$$= -\left(\frac{2 + 35.69 D^{3/4}}{D} \right) \left(\frac{2(1.204)(6.35 \times 10^{-6})(3.116 \times 10^{-4})}{1145} \right)$$

$$= (-4.161 \times 10^{-12}) \left(\frac{2 + 35.69 D^{3/4}}{D} \right)$$

This equation can be integrated from the initial diameter D_0 to zero:

$$(4.161 \times 10^{-12}) \int_0^T dt = \int_0^{D_0=0.025 \text{ m}} \frac{D dD}{(2 + 35.69 D^{3/4})} = 8.766 \times 10^{-5}$$

where the integral was evaluated numerically (in this case, using wolframalpha.com). Solving for the time, T :

$$T = \frac{8.766 \times 10^{-5}}{4.161 \times 10^{-12}} = 2.107 \times 10^7 \text{ sec} = 243.8 \text{ days} \quad \longleftarrow \text{Answer}$$

The mothball lasts about 8 months.

Comment 1: The vapor pressure rises very rapidly with temperature. If the closet is warmer, the mothball lifetime will be much shorter.

Comment 2: Air circulation in the closet (as from drafts, HVAC systems, or room scale natural convection) would increase the mass transfer coefficient and shorten the lifetime of the mothball. Such circulation is more likely than not.

Comment 3: If the mothball is placed in a small closed container, such as a drawer or box, the concentration of naphthalene may eventually rise to match the vapor pressure of naphthalene at the surface of the mothball. In this equilibrium condition, the sublimation rate would drop to zero.

Comment 4: Naphthalene is considered to pose health hazards. Its use in mothballs has been banned in the EU since 2008.

Comment 5: A fuller equation for the vapor pressure of solid naphthalene from 230 K to $T_{\text{tp}} = 353.34$ K is given by: D. Ambrose, I.J. Lawrenson, C.H.S. Sprake, "The vapour pressure of naphthalene," *J. Chemical Thermodynamics*, **7**(12):1173–1176, 1975. [doi:10.1016/0021-9614\(75\)90038-5](https://doi.org/10.1016/0021-9614(75)90038-5)

PROBLEM 11.45 In contrast to the naphthalene mothball described in Problem 11.44, other mothballs are made from paradichlorobenzene (PDB). Estimate the lifetime of a 2.5 cm diameter PDB mothball using the following room temperature property data:

$$\begin{aligned}\sigma &= 5.76 \text{ \AA} & \varepsilon/k_B &= 578.9 \text{ K} & M_{\text{PDB}} &= 147.0 \text{ kg/kmol} \\ \log_{10}(p_v \text{ mmHg}) &= 11.985 - 3570/(T \text{ K}) \\ \rho_{\text{PDB}} &= 1248 \text{ kg/m}^3\end{aligned}$$

SOLUTION Natural convection is driven by a higher concentration of paradichlorobenzene near the mothball. At 20°C (293.15 K) for 1 atm = 760 mmHg, with $M_{\text{PDB}} = 147.0$ kg/kmol,

$$\begin{aligned}p_v &= 0.6411 \text{ mmHg} \quad (136.8 \text{ Pa}) \\ x_{\text{PDB},s} &= p_v / p_{\text{atm}} = 0.6411 / 760 = 8.436 \times 10^{-4} \\ m_{\text{PDB},s} &= \frac{(x_{\text{PDB},s})(147.0)}{[(x_{\text{PDB},s})(147.0) + (1 - x_{\text{PDB},s})(28.96)]} = 4.267 \times 10^{-3}\end{aligned}$$

The closet should maintain only a very low concentration of paradichlorobenzene, so $m_{\text{PDB},s} \cong 0$. Further, the concentration of paradichlorobenzene is low even close to the mothball, so we can use the properties of air for all properties *except for* the gas density near the mothball.

To find a mass transfer coefficient, we must estimate the diffusion coefficient with eqn. (11.108)

$$\mathcal{D}_{AB} = \frac{(1.8583 \times 10^{-7})T^{3/2}}{p\sigma_{AB}^2\Omega_D} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (11.108)$$

for p in atm, T in K, and \mathcal{D}_{AB} in m^2/s . We use eqns. (11.14-15) and Tables 11.2 and 11.3 to find the necessary constants at $T = 293.15$ K:

$$\begin{aligned}\sigma_{AB} &= (\sigma_{\text{PDB}} + \sigma_{\text{air}})/2 = (5.76 + 3.711)/2 = 4.736 \text{ \AA} \\ \varepsilon_{AB} / k_B &= \sqrt{(578.9)(78.6)} = 213 \text{ K}, \quad k_B T / \varepsilon_{AB} = 1.374 \\ \Omega_D(1.374) &= 1.244\end{aligned}$$

so that

$$\mathcal{D}_{\text{PDB,air}} = \frac{(1.8583 \times 10^{-7})(293.15)^{3/2}}{(1)(4.95)^2(1.244)} \sqrt{\frac{1}{147.0} + \frac{1}{28.96}} = 6.23 \times 10^{-6} \text{ m}^2/\text{s}$$

and with $\nu_{\text{air}} = 1.51 \times 10^{-5} \text{ m}^2/\text{s}$, the Schmidt number is

$$\text{Sc} = \nu / \mathcal{D}_{\text{PDB,air}} = 1.51 \times 10^{-5} / 6.23 \times 10^{-6} = 2.42$$

Now, the p -dichlorobenzene containing air near the mothball will be denser than the fresh air farther away, so a natural convection boundary layer will form. For natural convection on a sphere, we use eqn. (8.33) with the analogy between heat transfer and low rate mass transfer

$$\overline{\text{Nu}}_{m,D} = 2 + \frac{0.589 \text{ Ra}_D^{1/4}}{[1 + (0.492/\text{Sc})^{9/16}]^{4/9}} \quad (8.33)$$

$$\frac{\bar{g}_m D}{\rho \mathcal{D}_{\text{PDB,air}}} = 2 + 0.5059 \text{ Ra}_D^{1/4} \quad (*)$$

$$\bar{g}_m = \left[2 + 0.5059 \text{ Ra}_D^{1/4} \right] \frac{\rho \mathcal{D}_{\text{PDB,air}}}{D} \quad (**)$$

where the diameter of the mothball, D , decreases in time. The Rayleigh number is

$$\text{Ra}_D = \frac{g \Delta \rho D^3}{\rho \nu \mathcal{D}_{\text{PDB,air}}}$$

We may find the densities using the ideal gas law. The mixture molar mass at the surface of the mothball is, with eqn. (11.8),

$$M_{\text{mix},s}^{-1} = \frac{4.267 \times 10^{-4}}{147.0} + \frac{1 - 4.267 \times 10^{-3}}{28.96} \implies M_{\text{mix},s} = 29.060 \text{ kg/kmol}$$

and

$$\rho_{\text{mix},s} = \frac{p M_{\text{mix},s}}{R^\circ T} = \frac{(101325)(29.060)}{(8314.46)(293.15)} = 1.20804 \text{ kg/m}^3$$

$$\rho_{\text{mix},e} = \frac{p M_{\text{air}}}{R^\circ T} = \frac{(101325)(28.96)}{(8314.46)(293.15)} = 1.20390 \text{ kg/m}^3$$

These densities differ by a very small amount, so a large number of digits must be carried. Then,

$$\text{Ra}_D = \frac{(9.806)(1.20804 - 1.20390)D^3}{(1.206)(1.51 \times 10^{-5})(6.35 \times 10^{-6})} = 3.49 \times 10^8 D^3$$

Because the density difference is small, so is the Rayleigh number: the initial value (for $D = 2.5 \text{ cm}$) is only 5446. However, from eqn. (*), we find that the Nusselt number varies between 2 and 6.35, so that both terms in eqn. (*) remain important.

A mass balance on the mothball gives us

$$\begin{aligned} \frac{d}{dt} \left(\rho_{\text{PDB,solid}} \frac{\pi}{6} D^3 \right) &= -\pi D^2 \bar{g}_m \Delta m_{\text{PDB}} = \pi D^2 \bar{g}_m m_{\text{PDB},s} \\ \left(\rho_{\text{PDB,solid}} \frac{\pi}{2} D^2 \right) \frac{dD}{dt} &= -\pi D^2 \bar{g}_m m_{\text{PDB},s} \end{aligned}$$

and with eqn. (**)

$$\begin{aligned} \frac{dD}{dt} &= -\bar{g}_m \frac{2m_{\text{PDB},s}}{\rho_{\text{PDB,solid}}} = \left[2 + 0.5058 (3.49 \times 10^8 D^3)^{1/4} \right] \frac{\rho \mathcal{D}_{\text{PDB,air}}}{D} \frac{2m_{\text{PDB},s}}{\rho_{\text{PDB,solid}}} \\ &= - \left(\frac{2 + 69.13 D^{3/4}}{D} \right) \left(\frac{2(1.206)(6.23 \times 10^{-6})(4.267 \times 10^{-3})}{1145} \right) \\ &= (-5.600 \times 10^{-11}) \left(\frac{2 + 69.13 D^{3/4}}{D} \right) \end{aligned}$$

This equation can be integrated from the initial diameter D_0 to zero:

$$(5.600 \times 10^{-11}) \int_0^T dt = \int_0^{D_0=0.025 \text{ m}} \frac{D dD}{(2 + 69.13 D^{3/4})} = 6.287 \times 10^{-5}$$

where the integral was evaluated numerically (in this case, using wolframalpha.com). Solving for the time, T :

$$T = \frac{6.287 \times 10^{-5}}{5.600 \times 10^{-11}} = 1.123 \times 10^6 \text{ sec} = 13.0 \text{ days} \quad \longleftarrow \text{Answer}$$

The mothball lasts about two weeks.

Comment 1: The vapor pressure rises rapidly with temperature. If the closet is warmer, the mothball lifetime will be much shorter.

Comment 2: Air circulation in the closet (as from drafts, HVAC systems, or room scale natural convection) would increase the mass transfer coefficient and shorten the lifetime of the mothball. Such circulation is more likely than not.

Comment 3: If the mothball is placed in a small closed container, such as a drawer or box, the concentration of paradichlorobenzene may eventually rise to match the vapor pressure of paradichlorobenzene at the surface of the mothball. In this equilibrium condition, the sublimation rate would drop to zero.

Comment 4: Paradichlorobenzene is considered to pose health hazards. Its use in mothballs has been banned in the EU since 2008.

11.46 Compute the diffusivity of methane in air using a.) equation (11.108) and b.) Blanc's Law. For part b.) ignore argon; use $x_{\text{methane}} = 0.05$, $T = 420^\circ\text{F}$, and $p = 10$ psia.

a) $\sigma_{\text{CH}_4\text{-air}} = 3.735 \text{ \AA}$, $(\epsilon/k)_{\text{CH}_4\text{-air}} = 108.1 \text{ K}$ from eqns. (11.106-107)

$kT/\epsilon = 4.523$ so, from Table 12.2, $\Omega_D = 0.8601$. The pressure is $p = (10/14.696) = 0.6805 \text{ atm}$. Eqn (11.108) gives:

$$D_{\text{CH}_4\text{-air}} = \frac{(1.8583 \times 10^{-7})(488.9)^{3/2}}{(3.735)^2 (0.6805)(0.8601)} \sqrt{\frac{1}{28.96} + \frac{1}{16.04}}$$

$$= \underline{7.658 \times 10^{-5} \text{ m}^2/\text{s}}$$

b) We need $D_{\text{O}_2\text{-CH}_4}$, $D_{\text{N}_2\text{-CH}_4}$, x_{O_2} , and x_{N_2} for eqn.

$\text{O}_2\text{-CH}_4$: $\sigma = 3.575 \text{ \AA}$, $\epsilon/k = 134.5 \text{ K}$, $\Omega_D = 0.9008$: $D = 7.840 \times 10^{-5} \text{ m}^2/\text{s}$

$\text{N}_2\text{-CH}_4$: $\sigma = 3.732 \text{ \AA}$, $\epsilon/k = 1.123 \text{ K}$, $\Omega_D = 0.8686$: $D = 7.463 \times 10^{-5} \text{ m}^2/\text{s}$

$x_{\text{air}} = 0.95$, so that: $x_{\text{N}_2} \approx (0.78)(0.95) = 0.74$, $x_{\text{O}_2} \approx (0.21)(0.95) = 0.20$

Thus, eqn. (11.109) yields:

$$D_{\text{CH}_4, \text{air}} = \left\{ \frac{0.74}{7.463} + \frac{0.20}{7.840} \right\}^{-1} \times 10^{-5} = \underline{8.021 \times 10^{-5} \text{ m}^2/\text{s}}$$

PROBLEM 11.47 In Section 11.5, $\rho\mathcal{D}_{12}$ or $c\mathcal{D}_{12}$ were at times assumed to be independent of position. Consider this approximation for gases. (a) Do these two groups depend on pressure, temperature, or the proportions of species 1 and 2? Are isobaric conditions necessary to hold either group constant? (b) For what type of mixture is $\rho\mathcal{D}_{12}$ most sensitive to composition? What does this indicate about mole versus mass-based analysis? (c) Do Pr or Sc depend on composition, temperature, or pressure?

SOLUTION

a) For ideal gases

$$c = \frac{p}{R^\circ T} \quad \text{and} \quad \rho = M \frac{p}{R^\circ T}$$

where M depends on the mole or mass fractions of species 1 and 2 from eqns. (11.8). The diffusion coefficient from eqn. (11.108),

$$\mathcal{D}_{12} = \frac{(1.8583 \times 10^{-7})T^{3/2}}{p\sigma_{12}^2\Omega_D} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}$$

does not depend on mass or mole fraction. Recall that Ω_D depends on temperature. Thus,

$$c\mathcal{D}_{12} \propto \frac{T^{1/2}}{\Omega_D} = \text{function of } T \text{ only}$$

$$\rho\mathcal{D}_{12} \propto \frac{MT^{1/2}}{\Omega_D} = \text{function of } T \text{ and mole fraction}$$

Neither group depends on pressure, so isobaric conditions are irrelevant. ← Answer

b) The molar mass is

$$M = x_1M_1 + x_2M_2$$

When the spatial variations of mole fraction are large, M can change significantly with position. However, if $M_1 \approx M_2$, the value of M is not sensitive to changes in mole fraction. The sensitivity to composition is greatest when M_1 and M_2 are very different. ← Answer

So, $\rho\mathcal{D}_{12}$ is nearly constant in isothermal mixtures of gases with similar molar mass, or when the composition does not vary much. On the hand, $c\mathcal{D}_{12}$ stays constant in an isothermal mixture of any pair of gases even if the concentration changes are large. ← Answer

c) We have

$$\text{Pr} = \frac{\nu}{\alpha} = \frac{\mu c_p}{k}$$

and we know from Section 11.10 that μ and k depend on T and composition, but not on p . Also, c_p is constant for an ideal gas. So, Pr is a function of temperature and composition.

Likewise,

$$\text{Sc} = \frac{\nu}{\mathcal{D}_{12}} = \frac{\mu}{\rho\mathcal{D}_{12}}$$

From the result of part (a), the denominator depends on T and composition. Thus Sc is also a function of T and composition.

Pr and Sc depend on temperature and composition, but neither depends on pressure. ← Answer

PROBLEM 11.48 A dilute aqueous solution containing potassium ions is subjected to a 1 V/cm electric field. A measurement suggests that the K^+ ions move at 4×10^{-4} cm/s in response to the field. Estimate the effective radius of K^+ ions if the solution is at 300 K. The charge of an electron is -1.609×10^{-19} C and $1 \text{ V/m} = 1 \text{ N/C}$.

SOLUTION The force on a K^+ ion is

$$F = (1.609 \times 10^{-19} \text{ C})(1 \text{ V/cm}) = 1.609 \times 10^{-17} \text{ N}$$

From the Einstein relation, eqn. (11.111), the diffusion coefficient is

$$\begin{aligned} \mathcal{D}_{K^+,H_2O} &= k_b T \left(\frac{v_{K^+}}{F_{K^+}} \right) \\ &= (1.38065 \times 10^{-23} \text{ J/K})(300 \text{ K}) \frac{(4 \times 10^{-4} \text{ cm/s})(0.01 \text{ m/cm})}{(1.609 \times 10^{-17} \text{ N})} \\ &= 1.03 \times 10^{-9} \text{ m}^2/\text{s} \end{aligned}$$

K^+ ions have a radius similar to water molecules, so eqn. (11.114b) is applicable. Rearranging that equation and taking μ_{H_2O} from Table A.3,

$$\begin{aligned} R_{K^+} &= \frac{k_b T}{4\pi\mu_{H_2O}\mathcal{D}_{K^+,H_2O}} \\ &= \frac{(1.38065 \times 10^{-23} \text{ J/K})(300 \text{ K})}{4\pi(8.54 \times 10^{-4} \text{ kg/m}\cdot\text{s})(1.03 \times 10^{-9} \text{ m}^2/\text{s})} \\ &= 3.75 \times 10^{-10} \text{ m} = 3.75 \text{ \AA} \quad \leftarrow \text{Answer} \end{aligned}$$

Comment 1: Ions in aqueous solution are surrounded by a shell of water molecules which are attracted by hydrogen bonding. This *hydration shell* can be several times the size of an isolated ion. For potassium, the hydration shell may consist of 5–7 water molecules [1]. The average reported radius of a hydrated potassium ion is 3.32 Å [2]

Comment 2: The “experiment” described here is completely made up!

REFERENCES:

[1] John Burgess, “Solvation numbers.” In John Burgess (ed.), *Ions in Solution*, Woodhead Publishing, 1999, Chapter 2, pp. 28–35, doi:10.1533/9781782420569.28.

[2] Bruce Railsback, *Some Fundamentals of Mineralogy and Geochemistry*, <http://railsback.org/Fundamentals/IonicChargeRadiusPlot06P.pdf>

- 11.49 a.) Obtain the following diffusion coefficients: (i) for dilute CCl_4 diffusing through liquid methanol at 340 K, (ii) for dilute benzene diffusing through water at 290 K, (iii) for dilute ethyl alcohol diffusing through water at 350 K, and (iv) for dilute acetone diffusing through methanol at 370 K. b.) Estimate the effective radius of a methanol molecule in a dilute aqueous solution.

a) Use eq'n (11.115) and App. A. (i) $\mu_{\text{methanol}} = 3.3 \times 10^{-4} \text{ kg/m}\cdot\text{s}$

$$D_{\text{CCl}_4\text{-meth.}} = \frac{(340)}{(3.3 \times 10^{-4})} (4.4 \times 10^{-15}) \left(\frac{0.042}{0.102}\right)^{1/6} \left(\frac{35.53}{29.93}\right)^{1/2}$$

$$= \underline{4.3 \times 10^{-9} \text{ m}^2/\text{s}}$$

(ii) $\mu_{\text{H}_2\text{O}} = 1.123 \times 10^{-3} \text{ kg/m}\cdot\text{s}$. Eq'n (11.115) gives: $D_{\text{benz-H}_2\text{O}} = \underline{9.94 \times 10^{-10} \text{ m}^2/\text{s}}$

(iii) $\mu_{\text{H}_2\text{O}} = 3.65 \times 10^{-4} \text{ kg/m}\cdot\text{s}$. Eq'n (11.115) gives: $D_{\text{ethyl-H}_2\text{O}} = \underline{3.49 \times 10^{-9} \text{ m}^2/\text{s}}$

(iv) $\mu_{\text{meth}} = 2.4 \times 10^{-4} \text{ kg/m}\cdot\text{s}$. Using eq'n (11.115) we have:

$$D_{\text{acet.-meth.}} = \frac{(370)}{(2.4 \times 10^{-4})} (4.4 \times 10^{-15}) \left(\frac{0.042}{0.074}\right)^{1/6} \left(\frac{35.53}{28.90}\right)^{1/2} = \underline{6.8 \times 10^{-9} \text{ m}^2/\text{s}}$$

b) Use eq'ns (11.114b) and (11.115). From (11.115), $D\mu/T =$

$4.11 \times 10^{-15} \text{ kg}\cdot\text{m}/\text{K}\cdot\text{s}^2$. Solving (11.114b) for R_{meth} we have:

$$R_{\text{meth}} = \frac{k_B}{4\pi} \left(\frac{D_{\text{meth-H}_2\text{O}} \mu_{\text{H}_2\text{O}}}{T} \right)^{-1} = \frac{(1.3805 \times 10^{-23})}{4\pi (4.11 \times 10^{-15})} = 2.67 \times 10^{-10} \text{ m}$$

$$= \underline{2.67 \text{ \AA}}$$

PROBLEM 11.50 Use eqn. (11.116) to calculate the dynamic viscosity, μ , of gaseous methane, hydrogen sulfide, and nitrous oxide, under the following conditions: 250 K and 1 atm, 500 K and 1 atm, 250 K and 2 atm, 250 K and 12 atm, 500 K and 12 atm. Is the calculation possible in every case?

SOLUTION

The dynamic viscosity of ideal gases is independent of pressure. However, we must also consider whether the fluid remains gaseous or liquefies as the pressure is increased. The six conditions described involve a maximum pressure of 12 atm and a minimum temperature of 250 K. So, we can start by checking whether each fluid is gaseous at 250 K and 12 atm, which requires us to obtain data outside this textbook, as from the NIST Chemistry Webbook, <https://webbook.nist.gov/chemistry/>.

To check for phase transitions, we can look at the 12 atm isotherm for each fluid to see whether the fluid remains gaseous at 250 K. Nitrous oxide remains gaseous at 12 atm. Hydrogen sulfide at 250 K liquefies at a pressure of 4.83 atm, so, we cannot evaluate gaseous μ for H₂S at 250 K and 12 atm. We must also check the 500 K isotherm, and we find that H₂S remains gaseous. Methane also remains a gas under the given conditions (in fact, these temperatures exceed the methane's critical point temperature of 190.6 K, with pressures below the critical point pressure of 46.1 bar, so methane is clearly gaseous).

Equation (11.25) is

$$\mu_A = (2.6693 \times 10^{-6}) \frac{\sqrt{M_A T}}{\sigma_A^2 \Omega_\mu} \quad (11.116)$$

so we need to find σ , M , and $\Omega_\mu(T)$ for each gas at each temperature.

Gas	σ [Å]	ε/k_B [K]	M [kg/kmol]	$T = 250$ K		$T = 500$ K	
				Ω_μ	μ [kg/m-s]	Ω_μ	μ [kg/m-s]
CH ₄	3.758	148.6	16.04	1.254	9.545×10^{-6}	1.010	1.676×10^{-5}
H ₂ S	3.623	301.1	34.08	1.747	1.075×10^{-5}	1.261	2.105×10^{-5}
N ₂ O	3.828	232.4	44.01	1.531	1.248×10^{-5}	1.145	2.360×10^{-5}

Equation (11.125) does not depend on pressure, so these values apply at 1 atm, 2 atm, and 12 atm, with the exception of H₂S for which the value does not apply at 12 atm.

Comment: These predictions can be compared to the more complex reference correlations in the NIST Webbook (below, in kg/m-s). The predictions are within $\pm 4\%$ or better of the NIST values.

Gas	$T = 250$ K		$T = 500$ K	
	$p = 1$ atm	$p = 12$ atm	$p = 1$ atm	$p = 12$ atm
CH ₄	9.471×10^{-6}	9.647×10^{-6}	1.690×10^{-5}	1.701×10^{-5}
H ₂ S	1.030×10^{-5}	liquid	2.108×10^{-5}	2.121×10^{-5}
N ₂ O	1.249×10^{-5}	1.299×10^{-6}	2.357×10^{-5}	2.375×10^{-5}

11.51 A student is studying the combustion of a premixed gaseous fuel with the molar composition: 10.3 percent methane, 15.4 percent ethane, and 74.3 percent oxygen. She passes $0.006 \text{ ft}^3/\text{s}$ of the mixture (at 70°F and 18 psia) through a smooth $3/8$ inch ID tube, 47 inches long. a.) What is the pressure drop? b.) The student's advisor recommends pre-heating the fuel mixture, using a nichrome strip heater wrapped around the last 5 inches of the duct. If the heater produces 0.8 W/inch , what is the wall temperature at the outlet of the duct? Let $c_{p,\text{CH}_4} = 2280 \text{ J/kg}\cdot^\circ\text{K}$, $\gamma_{\text{CH}_4} = 1.3$, $c_{p,\text{C}_2\text{H}_6} = 1730 \text{ J/kg}\cdot^\circ\text{K}$, $\gamma_{\text{C}_2\text{H}_6} = 1.2$, and approximate the properties at the inlet conditions.

First determine the properties of the gas mixture at (70°F , 18 psi)
 $= (294.4 \text{ K}, 1.225 \text{ atm})$. Use eqns. (11.119) for the mixture. From

Appendix A, $\mu_{\text{O}_2} = 2.032 \times 10^{-6} \text{ kg/ms}$, $k_{\text{O}_2} = 0.02629 \text{ W/mK}$. For CH_4 , C_2H_6 use (11.116) (11.116)

	$\sigma (\text{\AA})$	$\epsilon/k (\text{K})$	$M (\frac{\text{kg}}{\text{kgmole}})$	kT/ϵ	Ω_μ	$\mu (\text{kg/ms})$
CH_4	3.758	148.6	16.04	1.981	1.179	1.102×10^{-6}
C_2H_6	4.443	215.7	30.07	1.365	1.368	9.300×10^{-6}

and from the given data: $k_{\text{CH}_4} = 0.03237 \text{ W/mK}$, $k_{\text{C}_2\text{H}_6} = 0.01944 \frac{\text{W}}{\text{mK}}$
 by (11.118). To compute ϕ_{ij} , let $\text{O}_2 = 1$, $\text{CH}_4 = 2$, $\text{C}_2\text{H}_6 = 3$. The
 results are: $\phi_{12} = 0.9378$, $\phi_{13} = 1.484$, $\phi_{23} = 1.476$,
 $\phi_{21} = 1.015$, $\phi_{31} = 0.7226$, $\phi_{32} = 0.6645$

Representing the sums in the denominators of (11.119ac) as $\Sigma_i \equiv \sum_{j=1}^3 \chi_j \phi_{ij}$, we have: $\Sigma_1 = 1.068$, $\Sigma_2 = 1.084$, $\Sigma_3 = 0.7593$.

Thus,
$$\mu_m = \left\{ \frac{(0.743)(2.032)}{1.068} + \frac{(0.103)(1.102)}{1.084} + \frac{(0.154)(0.930)}{0.7593} \right\} \times 10^{-5}$$

$$= \underline{1.71 \times 10^{-5} \text{ kg/ms}}$$

$$k_m = \underline{0.0253 \text{ W/mK}}$$

(a) Use eqn. (3.25): $\Delta p = (L/D)(\rho u_{av}^2/2)f$. $u_{av} = \dot{m}/\rho A$ where $\dot{m}/\rho = 0.006 \text{ ft}^3/\text{s} = 1.70 \times 10^{-4} \text{ m}^3/\text{s}$ and $A = \frac{\pi}{4}(\frac{3}{8})^2 \text{ in}^2 = 7.13 \times 10^{-5} \text{ m}^2$, so that $u_{av} = 2.38 \text{ m/s}$. The density of the mixture is, by

(12.8) and the ideal gas law: $M = 30.06 \text{ kg/kgmole}$, $\rho = (101325)(1.225)(30.06)/(8314.3)(294.4) = 1.524 \text{ kg/m}^3$. The

Reynolds number is: $Re_D = (1.524)(2.38)(\frac{3}{8})(0.0254)/(1.71 \times 10^{-5}) = 2020$, barely laminar. From Fig 7.6, $f = 64/Re_D = 0.0317$

so: $\Delta p = \left(\frac{47}{38}\right) \left(\frac{(1.524)(2.38)^2}{2}\right) (0.0317) = \underline{17.2 \text{ N/m}^2} = \underline{2.49 \times 10^{-3} \text{ psi}}$

The pressure drop is entirely negligible.

(b) At the end of the tube we should have fully developed laminar flow: $Nu = 4.368$, eqn. (7.21). From Ex. 7.1 and eqn. (7.21)

$$T_w(L) = 294.4^\circ\text{K} + \frac{4q_w \alpha}{u_{av} D k} L + \frac{11}{48} \frac{q_w D}{k}, \quad L = 5''.$$

Now, $\alpha/k = k/\rho c_p k = 1/\rho c_p$. From App. A, $c_{p_{O_2}} = 919.8 \text{ J/kg K}$

and $c_{p_m} = \sum_i \chi_i c_{p_i} = \frac{1}{M} \sum_i \chi_i c_{p_i} M_i = 1119 \text{ J/kg K}$. Thus:

$$T_w(\text{exit}) = 294.4^\circ\text{K} + q_w \left\{ \frac{11}{48} \frac{\frac{3}{8}(0.0254)}{(0.0253)} + \frac{4(5'')}{(2.38)(\frac{3}{8})(1.524)(1119)} \right\}$$

$$= 294.4^\circ\text{K} + 0.09942 q_w$$

The wall heat flux is $q_w = (0.8 \text{ W/in})/\pi D = (0.8)/\pi(\frac{3}{8})(0.0254)^2 = 1053 \text{ W/m}^2$, so that

$$T_w(\text{exit}) = \underline{399.1 \text{ K}}$$

- 11.52 a.) Show that $k = (5/2)\mu c_v$ for a monatomic gas. b.) Obtain Eucken's formula for the Prandtl number of a dilute gas

$$Pr = 4\gamma / (9\gamma - 5)$$

c.) Recall that for an ideal gas $\gamma \cong (D + 2)/D$ where D is the number of modes of energy storage of its molecules. Obtain an expression for Pr as a function of D and describe what it means. d.) Use Eucken's formula to compute Pr for gaseous Ar, N_2 , and H_2O . Compare the result to data in Appendix A over the range of temperatures. Explain the results obtained for steam as opposed to Ar and N_2 . (Note that for each mode of vibration there are two modes of energy storage, but that vibration is normally inactive until T is very high.)

- (a) The simplest approach is to divide eqn. (11.116) into (11.117)

$$k = \left(\frac{0.083228}{2.6693 \times 10^6} \right) \left(\frac{\mu}{M} \right) = (3.118 \times 10^4 \text{ J/kg}\cdot\text{K}) \left(\frac{\mu}{M} \right)$$

For a monatomic gas

$$c_v = \frac{3}{2} (R^0/M) \quad \text{and} \quad \frac{5}{2} \left(\frac{3}{2} R^0 \right) = 3.118 \times 10^4 \text{ J/kg}\cdot\text{K}$$

Therefore,

$$\underline{k = \frac{5}{2} \mu c_v} \longleftarrow$$

compare to eqns. (6.45cd)

- (b) The Eucken correction (11.118) gives

$$k = \left(\frac{9\gamma - 5}{4\gamma} \right) \mu c_p$$

and $Pr = (\mu c_p / k)$ so: $\underline{Pr = \left(\frac{4\gamma}{9\gamma - 5} \right)} \longleftarrow$

- (c) Substituting the expression stated into Eucken's formula for Pr , we have:

$$\underline{Pr = \frac{4(D+2)}{9(D+2) - 5D} = 2 \left(\frac{D+2}{2D+9} \right)} \longleftarrow$$

Pr tends to unity as D becomes large, as for complex molecules and at high temperature when vibrational modes become more important.

- (d) The value of γ must be specified. For monatomic Ar, $D=3$ (3 translational modes) so $\gamma = 5/3$ and $Pr = 2/3$. For diatomic N_2 we add two rotational modes. $D=5$ and $\gamma = 7/5$ so $Pr = 28/38 = 14/19$. For triatomic H_2O , we have an additional rotational mode, so D is at least 6, and $Pr = 16/21$. H_2O may also be more susceptible to vibrational modes.

	Ar		N ₂		H ₂ O	
	T [K]	Pr	T [K]	Pr	T [K]	Pr
Eucken	-	0.666	-	0.737	-	0.762
Data	100	0.692	100	0.738	373	1.018
	200	0.669	300	0.721	473	0.961
	300	0.667	500	0.709	573	0.941
	400	0.666	800	0.707	673	0.924
	500	0.666	1200	0.712	873	0.899
	700	0.665	1600	0.715	1073	0.882

The Eucken relation predicts the data for argon to within 4% at 100 K, but within 0.5% or better for $T \geq 200$ K. For nitrogen, the agreement is within 4% over the entire temperature range. For steam, the disagreement ranges from 16% to 34%; coupling between rotational and vibrational modes may be a factor.

PROBLEM 11.53 Three simplifications of the Maxwell-Stefan equations, (11.139), lead to an effective, binary Fickian diffusion coefficient, \mathcal{D}_{im} . (a) Show that Blanc's law, eqn. (11.109), applies when species i at low concentration diffuses into an otherwise uniform mixture. (b) Show that if \mathcal{D}_{ij} has the same value for each pair of species and the mixture is ideal, then $\mathcal{D}_{im} = \mathcal{D}_{ij}$. (c) Show that if species $i = 1, 2, 3, \dots, n-1$ all have low concentrations, then $\mathcal{D}_{im} = \mathcal{D}_{i,n}$, where species n is the dominant species (or solvent), as stated in eqn. (11.110).

SOLUTION

a) Because species i is dilute ($x_i \ll 1$), it may be considered ideal, with $\gamma_i = 1$. Then $\Gamma_{ij} = \delta_{ij}$, from eqn. (11.137b). The Maxwell-Stefan equations, (11.139) are

$$\sum_{j=1}^{n-1} \Gamma_{ij} \nabla_{T,p} x_j = \nabla_{T,p} x_i = \sum_{j=1}^n \frac{x_i \vec{J}_j - x_j \vec{J}_i}{c \mathcal{D}_{ij}}$$

and because species other than i are approximately uniform, $\vec{J}_j \cong 0$ for $j \neq i$:

$$\nabla_{T,p} x_i = - \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j \vec{J}_i}{c \mathcal{D}_{ij}} = - \frac{\vec{J}_i}{c} \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{\mathcal{D}_{ij}}$$

Putting this into the form of Fick's law

$$\vec{J}_i = -c \nabla_{T,p} x_i \left/ \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{\mathcal{D}_{ij}} \right. = -c \mathcal{D}_{im} \nabla_{T,p} x_i$$

where

$$\mathcal{D}_{im}^{-1} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{\mathcal{D}_{ij}} \quad \leftarrow \text{Answer}$$

b) For an ideal mixture (such as an ideal gas mixture), $\Gamma_{ij} = \delta_{ij}$. The Maxwell-Stefan equations, (11.139), reduce to eqns. (11.129b). Then

$$\begin{aligned} \nabla_{T,p} x_i &= \sum_{j=1}^n \frac{x_i \vec{J}_j - x_j \vec{J}_i}{c \mathcal{D}_{ij}} \\ &= \frac{1}{c \mathcal{D}_{ij}} \sum_{j=1}^n (x_i \vec{J}_j - x_j \vec{J}_i) \\ &= \frac{1}{c \mathcal{D}_{ij}} \left(x_i \underbrace{\sum_{j=1}^n \vec{J}_j}_{=0} - \vec{J}_i \underbrace{\sum_{j=1}^n x_j}_{=1} \right) = - \frac{\vec{J}_i}{c \mathcal{D}_{ij}} \end{aligned}$$

so that

$$\vec{J}_i = -c \mathcal{D}_{ij} \nabla_{T,p} x_i = -c \mathcal{D}_{im} \nabla_{T,p} x_i$$

with

$$\mathcal{D}_{im} = \mathcal{D}_{ij} \quad \leftarrow \text{Answer}$$

- c) Because species 1, 2, 3, ..., $n - 1$ have low concentrations, they behave as ideal: $\Gamma_{ij} = \delta_{ij}$. The Maxwell-Stefan equations again reduce to eqns. (11.129b). Further, with $x_i \ll x_n \cong 1$ for $i \neq n$, many terms are negligible:

$$\begin{aligned} \nabla_{T,p} x_i &= \sum_{j=1}^n \frac{x_i \vec{J}_j - x_j \vec{J}_i}{c\mathcal{D}_{ij}} \\ &= x_i \sum_{j=1}^n \frac{\vec{J}_j}{c\mathcal{D}_{ij}} - \sum_{j=1}^n \frac{x_j \vec{J}_i}{c\mathcal{D}_{ij}} \\ &\cong x_i \sum_{j=1}^n \frac{\vec{J}_j}{c\mathcal{D}_{i,j}} - \frac{x_n \vec{J}_i}{c\mathcal{D}_{i,n}} \\ &\cong -\frac{\vec{J}_i}{c\mathcal{D}_{i,n}} \end{aligned}$$

and so

$$\vec{J}_i = -c\mathcal{D}_{i,n} \nabla_{T,p} x_i \quad i \neq n \quad \leftarrow \text{Answer}$$

We see that $\mathcal{D}_{im} = \mathcal{D}_{i,n} = \mathcal{D}_{i,n}$.

PROBLEM 11.54 A dilute solute A in a liquid solution diffuses down the gradient of the chemical potential, μ_A , because a gradient in potential energy causes a force per mole of A . Compute this force and combine the result with the molar form of Fick's law to derive the Einstein relation, eqn. (11.111). Note that the Einstein relation considers the force per molecule and that $R^\circ = k_B N_A$, where N_A is Avogadro's number.

SOLUTION The gradient in potential energy, or chemical potential, provides the force that drives the diffusion of a solute A against the opposing drag of the solvent molecules. From classical mechanics, the force \vec{F} resulting from a gradient in a potential energy E is

$$\vec{F} = -\nabla E \quad \text{or in 1-D} \quad F = -\frac{dE}{dz}$$

In the case of a dilute solute, the potential energy is the chemical potential of species A in J/mol, eqn. (11.131):

$$\mu_A(x) = \mu_A^\circ + R^\circ T \ln(x_A)$$

The force driving species A down the potential gradient, against the drag of solvent B , is then

$$F_{AB} = -\frac{d\mu_A}{dz} = -\frac{R^\circ T}{x_A} \frac{dx_A}{dz} \quad (*)$$

in units of N/mol, as given by eqn. (11.134). The drag force of the solvent on the solute is equal and opposite the force caused by the potential gradient (i.e., acceleration is zero).

From here, we use the molar form of Fick's law, eqn. (11.30), taken as an empirical premise:

$$J_A = -c \mathcal{D}_{AB} \frac{dx_A}{dz}$$

Combining these equations,

$$F_{AB} = \frac{R^\circ T}{c_A} \frac{J_A}{\mathcal{D}_{AB}} \quad (**)$$

Further, we recall that J_A is defined by eqn. (11.23) as

$$J_A = c_A(v_A - v^*)$$

We put this into eqn. (**), and also notice that Einstein stated the drag per molecule, $F_A = F_{AB}/N_A$:

$$F_A = \frac{k_B T(v_A - v^*)}{\mathcal{D}_{AB}}$$

To complete the calculation, we note that solute A is dilute, so that eqn. (11.22) gives $v^* \cong v_B$:

$$F_A = \frac{k_B T(v_A - v_B)}{\mathcal{D}_{AB}}$$

The velocity difference is just \hat{v}_A in eqn. (11.111), so we can rearrange to finish:

$$\mathcal{D}_{AB} = k_B T(\hat{v}_A/F_A) \quad \longleftarrow \text{Answer}$$

PROBLEM 11.55 In Section 11.11, we evaluated the drag on one species as it diffuses past another. Show that this force also leads to the Einstein relation, eqn. (11.111). Note that the Einstein relation considers the force per molecule and that $R^\circ = k_B N_A$, where N_A is Avogadro's number.

SOLUTION We evaluated the drag force on the diffusing solute A by the solvent B , per unit volume, in eqn. (11.126):

$$f_{AB} = (cR^\circ T) \frac{x_A x_B (v_A - v_B)}{\mathcal{D}_{AB}}$$

Since species A is dilute, $x_B \cong 1$; and $c_i = x_i c$:

$$f_{AB} = \frac{c_i R^\circ T (v_A - v_B)}{\mathcal{D}_{AB}}$$

Einstein's relation gives the drag force F_A per molecule (not per mole). The number of molecules of species i per unit volume is $c_i N_A$. Dividing

$$F_A = \frac{R^\circ T (v_A - v_B)}{N_A \mathcal{D}_{AB}} = \frac{k_B T (v_A - v_B)}{\mathcal{D}_{AB}}$$

With $\hat{v}_A = v_A - v_B$, we obtain the final result

$$\mathcal{D}_{AB} = k_B T (\hat{v}_A / F_A) \quad \longleftarrow \text{Answer}$$

PROBLEM 11.56 Consider a solvent n that contains $n - 1$ dilute solutes with $x_i \ll x_n \cong 1$. (a) Work Problem 11.53c. (b) Show that $\vec{v}^* \cong \vec{v}_n \cong \vec{v}$ if the solutes are dilute. (c) Suppose the solutes are charged ions, such as Na^+ and Cl^- for table salt dissolved in water. An electric potential gradient, $-\nabla\phi$, applied to the solution will create a force per mole of ion, $-z_i\mathcal{F}\nabla\phi$, where z_i is the ion's valence (± 1 for Na^+ and Cl^-) and $\mathcal{F} = 9.6485 \times 10^4$ C/mol is Faraday's constant. Starting with the Maxwell-Stefan equations, derive the *Nernst-Planck equation*:

$$\vec{N}_i = -c\mathcal{D}_{i,n}\nabla x_i + c_i\vec{v}_n - c_i\mathcal{D}_{i,n}z_i\frac{\mathcal{F}}{R^\circ T}\nabla\phi$$

SOLUTION

b) With eqn. (11.22), if $x_i \ll x_n \cong 1$,

$$c\vec{v}^* = \sum_i c_i\vec{v}_i = c \sum_i x_i\vec{v}_i \cong cx_n\vec{v}_n \cong c\vec{v}_n$$

so $\vec{v}^* \cong \vec{v}_i$. With eqn. (11.16), if $m_i \ll m_n \cong 1$,

$$\rho\vec{v} = \sum_i \rho_i\vec{v}_i = \rho \sum_i m_i\vec{v}_i \cong \rho m_n\vec{v}_n \cong \rho\vec{v}_n$$

so $\vec{v} \cong \vec{v}_n \cong \vec{v}^*$. Note that this condition implies that $\vec{J}_n \equiv c_n(v_n - v^*) \cong 0$, by eqn. (11.23).

c) We add the electrostatic force to the left-hand side of eqn. (11.138):

$$-c_i\nabla\mu_i - c_i z_i \mathcal{F} \nabla\phi = -cR^\circ T \sum_{j=1}^n \frac{x_i \vec{J}_j - x_j \vec{J}_i}{c\mathcal{D}_{ij}} \quad (*)$$

In other words, we add the electrostatic force to the chemical potential driving force per unit volume, $-c_i\nabla\mu_i$, and equate the sum to the drag force from other species.

For dilute solutions, we have the same simplification as in Problem 11.53c, so that

$$\sum_{j=1}^n \frac{x_i \vec{J}_j - x_j \vec{J}_i}{c\mathcal{D}_{ij}} \cong -\frac{\vec{J}_i}{c\mathcal{D}_{i,n}}$$

and because dilute solutions are nearly ideal

$$c_i\nabla\mu_i \cong cR^\circ T\nabla x_i$$

Putting these modifications into eqn. (*)

$$-cR^\circ T\nabla x_i - c_i z_i \mathcal{F} \nabla\phi = \frac{R^\circ T}{\mathcal{D}_{i,n}} \vec{J}_i$$

or

$$\vec{J}_i = -c\mathcal{D}_{i,n}\nabla x_i - c_i\mathcal{D}_{i,n}z_i\frac{\mathcal{F}}{R^\circ T}\nabla\phi$$

From part (b), $\vec{v}^* \cong \vec{v}_n \cong \vec{v}$. Then, with $\vec{N}_i \equiv \vec{J}_i + c_i\vec{v}^* \cong \vec{J}_i + c_i\vec{v}_n$ and $\mathcal{D}_{i,n} = \mathcal{D}_{i,n}$ from Problem 11.53c,

$$\vec{N}_i = -c\mathcal{D}_{i,n}\nabla x_i + c_i\vec{v}_n - c_i\mathcal{D}_{i,n}z_i\frac{\mathcal{F}}{R^\circ T}\nabla\phi \quad \longleftarrow \text{Answer}$$

The *Nernst-Planck equation* is widely used in the study of electrochemical systems. The terms on the right-hand side represent diffusion, convection, and electromigration.

PROBLEM 11.57 A liquid mixture of acetone and methanol sits at the bottom of a Stefan tube that is 23.8 cm tall. The top is swept by a flow of pure air. Let species 1 be acetone, species 2 be methanol, and species 3 be air. The temperature is 328.5 K, and the pressure is 745.2 mmHg. The mole fractions just above the liquid are $x_{1,s} = 0.319$ and $x_{2,s} = 0.528$. For these gases, $D_{12} = 0.0848 \text{ cm}^2/\text{s}$, $D_{13} = 0.1372 \text{ cm}^2/\text{s}$, and $D_{23} = 0.1991 \text{ cm}^2/\text{s}$ [1].

- Write the Maxwell-Stefan equations as a matrix o.d.e. for the vector $\mathbf{X}(z) = \{x_1(z), x_2(z)\}$. What is the mole flux of air, N_3 ? What are the boundary conditions at the liquid surface ($z = 0$) and at the top of the tube ($z = 23.8 \text{ cm}$)?
- Use the software of your choice to solve your equation from part (a) and plot the three concentrations as a function of z . Note that the mole fluxes N_1 and N_2 are not known, so that the equations must be solved iteratively to determine value correspond to the boundary condition at the top of the tube. [Ans: $N_1 = 1.782 \times 10^{-7} \text{ mol/cm}^2\text{s}$, $N_2 = 3.126 \times 10^{-7} \text{ mol/cm}^2\text{s}$.]
- If part (b) seems too complex, instead use the answers given for part (b) to solve the equations as if the fluxes were known. Does your solution meet the boundary conditions at the top of the tube? (It should.)
- Does $J_{\text{air}} = 0$ at $z = 0$? Explain.

SOLUTION

- Only two of the three MS equations are independent because $\sum x_i = 1$. Further, in a quasi-steady system, the mole fluxes are constant along the length of the tube. And, because air does not pass through the liquid surface, $N_3 = 0$.

Equations (11.129a) can be written for x_1 and x_2 as

$$c \frac{d}{dz} x_1 = \sum_{j=1}^3 \frac{x_1 N_j - x_j N_1}{D_{1j}} = \frac{x_1 N_2 - x_2 N_1}{D_{12}} + \frac{x_1 N_3^0 - x_3 N_1}{D_{13}}$$

$$c \frac{d}{dz} x_2 = \sum_{j=1}^3 \frac{x_2 N_j - x_j N_2}{D_{2j}} = \frac{x_2 N_1 - x_1 N_2}{D_{21}} + \frac{x_2 N_3^0 - x_3 N_2}{D_{23}}$$

But $x_3 = 1 - x_1 - x_2$ and $D_{ij} = D_{ji}$, so

$$c \frac{d}{dz} x_1 = \frac{x_1 N_2 - x_2 N_1}{D_{12}} - \frac{(1 - x_1 - x_2) N_1}{D_{13}}$$

$$= x_1 \left(\frac{N_2}{D_{12}} + \frac{N_1}{D_{13}} \right) + x_2 \left(\frac{N_1}{D_{13}} - \frac{N_1}{D_{12}} \right) - \frac{N_1}{D_{13}}$$

$$c \frac{d}{dz} x_2 = \frac{x_2 N_1 - x_1 N_2}{D_{12}} - \frac{(1 - x_1 - x_2) N_2}{D_{23}}$$

$$= x_1 \left(\frac{N_2}{D_{12}} - \frac{N_2}{D_{13}} \right) + x_2 \left(\frac{N_1}{D_{12}} + \frac{N_2}{D_{23}} \right) - \frac{N_2}{D_{23}}$$

And in matrix form, these equations are

$$c \frac{d}{dz} \underbrace{\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}}_{=\mathbf{X}} = \underbrace{\begin{pmatrix} \frac{N_2}{D_{12}} + \frac{N_1}{D_{13}} & \frac{N_1}{D_{13}} - \frac{N_1}{D_{12}} \\ \frac{N_2}{D_{12}} - \frac{N_2}{D_{13}} & \frac{N_1}{D_{12}} + \frac{N_2}{D_{23}} \end{pmatrix}}_{=\mathbf{A}} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} - \underbrace{\begin{pmatrix} \frac{N_1}{D_{13}} \\ \frac{N_2}{D_{23}} \end{pmatrix}}_{=\mathbf{B}}$$

or just

$$c \frac{d}{dz} \mathbf{X} = \mathbf{A}\mathbf{X} - \mathbf{B} \quad \leftarrow \text{Answer}$$

The boundary conditions are

$$\mathbf{X} = \begin{pmatrix} 0.319 \\ 0.528 \end{pmatrix} \text{ at } z = 0, \quad \mathbf{X} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \text{ at } z = 23.8 \text{ cm} \quad \leftarrow \text{Answer}$$

b) An example of appropriate code follows, using MATLAB.

```

1 % Solve ODEs iteratively to find fluxes that match bc: x1 = x2 = 0
  at top of tube
2 % species 1 = acetone; species 2 = methanol; species 3 = air
3 % Carty & Schrodtt had: N(1) = 1.779e-7, N(2) = 3.121e-7 [mol/cm^2-s]
4 %
5 % xi = mole fraction;
6 % D_ij = MS diffusivity [cm^2/s]
7 % N(i) = mole flux [mol/cm^2-s]
8
9 global zmax
10 zmax = 23.8; % length of Stefan tube [cm]
11
12 % iterative root finding: get fluxes that make top-end mole
  fractions zero.
13 fun = @root2d;
14 N0 = [0,0]; % initial guess for fluxes
15 options = optimset('Display','off'); % don't show fsolve message
16 N = fsolve(fun,N0,options) % iteratively solve ODE system in fun
17
18 [x1,x2,x3] = Conc(N) % display final solutions
19
20 % Plot results and save as a pdf file
21 clf
22 fplot(x2,'LineWidth',2);
23 ax = gca;
24 ax.FontSize = 16;
25 xlabel('Distance from surface, z [cm]')
26 ylabel('Mole fraction')
27 axis([0 zmax 0 1])
28 grid on
29 hold on
30 fplot(x1,'LineWidth',2)
31 fplot(x3,'LineWidth',2)

```



```

32 legend('Methanol','Acetone','Air','Location','northwest')
33 print('Ternary_Stefan_tube_concentrations', '-dpdf', '-r600'); % 600
    dpi, pdf
34
35 %% function that evaluates mole fractions at zmax as function of
    flux vector N
36 function F = root2d(N);
37     [x1,x2,x3] = Conc(N);
38     global zmax;
39     F(1) = double(subs(x1,zmax)); % convert symbols to numbers for
    fsolve
40     F(2) = double(subs(x2,zmax));
41 end
42
43 %% function that solves M-S odes for given values of flux vector N
44 function [x1,x2,x3] = Conc(N);
45     % data reported by Carty & Schrodt (1975)
46     D12 = 0.0848; % cm^2/s
47     D13 = 0.1372;
48     D23 = 0.1991;
49     cden = 3.6375e-5; % molar density [mol/cm3] calculated for their
    conditions
50
51     % initial conditions (bottom boundary condition)
52     x10 = 0.319; % solution is very sensitive to these ICs.
53     x20 = 0.528; % ICs are mole fractions above liquid surface.
54
55     % Maxwell-Stefan equations in matrix form, after eliminating eqn
    for x3
56     B1 = -N(1)/D13;
57     B2 = -N(2)/D23;
58     A11 = N(1)/D13+N(2)/D12;
59     A12 = N(1)*(1/D13-1/D12);
60     A21 = N(2)*(1/D23-1/D12);
61     A22 = N(1)/D12+N(2)/D23;
62
63     % https://www.mathworks.com/help/symbolic/solve-a-system-of-
    differential-equations.html
64     % X' = AX+B
65     sympref('FloatingPointOutput',true);
66     syms x1(z) x2(z) x3(z)
67     X = [x1; x2];
68     A = [A11 A12; A21 A22]/cden;
69     B = [B1; B2]/cden;
70     C = X(0) == [x10; x20]; % initial conditions
71
72     odes = diff(X) == A*X + B;
73     [x1Sol(z),x2Sol(z)] = dsolve(odes,C);
74
75     % solutions for yi(z)

```

```

76 x1(z) = simplify(x1Sol(z)); % acetone
77 x2(z) = simplify(x2Sol(z)); % methanol
78 x3(z) = 1 - x1(z) - x2(z) ; % air
79 end

```

The computed results are shown in Figure 1. The code returns $N_1 = 1.782 \times 10^{-7}$ mol/cm²s and $N_2 = 3.126 \times 10^{-7}$ mol/cm²s.

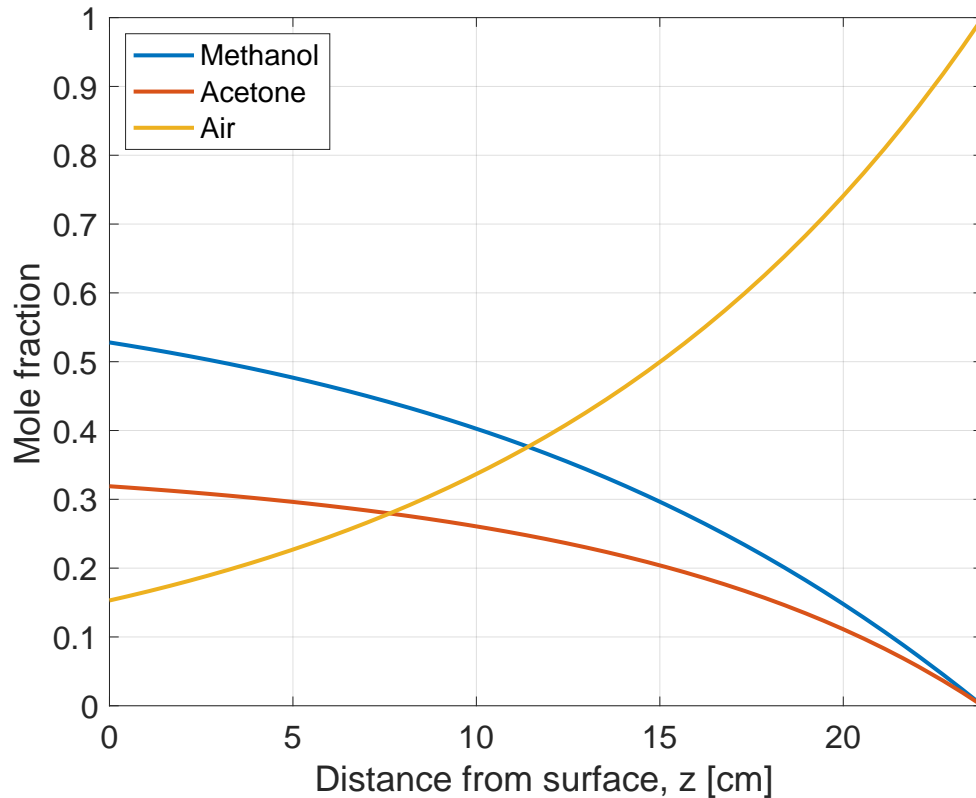


FIGURE 1. Concentration distribution of ternary gas mixture in Stefan tube, computed from Maxwell-Stefan equations. Liquid mixture of acetone and methanol (at $z = 0$) evaporates into tube swept by pure air at the top ($z = 23.8$ cm).

- c) The simpler code follows. The results are almost exactly the same, and the top boundary condition is well met.

```

1 % Values reported by Carty & Schrodtt (1975) in cgs units
2 % 1 = acetone; 2 = methanol; 3 = air
3 % y = mole fraction; N_i = mole flux; D_ij = MS diffusivity;
4 N1 = 1.779e-7; % mol/cm^2-s
5 N2 = 3.121e-7;
6 D12 = 0.0848; % cm^2/s
7 D13 = 0.1372;
8 D23 = 0.1991;
9

```

```

10 cden = 3.6375e-5; % molar density [mol/cm3] calculated for their
    conditions
11
12 y10 = 0.319; % the solution is very sensitive to these ICs.
13 y20 = 0.528;
14 zmax = 23.8; % length of Stefan tube [cm]
15
16 % Maxwell-Stefan equations in matrix form, after eliminating x3
17 B1 = -N1/D13;
18 B2 = -N2/D23;
19 A11 = N1/D13+N2/D12;
20 A12 = N1*(1/D13-1/D12);
21 A21 = N2*(1/D23-1/D12);
22 A22 = N1/D12+N2/D23;
23
24 % https://www.mathworks.com/help/symbolic/solve-a-system-of-
    differential-equations.html
25 %  $Y' = AY+B$ 
26 sympref('FloatingPointOutput',true);
27 syms y1(z) y2(z) y3(z)
28 Y = [y1; y2];
29 A = [A11 A12; A21 A22]/cden;
30 B = [B1; B2]/cden;
31 C = Y(0) == [y10; y20];
32
33 odes = diff(Y) == A*Y + B
34 [y1Sol(z),y2Sol(z)] = dsolve(odes,C);
35
36 y1Sol(z) = simplify(y1Sol(z))
37 y2Sol(z) = simplify(y2Sol(z))
38
39 % Air mole fraction can be obtained from  $y1 + y2 + y3 = 1$ 
40 y3(z) = 1 - y1Sol(z) - y2Sol(z);
41
42 clf
43 fplot(y2Sol, 'LineWidth',2);
44 ax = gca;
45 ax.FontSize = 16;
46 xlabel('Distance from surface, z [cm]')
47 ylabel('Mole fraction')
48 axis([0 zmax 0 1])
49 grid on
50 hold on
51 fplot(y1Sol, 'LineWidth',2)
52 fplot(y3, 'LineWidth',2)
53 legend('Methanol', 'Acetone', 'Air', 'Location', 'northwest')
54 print('Ternary_Stefan_tube_concentrations', '-dpdf', '-r600'); % 600
    dpi, pdf

```

- d) We now know that $N = N_1 + N_2 = 1.782 \times 10^{-7} + 3.126 \times 10^{-7} = 4.908 \times 10^{-7} \text{ mol/cm}^2\text{s}$. We also know that $N_3 = N_{\text{air}} = 0$ and that $x_3 = x_{\text{air}} = 1 - 0.319 - 0.528 = 0.153$ at $z = 0$. Thus

$$J_{\text{air}} = J_3 = \overset{0}{N_3} - x_3 N = -(0.153)(4.908 \times 10^{-7}) = -0.751 \times 10^{-7} \text{ mol/cm}^2\text{s}$$

The diffusional flux of air is not zero because the net mass transfer away from the surface produces convection. Because the air mole flux at the surface is zero, the concentration gradient will have steepened until air diffuses toward the surface at just the rate it is being convected away from the flux.

Comment 1: The linear differential equations can of course be solved analytically (as an initial value problem from $z = 0$), but the boundary conditions at the top must still be matched by a correct choice of the mole fluxes. MATLAB returns the following equations for the concentration profiles with the correct fluxes, for z in cm:

$$\begin{aligned}x_1 &= 0.3631 - 0.0020 e^{0.1591 z} - 0.0421 e^{0.0789 z} \\x_2 &= 0.0020 e^{0.1591 z} - 0.1109 e^{0.0789 z} + 0.6369 \\x_3 &= 0.1530 e^{0.0789 z}\end{aligned}$$

Comment 2: The curves are plotted in Fig. 2 with one of the data sets from Carty's dissertation (Table 1).

TABLE 1. Data from Carty's Ternary Run T-5 [2]

Position [cm]	x_{acetone}	x_{methanol}	x_{air}
4.472	0.2684	0.4568	0.2748
6.954	0.2515	0.4574	0.2911
9.437	0.2332	0.4218	0.3450
11.920	0.2205	0.3799	0.3996
14.402	0.1856	0.3047	0.5096
16.884	0.1551	0.2457	0.5992
19.367	0.1137	0.1668	0.7195

REFERENCES:

- [1] R. Carty and J. Thomas Schrod, "Concentration Profiles in Ternary Gaseous Diffusion," *Industrial & Engineering Chemistry Fundamentals*, **14**(3):276–278, 1975. doi:10.1021/i160055a025.
- [2] Ronald Haden Carty, *Concentration Profiles in a Ternary Gaseous Diffusion System*, PhD Dissertation, Department of Chemical Engineering, University of Kentucky, 1973.

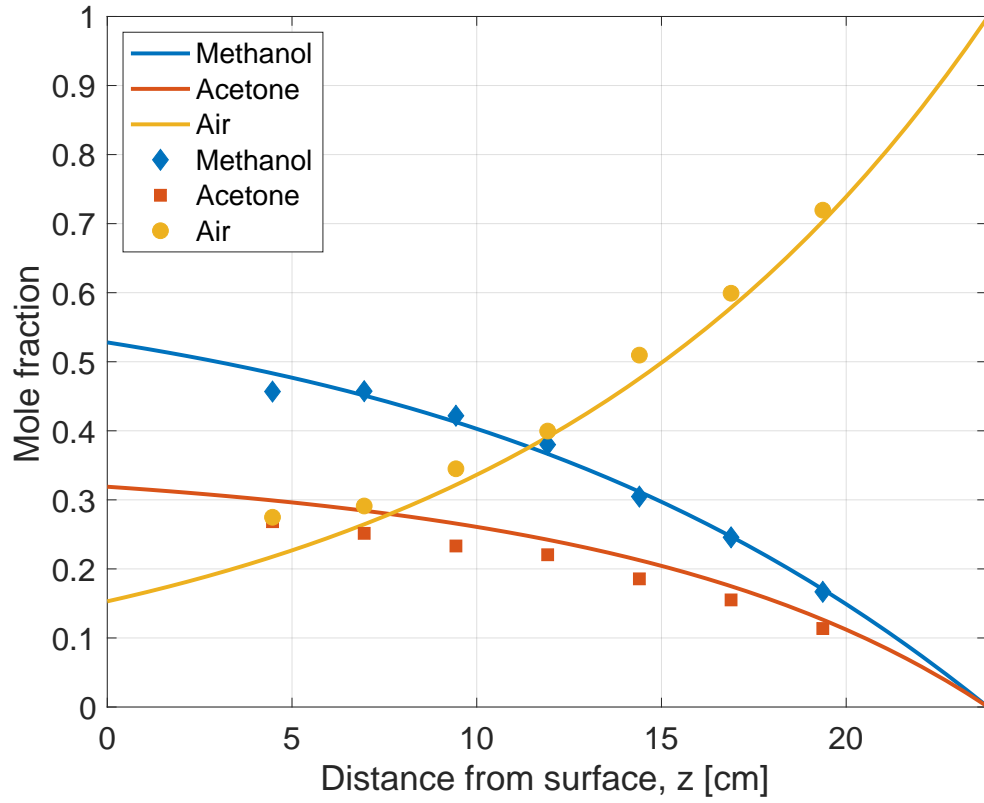
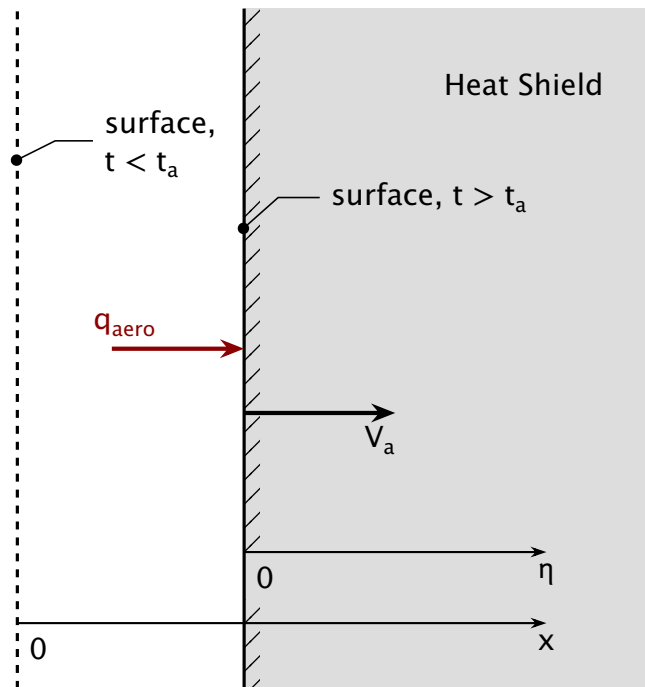


FIGURE 2. Concentration distribution of ternary gas mixture in Stefan tube, computed from Maxwell-Stefan equations, with measurements from [2].

PROBLEM 11.58 A simple model of an ablating heat shield assumes that ablated material is rapidly removed without effecting the flow and that the aerodynamic heat flux, q_{aero} , is constant.

- If the shield is at T_0 when heating starts at $t = 0$, how long until the surface reaches the ablation temperature, T_a , for either melting or sublimation?
- Once ablation starts, assume the surface recedes at a constant speed, V_a . Find the temperature distribution in the material below the surface for $t > t_a$. *Hint:* Change to a coordinate $\eta = x - V_a(t - t_a)$ attached to the receding surface, and ignore the initial distribution of T .
- Use an energy balance to determine V_a in terms of material properties and q_{aero} .
- What combination of material properties best reduces the heat conducted into the heat shield?



SOLUTION

- Using eqn. (5.56), the time to reach the ablation temperature, t_a , is

$$T_a = T_0 + 2 \frac{q_{\text{aero}}}{k} \sqrt{\frac{\alpha t_a}{\pi}}$$

or

$$t_a = \frac{\pi}{\alpha} \left[\frac{k(T_a - T_0)}{2q_{\text{aero}}} \right]^2 = \frac{\pi}{4} (k\rho c_p) \left[\frac{(T_a - T_0)}{q_{\text{aero}}} \right]^2 \quad \leftarrow \text{Answer}$$

- The governing equation is simply the 1D unsteady heat conduction equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

where: x is measured from the initial position of the surface; $T \rightarrow T_0$ as $x \rightarrow \infty$; and $T = T_a$ for $x = V_a t$. The last boundary condition is at the ablating surface for $t > t_a$. Define

a similarity coordinate, $x - V_a(t - t_a)$, which is attached to the receding surface. Then

$$\begin{aligned}\frac{\partial T}{\partial t} &= \frac{\partial T}{\partial \eta} \frac{\partial \eta}{\partial t} = -V_a \frac{dT}{d\eta} \\ \frac{\partial T}{\partial x} &= \frac{\partial T}{\partial \eta} \frac{\partial \eta}{\partial x} = \frac{dT}{d\eta} \\ \frac{\partial^2 T}{\partial x^2} &= \frac{\partial \eta}{\partial x} \frac{\partial}{\partial \eta} \frac{\partial T}{\partial \eta} = \frac{d^2 T}{d\eta^2}\end{aligned}$$

so that

$$-V_a \frac{dT}{d\eta} = \alpha \frac{d^2 T}{d\eta^2}$$

Integrating once (use the trick $y = dT/d\eta$ to do this)

$$\frac{dT}{d\eta} = C \exp\left(-\frac{V_a \eta}{\alpha}\right)$$

where C is a constant. A second integration gives us (collecting constant terms)

$$T(\eta) = C_1 + C_2 \exp(-V_a \eta / \alpha)$$

The surface is at $\eta = 0$ where $T = T_a$, and for $\eta \rightarrow \infty$, $T \rightarrow T_0$. Applying these conditions

$$T(\eta) = T_0 + (T_a - T_0) \exp(-V_a \eta / \alpha) \quad \leftarrow \text{Answer}$$

- c) At the surface, q_{aero} is divided between conduction into the material and the latent heat of melting or subliming (call this L in J/kg). Material is removed from the surface at a rate of ρV_a in kg/m²s. Then

$$q_{\text{aero}} = -k \left. \frac{\partial T}{\partial \eta} \right|_{\eta=0} + \rho L V_a$$

and the first right-hand side term is

$$q_{\text{cond}} = -k \left. \frac{\partial T}{\partial \eta} \right|_{\eta=0} = -k(T_a - T_0)(-V_a/\alpha) = +\rho c_p (T_a - T_0) V_a$$

so that

$$V_a = \frac{q_{\text{aero}}}{\rho [c_p (T_a - T_0) + L]} \quad \leftarrow \text{Answer}$$

- d) The heat shield should prevent heat from being conducted into the spacecraft behind the shield, so the following ratio should be low

$$\frac{q_{\text{cond}}}{q_{\text{aero}}} = \frac{\rho V_a c_p (T_a - T_0)}{\rho V_a [c_p (T_a - T_0) + L]} = \frac{1}{1 + L/c_p (T_a - T_0)} \quad \leftarrow \text{Answer}$$

Thus, to ensure that $q_{\text{cond}} \ll q_{\text{aero}}$, the shield material should have $L \gg c_p (T_a - T_0)$. In addition, V_a should be minimized, which favors high values of both ρL and $\rho c_p (T_a - T_0)$.

Comment: The initial condition for the moving surface problem should be the temperature distribution of the solution of part (a) at t_a . We have not provided an equation for that temperature profile in the text, but it is [2]

$$T(x, t_a) = T_0 + \frac{2q_{\text{aero}}\sqrt{\alpha t_a}}{k} \text{ierfc}\left(\frac{x}{2\sqrt{\alpha t_a}}\right)$$

where ierfc is an integral of the error function, also tabulated as a special function. This profile is similar to a decaying exponential function in x . Since we know t_a from part (a), we can do some algebra to show

$$\frac{T(x, t_a) - T_0}{(T_a - T_0)} = \sqrt{\pi} \text{ierfc}\left(\frac{x}{2\sqrt{\alpha t_a}}\right) \quad (*)$$

where we note that $\text{ierfc}(0) = 1/\sqrt{\pi}$.

On the other hand, evaluating the result of part (b) at $\eta = x - V_a(t_a - t_a)$ gives a different decaying function of x

$$T(x, t_a) = T_0 + (T_a - T_0) \exp(-V_a x / \alpha)$$

or

$$\frac{T(x, t_a) - T_0}{(T_a - T_0)} = \exp(-V_a x / \alpha) \quad (**)$$

Equations (*) and (**) both go from 1 at $x = 0$ to 0 as $x \rightarrow \infty$, but they are otherwise different functions. We cannot do a detailed comparison unless we choose a specific material. Given that we have already made the *vast* simplification of a constant heat flux, the smaller difference in the shape of the initial condition is not very significant.

REFERENCES:

[1] P. M. Sforza, "Thermal protection systems." In P. M. Sforza, ed., *Manned Spacecraft Design Principles*, Chapter 9, pp. 391-452. Butterworth-Heinemann, Boston, 2016. doi:10.1016/B978-0-12-804425-4.00009-X

[2] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., Oxford University Press, 1959, §2.9.