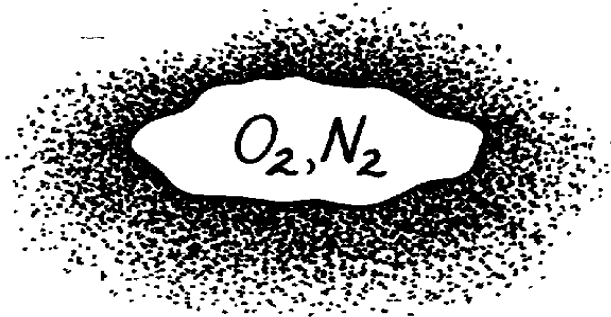# PROBLEM 14.1

KNOWN: Mixture of O_2 and N_2 with partial pressures in the ratio 0.21 to 0.79.

FIND: Mass fraction of each species in the mixture.

SCHEMATIC:

$$\frac{p_{O_2}}{p_{N2}} = \frac{0.21}{0.79}$$

$$M_{O_2} = 32 \text{ kg/kmol}$$

$$M_{N_2} = 28 \text{ kg/kmol}$$

ASSUMPTIONS: (1) Perfect gas behavior.

ANALYSIS: From the definition of the mass fraction,

$$m_i = \frac{r_i}{r} = \frac{r_i}{\Sigma r_i}$$

Hence, with

$$r_i = \frac{p_i}{R_i T} = \frac{p_i}{(\Re / M_i)T} = \frac{M_i p_i}{\Re T}.$$

Hence

$$m_i = \frac{M_i p_i / \Re T}{\Sigma M_i p_i / \Re T}$$

or, cancelling terms and dividing numerator and denominator by the total pressure p,

$$m_i = \frac{M_i x_i}{\Sigma M_i x_i}.$$

With the mole fractions as

$$x_{O_2} = p_{O_2}/p = \frac{0.21}{0.21 + 0.79} = 0.21$$

$$x_{N_2} = p_{N_2}/p = 0.79,$$

find the mass fractions as

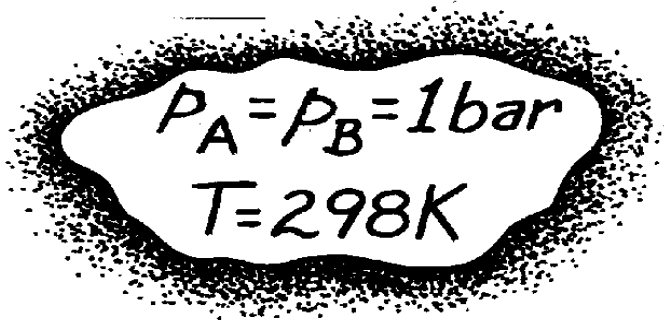$$m_{O_2} = \frac{32 \times 0.21}{32 \times 0.21 + 28 \times 0.79} = 0.233 \qquad <$$

$$m_{N_2} = 1 - m_{O_2} = 0.767. \qquad <$$

PROBLEM 14.2

KNOWN: Partial pressures and temperature for a mixture of CO_2 and N_2.

FIND: Molar concentration, mass density, mole fraction and mass fraction of each species.

SCHEMATIC:

$A \rightarrow CO_2, M_A = 44$ kg/kmol

$B \rightarrow N_2, M_B = 28$ kg/kmol

ASSUMPTIONS: (1) Perfect gas behavior.

ANALYSIS: From the equation of state for an ideal gas,

$$C_i = \frac{p_i}{\Re T}.$$

Hence, with $p_A = p_B$,

$$C_A = C_B = \frac{1\,bar}{8.314 \times 10^{-2}\ m^3 \cdot bar/kmol \cdot K \times 298\,K}$$

$$C_A = C_B = 0.040\ kmol/m^3. \qquad <$$

With $r_i = M_i C_i$, it follows that

$$r_A = 44\ kg/kmol \times 0.04\ kmol/m^3 = 1.78 kg/m^3 \qquad <$$

$$r_B = 28\ kg/kmol \times 0.04\ kmol/m^3 = 1.13\ kg/m^3. \qquad <$$

Also, with

$$x_i = C_i / \Sigma_i C_i$$

find

$$x_A = x_B = 0.04/0.08 = 0.5 \qquad <$$

and with

$$m_i = r_i / \Sigma r_i$$

find

$$m_A = 1.78/(1.78 + 1.13) = 0.61 \qquad <$$

$$m_B = 1.13/(1.78 + 1.13) = 0.39. \qquad <$$

PROBLEM 14.3

KNOWN: Mole fraction (or mass fraction) and molecular weight of each species in a mixture of n species. Equal mole fractions (or mass fractions) of O_2, N_2 and CO_2 in a mixture.

FIND:

SCHEMATIC:

$$x_{O_2} = x_{N_2} = x_{CO_2} = 0.333$$

or

$$m_{O_2} = m_{N_2} = m_{CO_2} = 0.333$$

$$M_{CO_2} = 44$$

$$M_{O_2} = 32, \; M_{N_2} = 28$$

ASSUMPTIONS: (1) Perfect gas behavior.

ANALYSIS: (a) With

$$m_i = \frac{r_i}{r} = \frac{r_i}{\sum_i r_i} = \frac{p_i / R_i T}{\sum_i p_i / R_i T} = \frac{p_i M_i / \Re T}{\sum_i p_i M_i / \Re T}$$

and dividing numerator and denominator by the total pressure p,

$$m_i = \frac{M_i x_i}{\sum_i M_i x_i}. \qquad\qquad <$$

Similarly,

$$x_i = \frac{p_i}{\sum_i p_i} = \frac{r_i R_i T}{\sum_i r_i R_i T} = \frac{(r_i / M_i) \Re T}{\sum_i (r_i / M_i) \Re T}$$

or, dividing numerator and denominator by the total density r

$$x_i = \frac{m_i / M_i}{\sum_i m_i / M_i}. \qquad\qquad <$$

(b) With

$$M_{O_2} x_{O_2} + M_{N_2} x_{N_2} + M_{CO_2} x_{CO_2} = 32 \times 0.333 + 28 \times 0.33 + 44 \times 0.333 = 34.6$$

$$m_{O_2} = 0.31, \qquad m_{N_2} = 0.27, \qquad m_{CO_2} = 0.42. \qquad <$$

With

$$m_{O_2} / M_{O_2} + m_{N_2} / M_{N_2} + m_{CO_2} / M_{CO_2} = 0.333/32 + 0.333/28 + 0.333/44$$
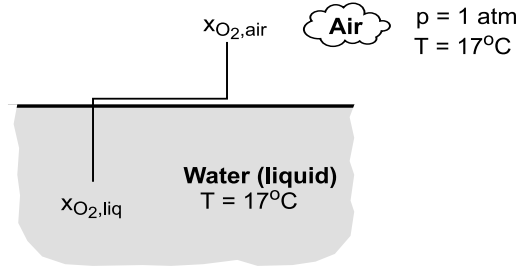
$$m_{O_2} = 2.987 \times 10^{-2}.$$

find

$$x_{O_2} = 0.35, \qquad x_{N_2} = 0.40, \qquad x_{CO_2} = 0.25. \qquad <$$

PROBLEM 14.4

KNOWN: Temperature of atmospheric air and water. Percentage by volume of oxygen in the air.

FIND: (a) Mole and mass fractions of water at the air and water sides of the interface, (b) Mole and mass fractions of oxygen in the air and water.

SCHEMATIC:

ASSUMPTIONS: (1) Perfect gas behavior for air and water vapor, (2) Thermodynamic equilibrium at liquid/vapor interface, (3) Dilute concentration of oxygen and other gases in water, (4) Molecular weight of air is independent of vapor concentration.

PROPERTIES: *Table A-6*, Saturated water (T = 290 K): p_{vap} = 0.01917 bars. *Table A-9*, O_2/water, H = 37,600 bars.

ANALYSIS: (a) Assuming ideal gas behavior, $p_{w,vap} = (N_{w,vap}/V) \cdot T$ and $p = (N/V) \cdot T$, in which case

$$x_{w,vap} = (p_{w,vap}/p_{air}) = (0.01917/1.0133) = 0.0194 \qquad <$$

With $m_{w,vap} = (\rho_{w,vap}/\rho_{air}) = (C_{w,vap} M_w / C_{air} M_{air}) = x_{w,vap}(M_w/M_{air})$. Hence,

$$m_{w,vap} = 0.0194 \,(18/29) = 0.0120 \qquad <$$

Assuming negligible gas phase concentrations in the liquid,

$$x_{w,liq} = m_{w,liq} = 1 \qquad <$$

(b) Since the partial volume of a gaseous species is proportional to the number of moles of the species, its mole fraction is equivalent to its volume fraction. Hence on the air side of the interface

$$x_{O2,air} = 0.205 \qquad <$$

$$m_{O2,air} = x_{O2,air}\left(M_{O_2}/M_{air}\right) = 0.205\,(32/29) = 0.226 \qquad <$$

The mole fraction of O_2 in the water is

$$x_{O2,liq} = p_{O2,air}/H = 0.208 \text{ bars}/37,600 \text{ bars} = 5.53 \times 10^{-6} \qquad <$$

where $p_{O2,air} = x_{O2,air}\,p_{atm} = 0.205 \times 1.0133$ bars $= 0.208$ bars. The mass fraction of O_2 in the water is

$$m_{O2,liq} = x_{O2,liq}\left(M_{O_2}/M_w\right) = 5.53 \times 10^{-6}\,(32/18) = 9.83 \times 10^{-6} \qquad <$$

COMMENTS: There is a large discontinuity in the oxygen content between the air and water sides of the interface. Despite the low concentration of oxygen in the water, it is sufficient to support the life of aquatic organisms.

PROBLEM 14.5

KNOWN: Air is enclosed at uniform pressure in a vertical, cylindrical container whose top and bottom surfaces are maintained at different temperatures.

FIND: (a) Conditions in air when bottom surface is colder than top surface, (b) Conditions when bottom surface is hotter than top surface.

SCHEMATIC:
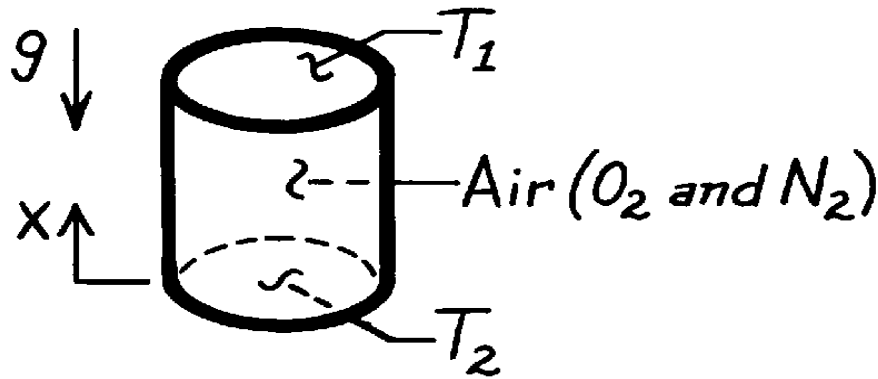
ASSUMPTIONS: (1) Uniform pressure, (2) Perfect gas behavior.

ANALYSIS: (a) If $T_1 > T_2$, the axial temperature gradient (dT/dx) will result in an axial density gradient. However, since $d\rho/dx < 0$ there will be no buoyancy driven, convective motion of the mixture.

There will also be axial species density gradients, $d r_{O_2}/dx$ and $d r_{N_2}/dx$. However, there is no gradient associated with the mass fractions $\left(dm_{O_2}/dx = 0, d m_{N_2}/dx = 0 \right)$. Hence, from Fick's law, Eq. 14.1, there is *no* mass transfer by diffusion.

(b) If $T_1 < T_2$, $d r/dx > 0$ and there will be a buoyancy driven, convective motion of the mixture. However, $dm_{O_2}/dx = 0$ and $dm_{N_2}/dx = 0$, and there is still *no* mass transfer. Hence, although there is motion of each species with the convective motion of the mixture, there is *no relative motion* between species.

COMMENTS: The commonly used special case of Fick's law,

$$j_A = -D_{AB} \frac{d r_A}{dx}$$

would be inappropriate for this problem since r is not uniform. If applied, this special case indicates that mass transfer would occur, thereby providing an incorrect result.

PROBLEM 14.6

KNOWN: Pressure and temperature of hydrogen stored in a spherical steel tank of prescribed diameter and thickness.

FIND: (a) Initial rate of hydrogen mass loss from the tank, (b) Initial rate of pressure drop in the tank.

SCHEMATIC:
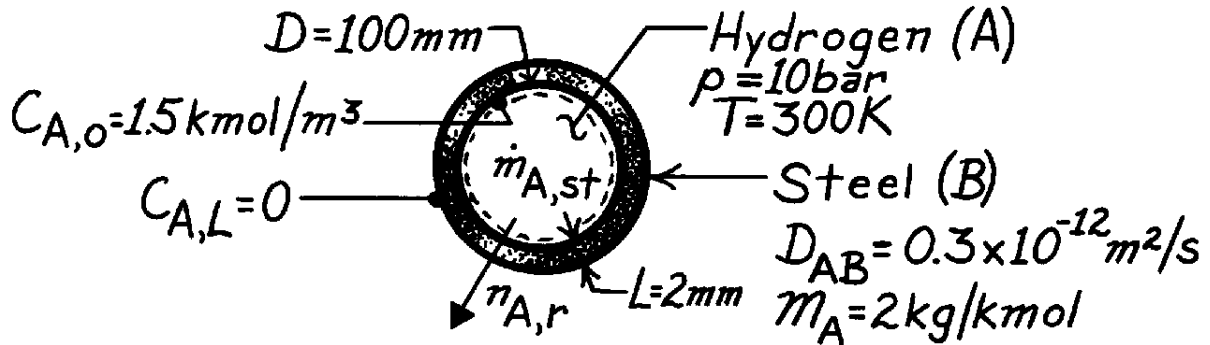
ASSUMPTIONS: (1) One-dimensional species diffusion in a stationary medium, (2) Uniform total molar concentration, C, (3) No chemical reactions.

ANALYSIS: (a) From Table 14.1

$$N_{A,r} = \frac{C_{A,o} - C_{A,L}}{R_{m,dif}} = \frac{C_{A,o}}{(1/4p D_{AB})(1/r_i - 1/r_o)}$$

$$N_{A,r} = \frac{4p\left(0.3 \times 10^{-12}\ m^2/s\right)1.5\ kmol/m^3}{(1/0.05\ m - 1/0.052\ m)} = 7.35 \times 10^{-12}\ kmol/s$$

or

$$n_{A,r} = M_A N_{A,r} = 2\ kg/kmol \times 7.35 \times 10^{-12}\ kmol/s = 14.7 \times 10^{-12}\ kg/s. \qquad <$$

(b) Applying a species balance to a control volume about the hydrogen,

$$\dot{M}_{A,st} = -\dot{M}_{A,out} = -n_{A,r}$$

$$\dot{M}_{A,st} = \frac{d(r_A V)}{dt} = \frac{pD^3}{6}\frac{dr_A}{dt} = \frac{pD^3}{6R_A T}\frac{dp_A}{dt} = \frac{pD^3 M_A}{6\Re T}\frac{dp_A}{dt}$$

Hence

$$\frac{dp_A}{dt} = -\frac{6\Re T}{pD^3 M_A} n_{A,r} = -\frac{6\left(0.08314\ m^3 \cdot bar/kmol \cdot K\right)(300\ K)}{p\left(0.1 m^3\right)2\ kg/kmol} \times 14.7 \times 10^{-12}\ kg/s$$

$$\frac{dp_A}{dt} = -3.50 \times 10^{-7}\ bar/s. \qquad <$$

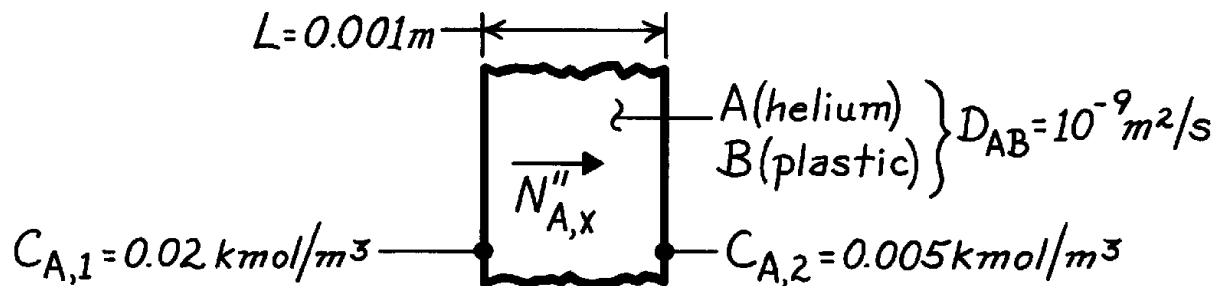**COMMENTS:** If the spherical shell is appoximated as a plane wall, $N_{a,x} = D_{AB}(C_{A,o})\ \pi D^2/L = 7.07 \times 10^{-12}$ kmol/s. This result is 4% lower than that associated with the spherical shell calculation.

KNOWN: Molar concentrations of helium at the inner and outer surfaces of a plastic membrane. Diffusion coefficient and membrane thickness.

FIND: Molar diffusion flux.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion in a plane wall, (3) Stationary medium, (4) Uniform $C = C_A + C_B$.

ANALYSIS: The molar flux may be obtained from Eq. 14.50,

$$N''_{A,x} = \frac{D_{AB}}{L}\left(C_{A,1} - C_{A,2}\right) = \frac{10^{-9}\ m^2/s}{0.001 m}\left(0.02 - 0.005\right) kmol/m^3$$

$$N''_{A,x} = 1.5 \times 10^{-8}\ kmol/s \cdot m^2. \qquad\qquad <$$

COMMENTS: The mass flux is

$$n''_{A,x} = M_A N''_{A,x} = 4\ kg/kmol \times 1.5 \times 10^{-8}\ kmol/s \cdot m^2 = 6 \times 10^{-8}\ kg/s \cdot m^2.$$

PROBLEM 14.8

KNOWN: Mass diffusion coefficients of two binary mixtures at a given temperature, 298 K.

FIND: Mass diffusion coefficients at a different temperature, T = 350 K.

ASSUMPTIONS: (a) Ideal gas behavior, (b) Mixtures at 1 atm total pressure.

PROPERTIES: *Table A-8*, Ammonia-air binary mixture (298 K), $D_{AB} = 0.28 \times 10^{-4} \ m^2/s$; Hydrogen-air binary mixture (298 K), $D_{AB} = 0.41 \times 10^{-4} \ m^2/s$.

ANALYSIS: According to treatment of Section 14.1.5, assuming ideal gas behavior,

$$D_{AB} \sim T^{3/2}$$

where T is in kelvin units. It follows then, that for

$$NH_3 - Air: \quad D_{AB}(350 \ K) = 0.28 \times 10^{-4} \ m^2/s \left(350 \ K / 298 \ K\right)^{3/2}$$

$$D_{AB}(350 \ K) = 0.36 \times 10^{-4} \ m^2/s \qquad\qquad <$$

$$H_2 - Air: \quad D_{AB}(350 \ K) = 0.41 \times 10^{-4} \ m^2/s \left(350/298\right)^{3/2}$$

$$D_{AB}(350 \ K) = 0.52 \times 10^{-4} \ m^2/s \qquad\qquad <$$

COMMENTS: Since the H_2 molecule is smaller than the NH_3 molecule, it follows that

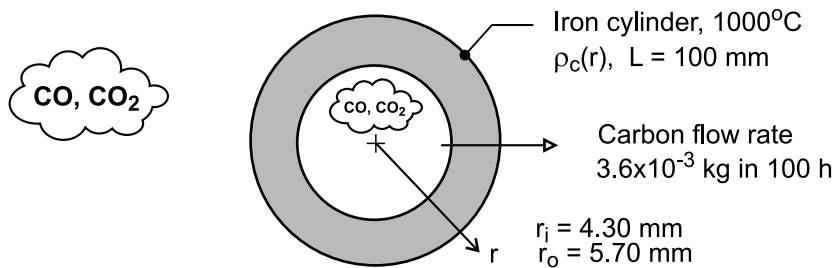$$D_{H_2-Air} > D_{NH_3-Air}$$

as indeed the numerical data indicate.

PROBLEM 14.9

KNOWN: The inner and outer surfaces of an iron cylinder of 100-mm length are exposed to a carburizing gas (mixtures of CO and CO_2). Observed experimental data on the variation of the carbon composition (weight carbon, %) in the iron at 1000°C as a function of radius. Carbon flow rate under steady-state conditions.

FIND: (a) Beginning with Fick's law, show that $d\rho_C / d(\ell n(r))$ is a constant if the diffusion coefficient, D_{C-Fe}, is a constant; sketch of the carbon mass density, $\rho_c(r)$, as function of ln(r) for such a diffusion process; (b) Create a graph for the experimental data and determine whether D_{C-Fe} for this diffusion process is constant, increases or decreases with increasing mass density; and (c) Using the experimental data, calculate and tabulate D_{C-Fe} for selected carbon compositions over the range of the experiment.

SCHEMATIC:

Iron cylinder, 1000°C
$\rho_c(r)$, L = 100 mm

CO, CO₂

co, CO₂

Carbon flow rate
3.6×10^{-3} kg in 100 h

r_i = 4.30 mm
r_o = 5.70 mm

PROPERTIES: *Iron* (1000°C). $\rho = 7730$ kg/m³. Experimental observations of carbon composition

r (mm)	4.49	4.66	4.79	4.91	5.16	5.27	5.40	5.53
Wt. C (%)	1.42	1.32	1.20	1.09	0.82	0.65	0.46	0.28

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional, radial diffusion in a stationary medium, and (3) Uniform total concentration.

ANALYSIS: (a) For the one-dimensional, radial (cylindrical) coordinate system, Fick's law is

$$j_A = -D_{AB} A_r \frac{d\rho_A}{dr} \tag{1}$$

where $A_r = 2\pi r L$. For steady-state conditions, j_A is constant, and if D_{AB} is constant, the product

$$r \frac{d\rho_A}{dr} = C_1 \tag{2}$$

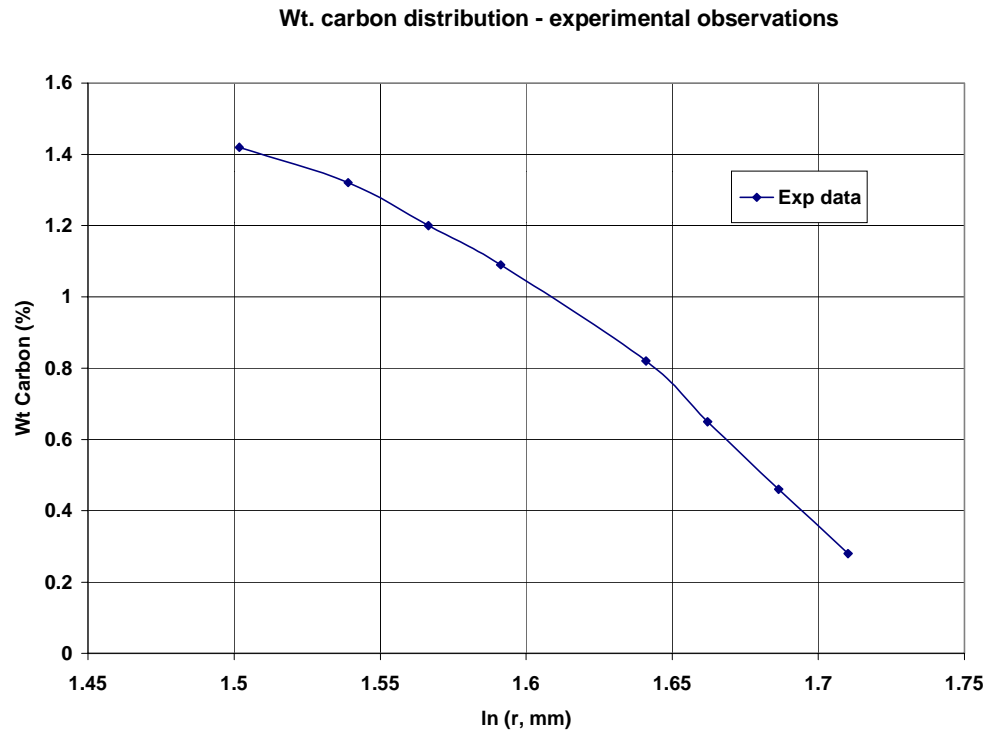must be a constant. Using the differential relation dr/r = d (ln r), it follows that

$$\frac{d\rho_A}{d(\ln r)} = C_1 \tag{3}$$

so that on a ln(r) plot, ρ_A is a straight line. See the graph below for this behavior.

(b) To determine whether D_{C-Fe} is a constant for the experimental diffusion process, the data are represented on a ln(r) coordinate.

Wt. carbon distribution - experimental observations

Since the plot is not linear, D_{C-Fe} is not a constant. From the treatment of part (a), if D_{AB} is not a constant, then

$$D_{AB} \frac{d\rho_A}{d(\ln r)} = C_2$$

must be constant. We conclude that D_{C-Fe} will be lower at the radial position where the gradient is higher. Hence, we expect D_{C-Fe} to increase with increasing carbon content.

(c) From a plot of Wt - %C vs. r (not shown), the mass fraction gradient is determined at three locations and Fick's law is used to calculate the diffusion coefficient,

$$j_c = -\rho \cdot A_r \cdot D_{C-Fe} \frac{\Delta (Wt - \% \ C)}{\Delta r}$$

where the mass flow rate is

$$j_c = 3.6 \times 10^{-3} \ \text{kg} / 100 \ \text{h} \ (3600 \ \text{s} / \text{h}) = 1 \times 10^{-8} \ \text{kg} / \text{s}$$

and $\rho = 7730 \ \text{kg/m}^3$, density of iron. The results of this analysis yield,

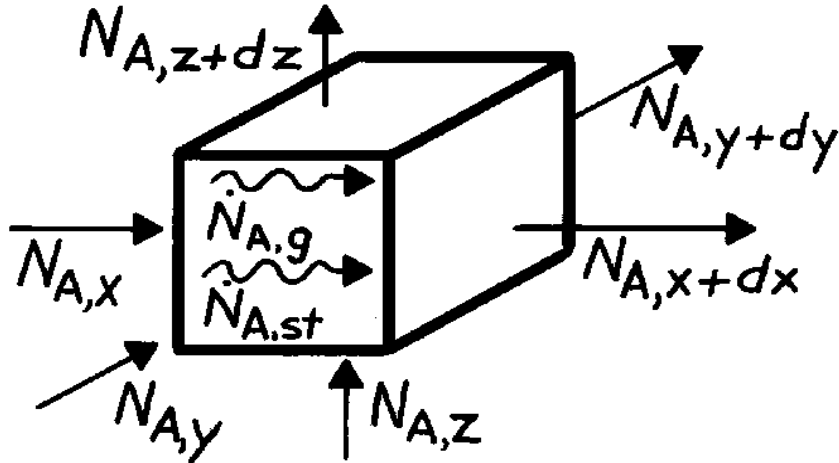| Wt - C (%)	r (mm)	Δ Wt-C/Δr (%/mm)	$D_{C-Fe} \times 10^{11} \ (\text{m}^2/\text{s})$
1.32	4.66	-0.679	6.51
0.955	5.04	-1.08	3.79
0.37	5.47	-1.385	2.72

PROBLEM 14.10

KNOWN: Three-dimensional diffusion of species A in a stationary medium with chemical reactions.

FIND: Derive molar form of diffusion equation.

SCHEMATIC:

ASSUMPTIONS: (1) Uniform total molar concentration, (2) Stationary medium.

ANALYSIS: The derivation parallels that of Section 14.2.2, except that Eq. 14.33 is applied on a molar basis. That is,

$$N_{A,x} + N_{A,y} + N_{A,z} + \dot{N}_{A,g} - N_{A,x+dx} - N_{A,y+dy} - N_{A,z+dz} = \dot{N}_{A,st}.$$

With

$$N_{A,x+dx} = N_{A,x} + \frac{\partial N_{A,x}}{\partial x} dx, \qquad\qquad N_{A,y+dy} = ...$$

$$N_{A,x} = -D_{AB} (dydz) \frac{\partial C_A}{\partial x}, \qquad\qquad N_{A,y} = ...$$

$$\dot{N}_{A,g} = \dot{N}_A (dxdydz), \qquad\qquad \dot{N}_{A,st} = \frac{\partial C_A}{\partial t} dxdydz$$

It follows that

$$\frac{\partial}{\partial x}\left(D_{AB} \frac{\partial C_A}{\partial x} \right) + \frac{\partial}{\partial y}\left(D_{AB} \frac{\partial C_A}{\partial y} \right) + \frac{\partial}{\partial z}\left(D_{AB} \frac{\partial C_A}{\partial z} \right) + \dot{N}_A = \frac{\partial C_A}{\partial t}. \qquad\qquad <$$
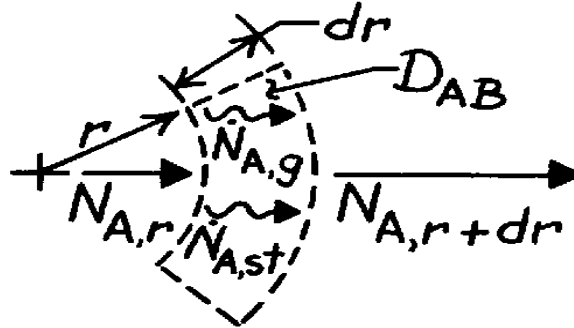
COMMENTS: If D_{AB} is constant, the foregoing result reduces to Eq. 14.38b.

PROBLEM 14.11

KNOWN: Gas (A) diffuses through a cylindrical tube wall (B) and experiences chemical reactions at a volumetric rate, $\dot{N}_A$.

FIND: Differential equation which governs molar concentration of gas in plastic.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional radial diffusion, (2) Uniform total molar concentration, (3) Stationary medium.

ANALYSIS: Dividing the species conservation requirement, Eq. 14.33, by the molecular weight, $_A$, and applying it to a differential control volume of unit length normal to the page,

$$N_{A,r} + \dot{N}_{A,g} - N_{A,r+dr} = \dot{N}_{A,st}$$

where

$$N_{A,r} = (2\boldsymbol{p}r \cdot 1)\, N''_{A,r} = -2\boldsymbol{p}r D_{AB} \frac{\partial C_A}{\partial r}$$

$$N_{A,r+dr} = N_{A,r} + \frac{\partial N_{A,r}}{\partial r} dr$$

$$\dot{N}_{A,g} = -\dot{N}_A (2\boldsymbol{p}r \cdot dr \cdot 1) \qquad \dot{N}_{A,st} = \frac{\partial \left[C_A (2\boldsymbol{p}r dr \cdot 1) \right]}{\partial t}.$$

Hence

$$-\dot{N}_A (2\boldsymbol{p}r dr) + 2\boldsymbol{p} D_{AB} \frac{\partial}{\partial r}\left(r \frac{\partial C_A}{\partial r} \right) dr = 2\boldsymbol{p}r dr \frac{\partial C_A}{\partial t}$$

or

$$\frac{D_{AB}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_A}{\partial r} \right) - \dot{N}_A = \frac{\partial C_A}{\partial t}. \qquad\qquad <$$

COMMENTS: (1) The minus sign in the generation term is necessitated by the fact that the reactions deplete the concentration of species A.

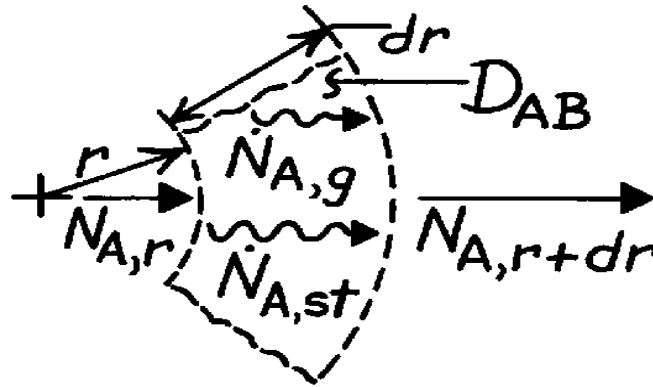(2) From knowledge of $\dot{N}_A (r,t)$, the foregoing equation could be solved for $C_A (r,t)$.

(3) Note the agreement between the above result and the one-dimensional form of Eq. 14.39 for uniform C.

PROBLEM 14.12

KNOWN: One-dimensional, radial diffusion of species A in a stationary, spherical medium with chemical reactions.

FIND: Derive appropriate form of diffusion equation.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional, radial diffusion, (2) Uniform total molar concentration, (3) Stationary medium.

ANALYSIS: Dividing the species conservation requirement, Eq. 14.33, by the molecular weight, $_A$, and applying it to the differential control volume, it follows that

$$N_{A,r} + \dot{N}_{A,g} - N_{A,r+dr} = \dot{N}_{A,st}$$

where

$$N_{A,r} = -D_{AB} 4p r^2 \frac{\partial C_A}{\partial r}$$

$$N_{A,r+dr} = N_{A,r} + \frac{\partial N_{A,r}}{\partial r} dr$$

$$\dot{N}_{A,g} = \dot{N}_A \left(4p r^2 dr \right), \qquad \dot{N}_{A,st} = \frac{\partial \left[C_A \left(4p r^2 dr \right) \right]}{\partial t}.$$

Hence

$$\dot{N}_A \left(4p r^2 dr \right) + 4p \frac{\partial}{\partial r} \left(D_{AB} r^2 \frac{\partial C_A}{\partial r} \right) dr = 4p r^2 \frac{\partial C_A}{\partial t} dr$$

or

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{AB} r^2 \frac{\partial C_A}{\partial r} \right) + \dot{N}_A = \frac{\partial C_A}{\partial t}. \qquad\qquad <$$
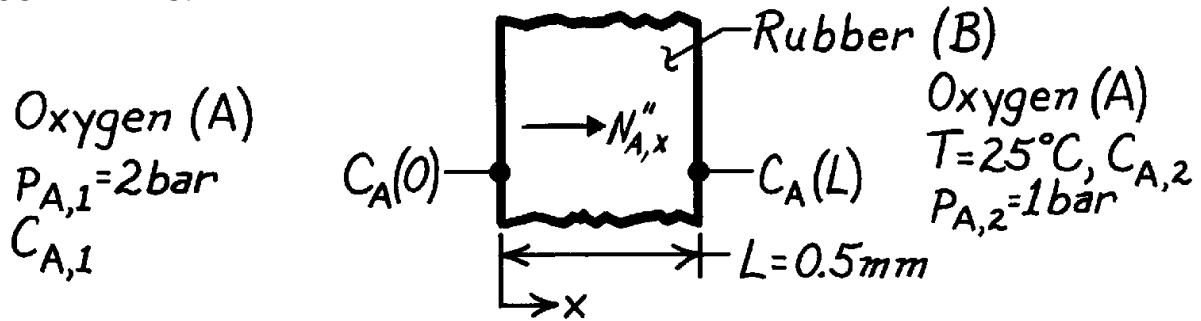
COMMENTS: Equation 14.40 reduces to the foregoing result if C is independent of r and variations in ϕ and θ are negligible.

PROBLEM 14.13

KNOWN: Oxygen pressures on opposite sides of a rubber membrane.

FIND: (a) Molar diffusion flux of O_2, (b) Molar concentrations of O_2 outside the rubber.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional, steady-state conditions, (2) Stationary medium of uniform total molar concentration, $C = C_A + C_B$, (3) Perfect gas behavior.

PROPERTIES: *Table A-8*, Oxygen-rubber (298 K): $D_{AB} = 0.21 \times 10^{-9}$ m^2/s; *Table A-10*, Oxygen-rubber (298 K): $S = 3.12 \times 10^{-3}$ $kmol/m^3 \cdot bar$.

ANALYSIS: (a) For the assumed conditions

$$N''_{A,x} = J^*_{A,x} = -D_{AB}\frac{dC_A}{dx} = D_{AB}\frac{C_A(0) - C_A(L)}{L}.$$

From Eq. 14.33,

$$C_A(0) = Sp_{A,1} = 6.24 \times 10^{-3} kmol/m^3$$

$$C_A(L) = Sp_{A,2} = 3.12 \times 10^{-3} lmol/m^3.$$

Hence

$$N''_{A,x} = 0.21 \times 10^{-9} m^2/s \frac{\left(6.24 \times 10^{-3} - 3.12 \times 10^{-3}\right)kmol/m^3}{0.0005 \text{ m}}$$

$$N''_{A,x} = 1.31 \times 10^{-9} kmol/s \cdot m^2. \qquad <$$

(b) From the perfect gas law

$$C_{A,1} = \frac{p_{A,1}}{\Re T} = \frac{2 \text{ bar}}{\left(0.08314 \text{ m}^3 \cdot bar/kmol \cdot K\right)298 \text{ K}} = 0.0807 \text{ kmol/m}^3 \qquad <$$

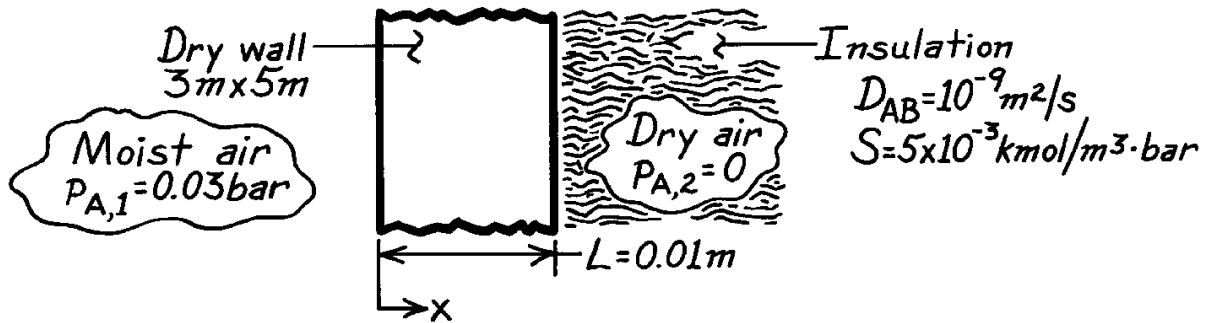$$C_{A,2} = 0.5C_{A,1} = 0.0404 \text{ kmol/m}^3. \qquad <$$

COMMENTS: Recognize that the molar concentrations outside the membrane differ from those within the membrane; that is, $C_{A,1} \neq C_A(0)$ and $C_{A,2} \neq C_A(L)$.

PROBLEM 14.14

KNOWN: Water vapor is transferred through dry wall by diffusion.

FIND: The mass diffusion rate through a $0.01 \times 3 \times 5$ m wall.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional species diffusion, (3) Homogeneous medium, (4) Constant properties, (5) Uniform total molar concentration, (6) Stationary medium with $x_A \ll 1$, (7) Negligible condensation in the dry wall.

ANALYSIS: From Eq. 14.46,

$$N''_{A,x} = -CD_{AB}\frac{dx_A}{dx} = -D_{AB}\frac{dC_A}{dx} = D_{AB}\frac{C_{A,1}-C_{A,2}}{L}.$$

From Eq. 14.33

$$C_{A,1} = Sp_{A,1} = 0.15\times10^{-3}\,\text{kmol/m}^3$$

$$C_{A,2} = Sp_{A,2} = 0\,\text{kmol/m}^3.$$

Hence

$$N''_A = 10^{-9}\,\text{m}^2/\text{s}\times\frac{0.15\times10^{-3}\,\text{kmol/m}^3}{0.01\,\text{m}} = 0.15\times10^{-10}\,\text{kmol/s}\cdot\text{m}^2.$$

Therefore

$$n_A = M_A\left(A\cdot N''_A\right) = 18\text{kg/kmol}\times15\,\text{m}^2\times0.15\times10^{-10}\,\text{kmol/s}\cdot\text{m}^2$$

or

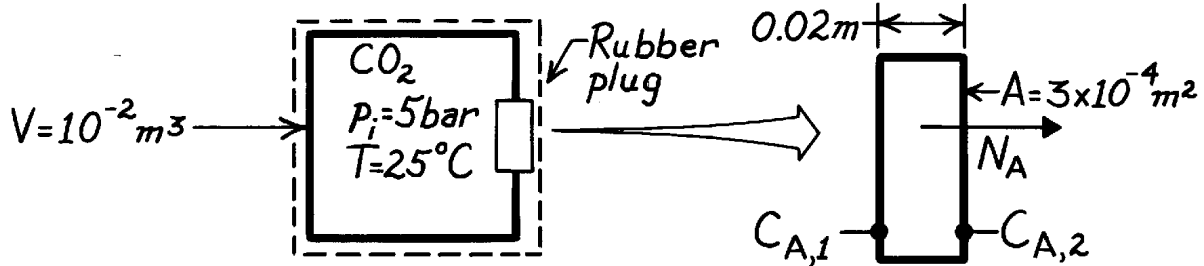$$n_A = 4.05\times10^{-9}\,\text{kg/s}. \qquad\qquad <$$

PROBLEM 14.15

KNOWN: Pressure and temperature of CO_2 in a container of prescribed volume. Thickness and surface area of rubber plug.

FIND: (a) Mass rate of CO_2 loss from container, (b) Reduction in pressure over a 24 h period.

SCHEMATIC:

ASSUMPTIONS: (1) Loss of CO_2 is only by diffusion through the rubber plug, (2) One-dimensional diffusion through a stationary medium, (3) Diffusion rate is constant over the 24 h period, (4) Perfect gas behavior, (5) Negligible CO_2 pressure outside the plug.

PROPERTIES: *Table A-8*, CO_2-rubber (298 K, 1 atm): $D_{AB} = 0.11 \times 10^{-9}$ m^2/s; *Table A-10*, CO_2-rubber (298 K, 1 atm): $S = 40.15 \times 10^{-3}$ kmol/m^3·bar.

ANALYSIS: (a) For diffusion through a stationary medium,

$$N_A = AD_{AB} \frac{C_{A,1} - C_{A,2}}{L}$$

where
$$C_{A,1} = Sp_{A,1} = 40.15 \times 10^{-3} \text{ kmol/m}^3 \cdot \text{bar} \times 5\text{bar} = 0.200 \text{ kmol/m}^3$$
$$C_{A,2} = Sp_{A,2} = 0.$$

Hence

$$N_A = 3 \times 10^{-4} \text{ m}^2 \left(0.11 \times 10^{-9} \text{ m}^2/\text{s}\right) \frac{(0.200 - 0) \text{ kmol/m}^3}{0.02 \text{ m}} = 3.30 \times 10^{-13} \text{ kmol/s}$$

and

$$n_A = M_A N_A = 44 \text{ kg/kmol} \times 3.30 \times 10^{-13} \text{ kmol/s} = 1.45 \times 10^{-11} \text{ kg/s}. \quad <$$

(b) Applying conservation of mass to a control volume about the container

$$\frac{d(r_A V)}{dt} = -n_A \qquad \text{or} \qquad \frac{d(C_A V)}{dt} = -N_A.$$

Hence, with $C_A = p_A/\Re T$,

$$\frac{dp_A}{dt} = -\frac{N_A \Re T}{V} = -\frac{3.3 \times 10^{-13} \text{kmol/s} \times 8.314 \times 10^{-2} \text{m}^3 \cdot \text{bar/kmol} \cdot \text{K} (298\text{K})}{10^{-2} \text{ m}^3} = -8.18 \times 10^{-10} \text{ bar/s}.$$
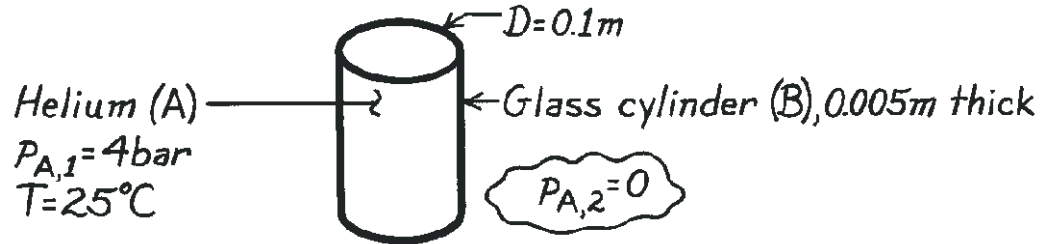
Hence

$$\Delta p_A = \left(\frac{dp_A}{dt}\right)\Delta t = -8.18 \times 10^{-10} \text{ bar/s} \times 24\text{h} \times 3600\text{s/h} = 7.06 \times 10^{-5} \text{ bar}. \quad <$$

PROBLEM 14.16

KNOWN: Pressure and temperature of helium in a glass cylinder of 100 mm inside diameter and 5 mm thickness.

FIND: Mass rate of helium loss per unit length.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional radial diffusion through cylinder wall, (3) Negligible end losses, (4) Stationary medium, (5) Uniform total molar concentration, (6) Negligible helium concentration outside cylinder.

PROPERTIES: *Table A-8*, He-SiO_2 (298 K): $D_{AB} \approx 0.4 \times 10^{-13}$ m^2/s; *Table A-10*, He-SiO_2 (298 K): $S \approx 0.45 \times 10^{-3}$ kmol/$m^3 \cdot$bar.

ANALYSIS: From Table 14.1,

$$N'_{A,r} = \frac{C_{A,S1} - C_{A,S2}}{\ln(r_2/r_1)/2\pi D_{AB}}$$

where, from Eq. 14.44, $C_{A,S} = Sp_A$. Hence

$$C_{A,S1} = Sp_{A,1} = 0.45 \times 10^{-3} \text{ kmol}/m^3 \cdot \text{bar} \times 4 \text{ bar} = 1.8 \times 10^{-3} \text{ kmol}/m^3$$

$$C_{A,S2} = SP_{A,2} = 0.$$

Hence

$$N'_{A,r} = \frac{1.8 \times 10^{-3} \text{ kmol}/m^3}{\ln(0.055/0.050)/2\pi\left(0.4 \times 10^{-13} \text{ m}^2/\text{s}\right)}$$

$$N'_{A,r} = 4.75 \times 10^{-15} \text{ kmol}/\text{s} \cdot \text{m}.$$

The mass loss is then

$$n'_{A,r} = M_A N'_{A,r} = 4 \text{ kg}/\text{kmol} \times 4.75 \times 10^{-15} \text{ kmol}/\text{s} \cdot \text{m}$$

$$n'_{A,r} = 1.90 \times 10^{-14} \text{ kg}/\text{s} \cdot \text{m}. \qquad\qquad <$$
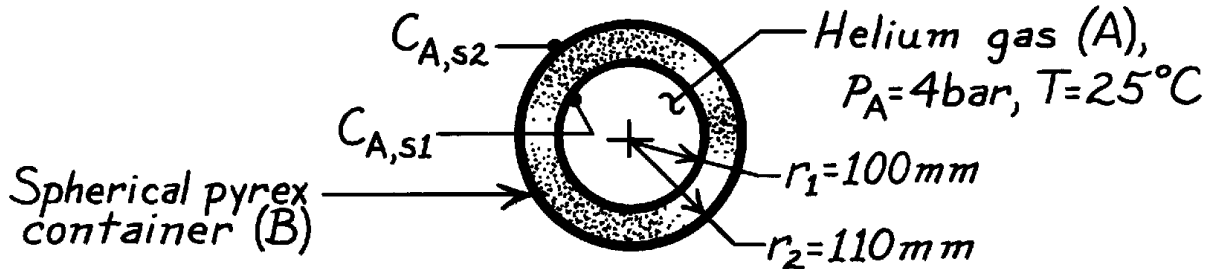
PROBLEM 14.17

KNOWN: Temperature and pressure of helium stored in a spherical pyrex container of prescribed diameter and wall thickness.

FIND: Mass rate of helium loss.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) Helium loss by one-dimensional diffusion in radial direction through the pyrex, (3) $C = C_A + C_B$ is independent of r, and $x_A \ll 1$, (4) Stationary medium.

PROPERTIES: *Table A-8*, He-SiO$_2$ (293 K): $D_{AB} = 0.4 \times 10^{-13}$ m^2/s; *Table A-10*, He-SiO$_2$ (293 K): $S = 0.45 \times 10^{-3}$ kmol/m^3·bar.

ANALYSIS: From Table 14.1, the molar diffusion rate may be expressed as

$$N_{A,r} = \frac{C_{A,S1} - C_{A,S2}}{R_{m,dif}}$$

where

$$R_{m,dif} = \frac{1}{4pD_{AB}}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{1}{4p\left(0.4 \times 10^{-13}\,\text{m}^2/\text{s}\right)}\left(\frac{1}{0.1\text{m}} - \frac{1}{0.11\text{m}}\right) = 1.81 \times 10^{12}\,\text{s}/\text{m}^3$$

with

$$C_{A,S1} = Sp_A = 0.45 \times 10^{-3}\,\text{kmol/m}^3 \cdot \text{bar} \times 4\ \text{bar} = 1.80 \times 10^{-3}\,\text{kmol/m}^3$$
$$C_{A,S2} = 0$$

find

$$N_{A,r} = \frac{1.80 \times 10^{-3}\,\text{kmol/m}^3}{1.81 \times 10^{12}\,\text{s}/\text{m}^3} = 10^{-15}\ \text{kmol/s}.$$

Hence

$$n_{A,r} = M_A N_{A,r} = 4\ \text{kg/mol} \times 10^{-15}\,\text{kmol/s} = 4 \times 10^{-15}\,\text{kg/s}. \qquad <$$

COMMENTS: Since $r_1 \approx r_2$, the spherical shell could have been approximated as a plane wall with L = 0.01 m and $A \approx 4pr_m^2 = 0.139$ m^2. From Table 14.1,

$$R_{m,dif} = \frac{L}{D_{AB}A} = \frac{0.01\text{m}}{\left(0.4 \times 10^{-13}\,\text{m}^2/\text{s}\right)\left(0.137\ \text{m}^2\right)} = 1.8 \times 10^{12}\,\text{s}/\text{m}^3$$

and

$$N_{A,x} = \frac{C_{A,S1} - C_{A,S2}}{R_{m,dif}} = \frac{1.80 \times 10^{-3}\,\text{kmol/m}^3}{1.8 \times 10^{12}\,\text{s}/\text{m}^3} = 10^{-15}\ \text{kmol/s}.$$
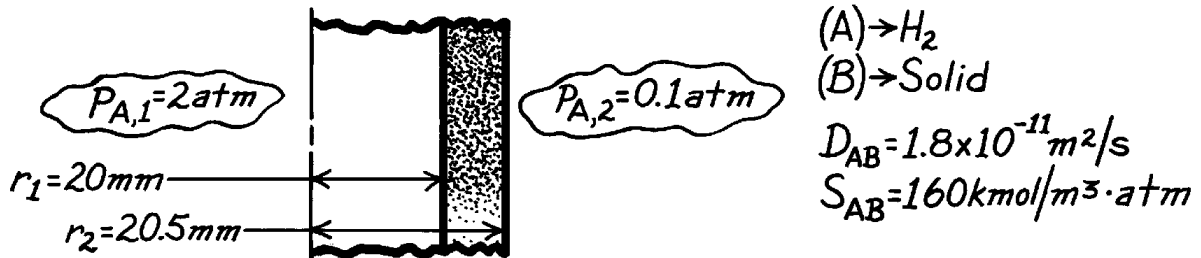
Hence the approximation is excellent.

PROBLEM 14.18

KNOWN: Pressure and temperature of hydrogen inside and outside of a circular tube. Diffusivity and solubility of hydrogen in tube wall of prescribed thickness and diameter.

FIND: Rate of hydrogen transfer through tube per unit length.

SCHEMATIC:

ASSUMPTIONS: (1) Steady diffusion in radial direction, (2) Uniform total molar concentration in wall, (3) No chemical reactions.

ANALYSIS: The mass transfer rate per unit tube length is

$$N'_{A,r} = \frac{C_A(r_1) - C_A(r_2)}{\ln(r_2/r_1)/2pD_{AB}}$$

where from Eq. 14.44, $C_{A,s} = Sp_a$,

$$C_A(r_1) = Sp_{A,1} = 160 \ \text{kmol/m}^3 \cdot \text{atm} \times 2 \ \text{atm} = 320 \ \text{kmol/m}^3$$

$$C_A(r_2) = Sp_{A,2} = 160 \ \text{kmol/m}^3 \cdot \text{atm} \times 0.1 \text{atm} = 16 \ \text{kmol/m}^3.$$

Hence,

$$N'_{A,r} = \frac{(320 - 16)\text{kmol/m}^3}{\ln(20.5/20)/2p \times 1.8 \times 10^{-11} \ \text{m}^2/s} = \frac{304 \ \text{kmol/m}^3}{2.18 \times 10^8 \ s/m^2}$$

$$N'_{A,r} = 1.39 \times 10^{-6} \ \text{kmol/s} \cdot \text{m}. \qquad <$$

COMMENTS: If the wall were assumed to be plane,

$$R'_{m,\text{dif}} = \frac{L}{D_{AB}pD} = \frac{5 \times 10^{-4} \ \text{m}}{1.8 \times 10^{-11} \ \text{m}^2/sp \ (0.04 \ \text{m})} = 2.21 \times 10^8 \ s/m^2$$
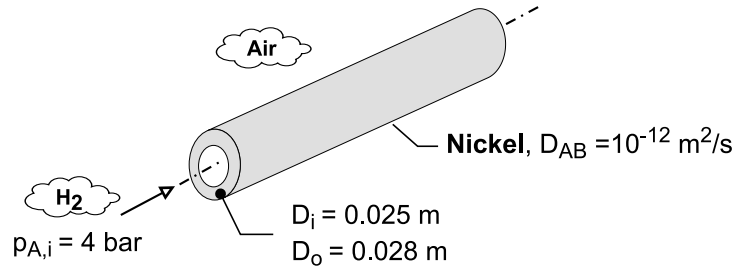
which is close to the value of 2.18×10^8 s/m^2 for the cylindrical wall.

PROBLEM 14.19

KNOWN: Dimensions of nickel tube and pressure of hydrogen flow through the tube. Diffusion coefficient.

FIND: Mass rate of hydrogen diffusion per unit tube length.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state, (2) One-dimensional diffusion through tube wall, (3) Negligible pressure of H_2 in ambient air, (4) Tube wall is a stationary medium of uniform total molar concentration, (5) Constant properties.

PROPERTIES: *Table A-10* (H_2 – Ni): $S = 9.01 \times 10^{-3}$ kmol/m³·bar.

ANALYSIS: From Table 14.1, the resistance to diffusion per unit tube length is $R_{m,dif} = \ln (D_o/D_i)/2\pi \, D_{AB}$, and the molar rate of hydrogen diffusion per unit length is

$$N_{A,r} = \frac{2\pi \, D_{AB} \left(C_{A,si} - C_{A,so} \right)}{\ln \left(D_o / D_i \right)}$$

From Eq. (14.44), the tube wall molar concentrations are

$$C_{A,si} = S \, p_{A,i} = 9.01 \times 10^{-3} \, \text{kmol} / \text{m}^3 \cdot \text{bar} \times 4 \, \text{bar} = 0.036 \, \text{kmol} / \text{m}^3$$

$$C_{A,so} = S \, p_{A,o} = 0$$

$$N_{A,r} = \frac{2\pi \times 10^{-12} \, \text{m}^2 / \text{s} \times 0.036 \, \text{kmol} / \text{m}^3}{\ln \left(0.028 / 0.025 \right)} = 2.00 \times 10^{-12} \, \text{kmol} / \text{s} \cdot \text{m}$$

With $\mathcal{M}_A = 2 \, \text{kg} / \text{kmol}$ for H_2,

$$n_{A,r} = \mathcal{M}_A N_{A,r} = 2 \, \text{kg} / \text{kmol} \times 2.00 \times 10^{-12} \, \text{kmol} / \text{s} \cdot \text{m} = 4.00 \times 10^{-12} \, \text{kg} / \text{s} \cdot \text{m} \qquad <$$
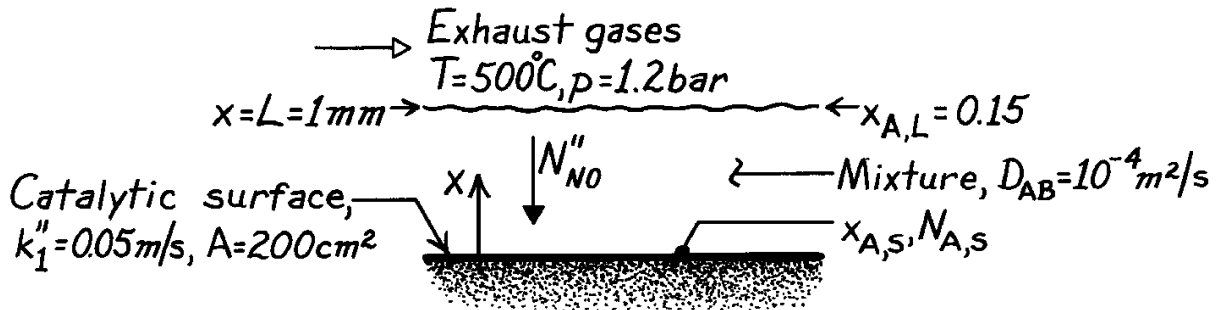
COMMENTS: The hydrogen loss is miniscule.

PROBLEM 14.20

KNOWN: Conditions of the exhaust gas passing over a catalytic surface for the removal of NO.

FIND: (a) Mole fraction of NO at the catalytic surface, (b) NO removal rate.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional species diffusion through the film, (3) Effects of bulk motion on NO transfer in the film are negligible, (4) No homogeneous reactions of NO within the film, (5) Constant properties, including the total molar concentration, C, throughout the film.

ANALYSIS: Subject to the above assumptions, the transfer of species A (NO) is governed by diffusion in a stationary medium, and the desired results are obtained from Eqs. 14.60 and 14.61. Hence

$$\frac{x_{A,s}}{x_{A,L}} = \frac{1}{1+\left(Lk_1''/D_{AB}\right)} \qquad x_{A,s} = \frac{0.15}{1+0.001\,\text{m}\times0.05\,\text{m/s}/\ 10^{-4}\,\text{m}^2/\text{s}} = 0.10. \quad <$$

Also

$$N_{A,s}'' = -\frac{k_1''C x_{A,L}}{1+\left(Lk_1''/D_{AB}\right)}$$

where, from the equation of state for a perfect gas,

$$C = \frac{p}{\Re T} = \frac{1.2\ \text{bar}}{8.314\times10^{-2}\,\text{m}^3\cdot\text{bar/kmol}\cdot\text{K}\times773\ \text{K}} = 0.0187\ \text{kmol/m}^3.$$

Hence

$$N_{A,s}'' = -\frac{0.05\ \text{m/s}\times0.0187\ \text{kmol/m}^3\times0.15}{1+\left(0.001\,\text{m}\times0.05\,\text{m/s}/10^{-4}\ \text{m}^2/\text{s}\right)} = -9.35\times10^{-5}\ \text{kmol/s}\cdot\text{m}^2$$

or

$$n_{A,S}'' = M_A N_{A,S}'' = 30\ \text{kg/kmol}\left(-9.35\times10^{-5}\ \text{kmol/s}\cdot\text{m}^2\right) = -2.80\times10^{-3}\ \text{kg/s}\cdot\text{m}^2.$$

The molar rate of NO removal for the entire surface is then

$$N_{A,s} = N_{A,s}'' A = -9.35\times10^{-5}\ \text{kmol/s}\cdot\text{m}^2\times0.02\ \text{m}^2 = -1.87\times10^{-6}\ \text{kmol/s}$$

or

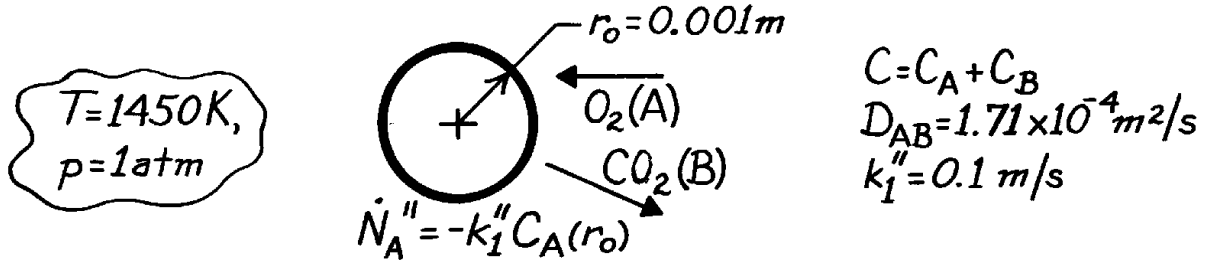$$n_{A,S} = -5.61\times10^{-5}\ \text{kg/s}. \qquad\qquad <$$

COMMENTS: Because bulk motion is likely to contribute significantly to NO transfer within the film, the above results should be viewed as a first approximation.

PROBLEM 14.21

KNOWN: Radius of coal pellets burning in oxygen atmosphere of prescribed pressure and temperature.

FIND: Oxygen molar consumption rate.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional diffusion in r, (2) Steady-state conditions, (3) Constant properties, (4) Perfect gas behavior, (5) Uniform C and T.

ANALYSIS: From Equation 14.53,

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

$$dC_A/dr = C_1/r^2 \qquad \text{or} \qquad C_A = -C_1/r + C_2.$$

The boundary conditions at $r \to \infty$ and $r = r_o$ are, respectively,

$$C_A(\infty) = C \;\to\; C_2 = C$$

$$\dot{N}_A'' = N_A''(r_o) = -CD_{AB}\left.\frac{dx_A}{dr}\right|_{r_o} = -D_{AB}\left.\frac{dC_A}{dr}\right|_{r_o}$$

Hence

$$-k_1''(-C_1/r_o + C) = -D_{AB}C_1/r_o^2$$

$$k_1''(C_1/r_o) + D_{AB}\left(C_1/r_o^2\right) = k_1''C \qquad \text{or} \qquad C_1 = \frac{k_1''C}{\left(k_1''/r_o\right) + \left(D_{AB}/r_o^2\right)}.$$

The oxygen molar consumption rate is

$$N_A''(r_o) = -D_{AB}\left.\frac{dC_A}{dr}\right|_{r_o} = -D_{AB}\frac{k_1''C}{k_1''r_o + D_{AB}}$$

where

$$C = \frac{p}{\mathfrak{R}T} = \frac{1\text{ atm}}{\left(8.205\times10^{-2}\,m^3\cdot atm/kmol\cdot K\right)1450\text{ K}} = 8.405\times10^{-3}\text{ kmol/m}^3.$$

Hence,

$$N_A''(r_o) = -1.71\times10^{-4}\,m^2/s\frac{0.1\,m/s\times8.405\times10^{-3}\,kmol/m^3}{\left(10^{-4} + 1.71\times10^{-4}\right)m^2/s} = -5.30\times10^{-4}\text{ kmol/s}\cdot m^2$$

$$N_A(r_o) = 4p r_o^2 N_A''(r_o) = 4p\,(0.001\text{ m})^2 \times 5.30\times10^{-4}\text{ kmol/s}\cdot m^2$$

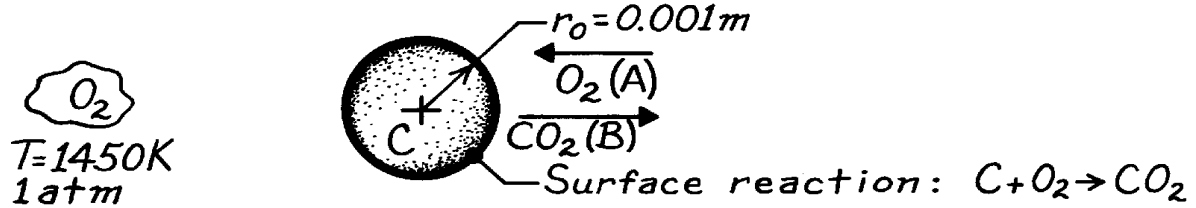$$N_A(r_o) = 6.66\times10^{-9}\text{ kmol/s.} \qquad\qquad\qquad <$$

COMMENTS: The O_2 consumption rate would increase with increasing k_1'' and approach a limiting *finite* value as k_1'' approaches infinity.

PROBLEM 14.22

KNOWN: Radius of coal particles burning in oxygen atmosphere of prescribed pressure and temperature.

FIND: (a) Radial distributions of O_2 and CO_2, (b) O_2 molar consumption rate.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional, steady-state conditions, (2) Uniform total molar concentration, (3) No homogeneous chemical reactions, (4) Coal is pure carbon, (5) Surface reaction rate is infinite (hence concentration of O_2 at surface, C_A, is zero), (6) Constant D_{AB}, (7) Perfect gas behavior.

PROPERTIES: *Table A-8*, $CO_2 \rightarrow O_2$; D_{AB} (273 K) $= 0.14 \times 10^{-4}$ m^2/s; D_{AB} (1450 K) $= D_{AB}$ (273 K) $(1450/273)^{3/2} = 1.71 \times 10^{-4}$ m^2/s.

ANALYSIS: (a) For the assumed conditions, Eq. 14.53 reduces to

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

$$r^2 (dC_A/dr) = C_1 \qquad \text{or} \qquad C_A = -(C_1/r) + C_2.$$

From the boundary conditions:

$$C_A(\infty) = C \rightarrow \qquad C_2 = C$$

$$C_A(r_o) = 0 \rightarrow \qquad 0 = -C_1/r_o + C \qquad\qquad C_1 = Cr_o.$$

Hence, recognizing that $C = C_A + C_B$,

$$C_A = C - C(r_o/r) = C(1 - r_o/r) \qquad\qquad C_B = C - C_A = C(r_o/r). \qquad <$$

(b) The conditions correspond to equimolar, counter diffusion $\left(N_A'' = -N_B'' \right)$, with

$$N_{A,r} = N_{A,r}'' \, 4\pi r^2 = -CD_{AB} \, 4\pi r^2 \frac{dx_A}{dr} = -D_{AB} \, 4\pi r^2 \frac{dC_A}{dr} = -4\pi D_{AB} r^2 \left(+ \frac{Cr_o}{r^2} \right) = -4\pi D_{AB} Cr_o.$$

With

$$C = \frac{p}{\Re T} = \frac{1 \text{ atm}}{8.205 \times 10^{-2} \text{ m}^3 \cdot \text{atm/kmol} \cdot \text{K} \times 1450 \text{ K}} = 8.405 \times 10^{-3} \text{ kmol/m}^3$$

find

$$N_{A,r} = -1.71 \times 10^{-4} \text{ m}^2/\text{s} \times 4\pi \times 8.405 \times 10^{-3} \text{ kmol/m}^3 \left(10^{-3} \text{ m} \right)$$
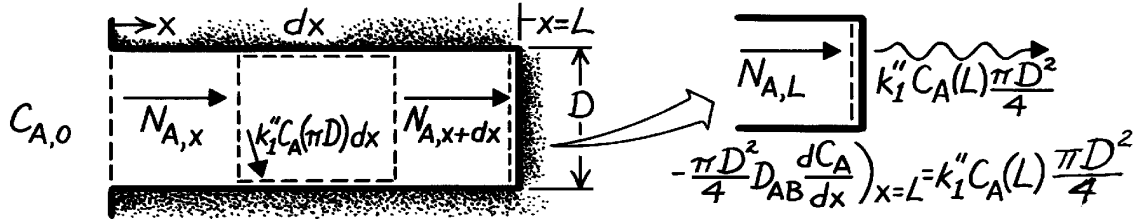
$$N_{A,r} = 1.81 \times 10^{-8} \text{ kmol/s}. \qquad\qquad <$$

PROBLEM 14.23

KNOWN: Pore geometry in a catalytic reactor. Concentration of reacting species at pore opening and order of catalytic reaction.

FIND: (a) Differential equation which determines concentration of reacting species, (b) Distribution of reacting species concentration along the pore.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion in x direction, (3) Stationary medium, (4) Uniform total molar concentration.

ANALYSIS: (a) Apply the species conservation requirement to the differential control volume,

$$N_{A,x} - k_1'' C_A \left(\boldsymbol{p} D \right) dx - N_{A,x+dx} = 0, \text{ where}$$

$$N_{A,x+dx} = N_{A,x} + \left(dN_{A,x} / dx \right) dx$$

and from Fick's law

$$N_{A,x} = \left(-CD_{AB} \frac{dx_A}{dx} \right) \frac{\boldsymbol{p} D^2}{4} = -\frac{\boldsymbol{p} D^2}{4} D_{AB} \frac{dC_A}{dx}.$$

Hence

$$-\frac{dN_A}{dx} dx - k_1'' C_A \left(\boldsymbol{p} D \right) dx = \frac{\boldsymbol{p} D^2}{4} D_{AB} \frac{d^2 C_A}{dx^2} - k_1'' C_A \left(\boldsymbol{p} D \right) dx = 0$$

$$\frac{d^2 C_A}{dx^2} - \frac{4 k_1''}{D D_{AB}} C_A = 0. \qquad \qquad <$$

(b) A solution to the above equation is readily obtained by recognizing that it is of exactly the same form as the energy equation for an extended surface of uniform cross section. Hence for boundary conditions of the form

$$C_A(0) = C_{A,0}, \qquad \qquad -D_{AB} \left(dC_A / dx \right)_{x=L} = k_1'' C_A(L)$$

the solution must be analogous to that obtained for a fin with a convection tip condition. With the analogous quantities

$$C_A \leftrightarrow \boldsymbol{q} \equiv T - T_\infty, \qquad m \equiv \left(4 k_1'' / D D_{AB} \right)^{1/2} \leftrightarrow \left(4h/Dk \right)^{1/2}$$

$$D_{AB} \leftrightarrow k, \qquad \qquad k_1'' \leftrightarrow h$$

the solution is, by analogy to Eq. 3.70

$$C_A(x) = \frac{\cosh\ m(L-x) + \left(k_1'' / m D_{AB} \right) \sinh\ m(L-x)}{\cosh\ mL + \left(k_1'' / m D_{AB} \right) \sinh\ mL}. \qquad \qquad <$$

COMMENTS: The total pore reaction rate is $-D_{AB}(\pi D^2 / 4) \ (dC_A/dx)_{x=0}$, which can be inferred by applying the analogy to Eq. 3.72.

PROBLEM 14.24

KNOWN: Pressure, temperature and mole fraction of CO in auto exhaust. Diffusion coefficient for CO in gas mixture. Film thickness and reaction rate coefficient for catalytic surface.

FIND: (a) Mole fraction of CO at catalytic surface and CO removal rate, (b) Effect of reaction rate coefficient on removal rate.

SCHEMATIC:
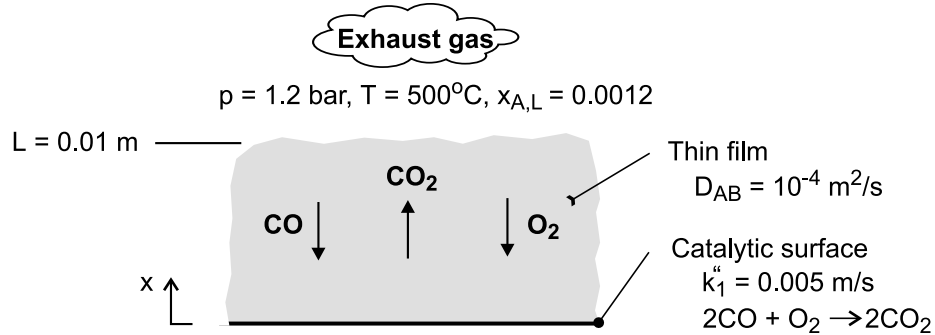
ASSUMPTIONS: (1) Steady-state, (2) One-dimensional species diffusion in film, (3) Negligible effect of advection in film, (4) Constant total molar concentration and diffusion coefficient in film.

ANALYSIS: From Eq. (14.60) the surface molar concentration is

$$x_A(0) = \frac{x_{A,L}}{1+\left(Lk_1''/D_{AB}\right)} = \frac{0.0012}{1+\left(0.01\,\text{m}\times0.005\,\text{m/s}/10^{-4}\,\text{m}^2/\text{s}\right)} = 0.0008 \qquad <$$

With $C = p/\bullet T = 1.2$ bar$/(8.314 \times 10^{-2}$ m$^3\cdot$bar/kmol$\cdot$K $\times$ 773 K$) = 0.0187$ kmol/m^3, Eq. (14.61) yields a CO molar flux, and hence a CO removal rate, of

$$N_{A,s}'' = -N_A''(0) = \frac{k_1'' C\, x_{A,L}}{1+\left(Lk_1''/D_{AB}\right)}$$

$$N_{A,s}'' = \frac{0.005\,\text{m/s}\times0.0187\,\text{kmol/m}^3\times0.0012}{1+\left(0.01\text{m}\times0.005\,\text{m/s}/10^{-4}\,\text{m}^2/\text{s}\right)} = 7.48\times10^{-8}\,\text{kmol/s}\cdot\text{m}^2 \qquad <$$

If the process is diffusion limited, $Lk_1''/D_{AB} \gg 1$ and

$$N_{A,s}'' = \frac{C\,D_{AB}\,x_{A,L}}{L} = \frac{0.0187\,\text{kmol/m}^3\times10^{-4}\,\text{m}^2/\text{s}\times0.0012}{0.01\text{m}} = 2.24\times10^{-7}\,\text{kmol/s}\cdot\text{m}^2 \qquad <$$

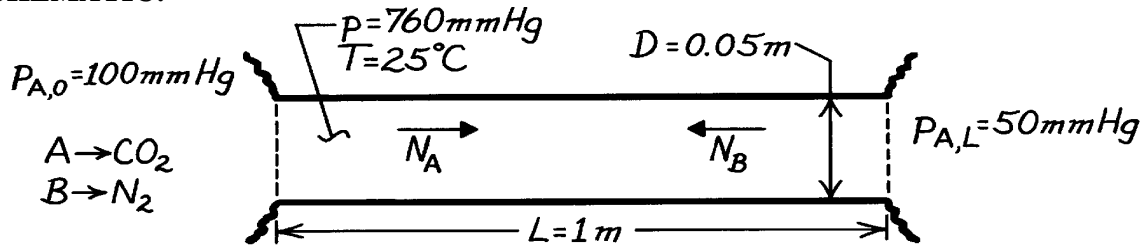**COMMENTS:** If the process is reaction limited, $N_{A,s}'' \to 0$ as $k_1'' \to 0$.

KNOWN: Partial pressures and temperatures of CO_2 at opposite ends of a circular tube which also contains nitrogen.

FIND: Mass transfer rate of CO_2 through the tube.

SCHEMATIC:

$p = 760 \, mmHg$
$T = 25°C$
$D = 0.05 \, m$
$P_{A,0} = 100 \, mmHg$
$P_{A,L} = 50 \, mmHg$
$A \rightarrow CO_2$
$B \rightarrow N_2$
N_A
N_B
$L = 1 \, m$

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion, (3) Uniform temperature and total pressure.

PROPERTIES: *Table A-8*, $CO_2 - N_2$ (T ≈ 298 K, 1 atm): $D_{AB} = 0.16 \times 10^{-4} \, m^2/s$.

ANALYSIS: From Eq. 14.70 the CO_2 molar transfer rate is

$$N_A = \frac{D_{AB}\left(pD^2/4\right)}{\Re T} \frac{p_{A,0} - p_{A,L}}{L}$$

$$N_A = \frac{0.16 \times 10^{-4} \, m^2/s \, (p/4)(0.05 \, m)^2}{0.08205 \, m^3 \cdot atm/kmol \cdot K \times 298 \, K} \frac{(100 - 50) \, mmHg}{1 \, m \times 760 \, mmHg/atm}$$

$$N_A = 8.45 \times 10^{-11} \, kmol/s.$$

The mass transfer rate is then

$$n_A = M_A N_A = 44 \, kg/kmol \times 8.45 \times 10^{-11} \, kmol/s$$

$$n_A = 3.72 \times 10^{-9} \, kg/s. \qquad <$$

COMMENTS: Although the molar transfer rate of N_2 in the opposite direction is $N_B = 8.45 \times 10^{-11}$ kmol/s, the mass transfer rate is

$$n_B = M_B N_B = 28 \, kg/kmol \times 8.45 \times 10^{-11} \, kmol/s = 2.37 \times 10^{-9} \, kg/s.$$

PROBLEM 14.26

KNOWN: Conditions associated with evaporation from a liquid in a column, with vapor (A) transfer occurring in a gas (B). In one case B has unlimited solubility in the liquid; in the other case it is insoluble.

FIND: Case characterized by the largest evaporation rate and ratio of evaporation rates if $p_A = 0$ at the top of the column and $p_A = p/10$ at the liquid interface.

SCHEMATIC:
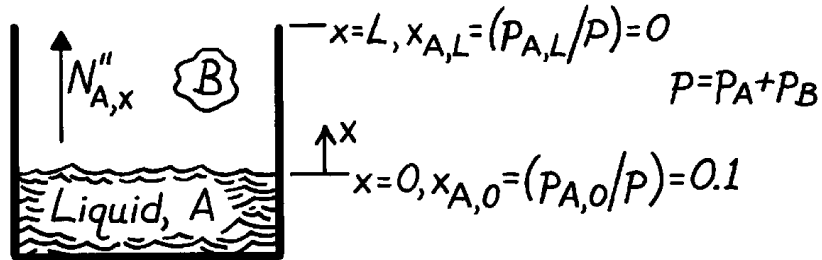
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional species transfer, (3) Uniform temperature and total pressure in the column, (4) Constant properties.

ANALYSIS: If gas B has unlimited solubility in the liquid, the solution corresponds to equimolar counter diffusion of A and B. From Eqs. 14.63 and 14.68, it follows that

$$N_{A,x}'' = -CD_{AB}\frac{dx_A}{dx} = CD_{AB}\frac{x_{A,0} - x_{A,L}}{L}. \tag{1}$$

If gas B is completely insoluble in the liquid, the diffusion of A is augmented by convection and from Eqs. 14.73 and 14.77

$$N_{A,x}'' = -CD_{AB}\frac{dx_A}{dx} + C_A v_x^* = \frac{CD_{AB}}{L}\ln\frac{1-x_{A,L}}{1-x_{A,0}}. \tag{2}$$

Comparing Eqs. (1) and (2), it is obvious that the evaporation rate for the second case exceeds that for the first case. Also

$$\frac{N_{A,x}''(\text{sol})}{N_{A,x}''(\text{insol})} = \frac{(CD_{AB}/L)(x_{A,0} - x_{A,L})}{(CD_{AB}/L)\ln(1-x_{A,L})/(1-x_{A,0})} = \frac{0.1-0}{\ln[(1-0)/(1-0.1)]}$$

$$\frac{N_{A,x}''(\text{sol})}{N_{A,x}''(\text{insol})} = 0.949. \qquad <$$

COMMENTS: The above result suggests that, since the mole fraction of the saturated vapor is typically small, the rate of evaporation in a column is well approximated by the result corresponding to equimolar counter diffusion.

PROBLEM 14.27

KNOWN: Water in an open pan exposed to prescribed ambient conditions.

FIND: Evaporation rate considering (a) diffusion only and (b) convective effects.

SCHEMATIC:
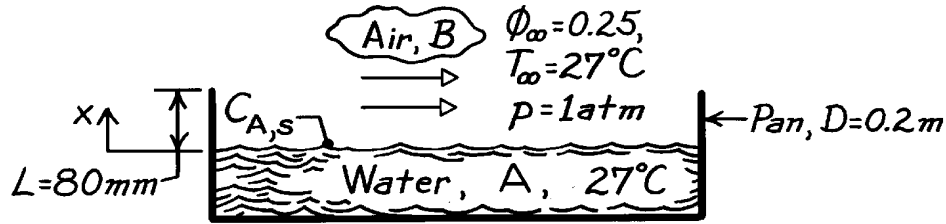
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion, (3) Constant properties, (4) Uniform T and p, (5) Perfect gas behavior.

PROPERTIES: *Table A-8*, Water vapor-air (T = 300 K, 1 atm), $D_{AB} = 0.26 \times 10^{-4}$ m^2/s; *Table A-6*, Water vapor (T = 300 K, 1 atm), $p_{sat} = 0.03513$ bar, $v_g = 39.13$ m^3/kg.

ANALYSIS: (a) The evaporation rate considering only diffusion follows from Eq. 14.63 simplified for a stationary medium. That is,

$$N_{A,x} = N''_{A,x} \cdot A = -D_{AB} A \frac{dC_A}{dx}.$$

Recognizing that $\phi \equiv p_A/p_{A,sat} = C_A/C_{A,sat}$, the rate is expressed as

$$N_{A,x} = -D_{AB} A \frac{C_{A,\infty} - C_{A,s}}{L} = \frac{D_{AB} A}{L} C_{A,sat} (1 - f_\infty)$$

$$N_{A,x} = \frac{0.26 \times 10^{-4} \text{ m}^2/\text{s} (p/4)(0.2\text{m})^2}{80 \times 10^{-3} \text{m}} \frac{1}{39.13 \text{ m}^3/\text{kg} \times 18 \text{ kg/kmol}} (1 - 0.25) = 1.087 \times 10^{-8} \text{kmol/s}$$

where $C_{A,s} = 1/(v_g M_A)$ with $M_A = 18$ kg/kmol.

(b) The evaporation rate considering convective effects using Eq. 14.77 is

$$N_{A,x} = N''_{A,x} \cdot A = \frac{C D_{AB} A}{L} \ln \frac{1 - x_{AL}}{1 - x_{A,0}}.$$

Using the perfect gas law, the total concentration of the mixture is

$$C = p/\Re T = 1.0133 \text{ bar}/\left(8.314 \times 10^{-2} \text{m}^3 \cdot \text{bar/kmol} \cdot \text{K} \times 300 \text{K}\right) = 0.04063 \text{ kmol/m}^3$$

where p = 1 atm = 1.0133 bar. The mole fractions at x = 0 and x = L are

$$x_{A,0} = \frac{p_{A,s}}{p} = \frac{0.03531 \text{bar}}{1.0133 \text{bar}} = 0.0348 \qquad x_{A,L} = f_\infty x_{A,0} = 0.0087.$$

Hence

$$N_{A,x} = \frac{0.04063 \text{ kmol/m}^3 \times 0.26 \times 10^{-4} \text{m}^2/\text{s} (p/4)(0.2 \text{ m})^2}{80 \times 10^{-3} \text{ m}} \ln \frac{1 - 0.0087}{1 - 0.0348} = 1.107 \times 10^{-8} \text{kmol/s}. \qquad <$$

COMMENTS: For this situation, the convective effect is very small but does tend to increase (by 1.5%) the evaporation rate as expected.

PROBLEM 14.28

KNOWN: Vapor concentrations at ends of a tube used to grow crystals. Presence of an inert gas. Ends are impermeable to the gas. Constant temperature.

FIND: Vapor molar flux and spatial distribution of vapor molar concentration. Location of maximum concentration gradient.

SCHEMATIC:
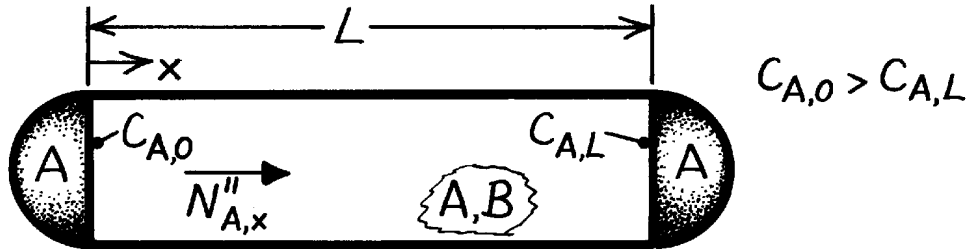
ASSUMPTIONS: (1) One-dimensional, steady-state conditions, (2) Constant properties, (3) Constant pressure, hence C is constant.

ANALYSIS: Physical conditions are analogous to those of the evaporation problem considered in Section 14.4.4 with

$C_{A,0} > C_{A,L} \rightarrow$ diffusion of vapor from source to crystal,

$C_{B,L} > C_{B,0} \rightarrow$ diffusion of inert gas from crystal to source,

Impermeable ends $\rightarrow$ absolute flux of species B is zero $\left(N''_{B,x} = 0 \right)$; hence $v_{B,x} = 0$.

Diffusion of B from crystal to source must be balanced by advection from source to crystal. The advective velocity is $v_x^* = N''_{A,x} / C$. The vapor molar flux is therefore determined by Eq. 14.77,

$$N''_{A,x} = \frac{CD_{AB}}{L} \ln\left(\frac{1 - x_{A,L}}{1 - x_{A,0}} \right) \qquad <$$

and the vapor molar concentration is given by Eq. 14.75,

$$x_A = \frac{C_A}{C} = 1 - \left(1 - x_{A,0} \right) \left(\frac{1 - x_{A,L}}{1 - x_{A,0}} \right)^{x/L}. \qquad <$$

From Eq. 14.72,

$$\frac{dx_A}{dx} = -N''_{A,x} \left(1 - x_A \right) / CD_{AB}$$

$$\frac{dC_A}{dx} = -\frac{N''_{A,x}}{D_{AB}} \left(1 - x_A \right).$$

Hence maximum concentration gradient corresponds to minimum x_A and occurs at
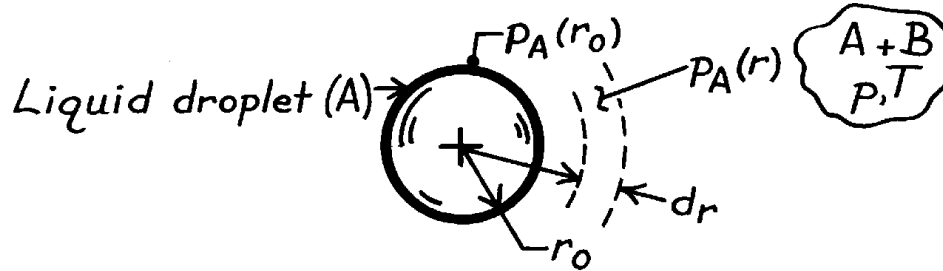
$$x = L.$$

COMMENTS: Vapor transfer is enhanced by the advection, which is induced by presence of the inert gas.

PROBLEM 14.29

KNOWN: Spherical droplet of liquid A and radius r_o evaporating into stagnant gas B.

FIND: Evaporation rate of species A in terms of $p_{A,sat}$, partial pressure $p_A(r)$, the total pressure p and other pertinent parameters.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional, radial, species diffusion, (3) Constant properties, including total concentration, (4) Droplet and mixter air at uniform pressure and temperature, (5) Perfect gas behavior.

ANALYSIS: From Eq. 14.31 for a radial spherical coordinate system, the evaporation rate of liquid A into a binary gas mixture A + B is

$$N_{A,r} = -D_{AB} A_r \frac{dC_A}{dr} + \frac{C_A}{C} N_{A,r}$$

where $A_r = 4\pi r^2$ and $N_{A,r} = N_A$, a constant,

$$N_A \left(1 - \frac{C_A}{C}\right) = -D_{AB} \cdot 4\boldsymbol{p}r^2 \cdot \frac{dC_A}{dr}.$$

From perfect gas behavior, $C_A = p_A / \Re T$ and $C = p / \Re T$,

$$N_A (p - p_A) = -D_{AB} \cdot 4\boldsymbol{p}r^2 \cdot \frac{p}{\Re T} \frac{dp_A}{dr}$$

Separating variables, setting definite limits, and integrating

$$-N_A \frac{\Re T}{p} \frac{1}{4\boldsymbol{p}D_{AB}} \int_{r_o}^r \frac{dr}{r^2} = \int_{p_{A,r_o}}^{p_{A,r}} \frac{dp_A}{p - p_A}$$

find that

$$N_A = 4\boldsymbol{p}r_o D_{AB} \frac{p}{\Re T} \frac{1}{1 - r_o / r} \ln \frac{p - p_A(r)}{p - p_{A,o}} \qquad <$$

where $p_{A,o} = p_A(r_o) = p_{A,sat}$, the saturation pressure of liquid A at temperature T.

COMMENTS: Compare the method of solution and result with the content of Section 14.4.4, Evaporation in a Column.

PROBLEM 14.30

KNOWN: Vent pipe on a methanol distillation system condenser discharges to atmosphere at 1 bar. Cooler and vent at 21°C. Vapor volume of cooler is 0.005 m^3.

FIND: (a) Weekly loss of methanol vapor due to diffusion out the vent pipe and (b) Weekly loss due to expulsion of methanol vapor in the cooler once per hour caused by process heat rate change.

SCHEMATIC:
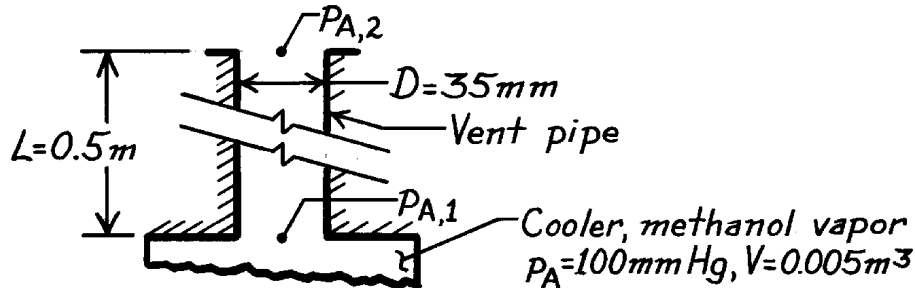
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional species transport, (3) Uniform temperature and total pressure in vent pipe, (4) Constant properties, (5) Perfect gas behavior.

PROPERTIES: Methanol-air mixture (given, 273 K): $D_{AB} = 0.13 \times 10^{-4}$ m^2/s.

ANALYSIS: (a) The methanol transfer rate through the vent follows from Eq. 14.77

$$N_{A,x} = N''_{A,x} \cdot A_c = \frac{pD^2}{4} \frac{CD_{AB}}{L} \ln\frac{1-p_{A,2}/p}{1-p_{A,1}/p}$$

where $p_{A,2} = 0$ and $p_{A,1} = p_A = 100$ mmHg = 0.1333 bar = 13.3 kPa,

$$C = \frac{p}{\Re T} = \frac{1\,bar}{8.314\times10^{-2}\,m^3 \cdot bar/kmol\cdot K(21+273)\,K} = 4.093\times10^{-2}\,kmol/m^3$$

$$D_{AB}(294K) = D_{AB}(273)(294/273)^{3/2} = 0.13\times10^{-4}\,m^2/s\,(294/273)^{3/2} = 0.145\times10^{-4}\,m^2/s.$$

Substituting numerical values, find the rate on a weekly basis as

$$N_A = \frac{p\,(0.035\,m)^2}{4} \times 4.093\times10^{-2}\,kmol/m^3 \times \frac{0.145\times10^{-4}\,m^2/s}{0.5\,m} \ln\frac{1-0}{1-0.1333/1}$$

$$\times 3600\,s/h\times24h/day\times7day/week = 9.883\times10^{-5}\,kmol/week$$

$$m_A = N_A M_A = 9.883\times10^{-5}\,kmol/week\times32\,kg/kmol = 0.00316\,kg/week. \qquad <$$

(b) The methanol vapor in the cooler of volume 0.005 m^3 is expelled once per hour, so that the additional mass loss is $m_A = n_A M_A$, where n_A is

$$n_A = \frac{p_A V}{\Re T} = \frac{0.1333bar\times0.005m^3}{8.314\times10^{-2}\,m^3 \cdot bar/kmol\cdot K\times294\,K} = 2.728\times10^{-5}\,kmol$$

from which it follows that

$$m_A = 2.728\times10^{-5}\,kmol/\times24\times7\times32\,kg/kmol = 0.1467\,kg/week. \qquad <$$

COMMENTS: Note that the loss through the vent is approximately 2% that lost by expulsion when the process heat rate is varied.

PROBLEM 14.31

KNOWN: Clean surface with pure steam has condensate rate of 0.020 kg/m²·s for the prescribed conditions. With the presence of stagnant air in the steam, the condensate surface drops from 28°C to 24°C and the condensate rate is halved.

FIND: Partial pressure of air in the air-steam mixture as a function of distance from the condensate film.

SCHEMATIC:
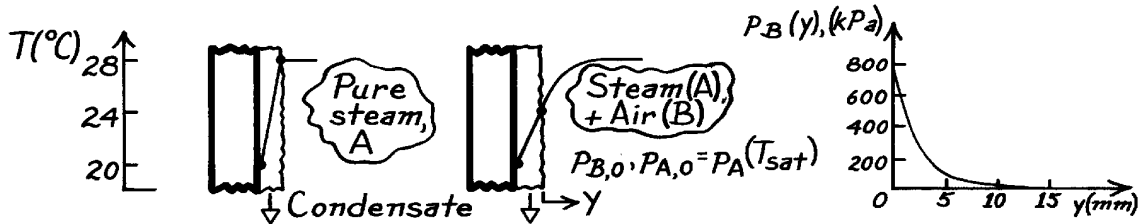
ASSUMPTIONS: (1) Steady-state conditions, (2) Constant properties including pressure in air-steam mixture, (3) Perfect gas behavior.

PROPERTIES: *Table A-6*, Water vapor: p_{sat} (28°C = 301 K) = 0.03767 bar; p_{sat} (24°C = 297 K) = 0.02983 bar; *Table A-8*, Water-air (298 K, 1 bar): $D_{AB} = 0.26 \times 10^{-4}$ m²/s.

ANALYSIS: The partial pressure distribution of the air as a function of distance y can be found from the species (A) rate expression, Eq. 14.77,

$$N''_{A,y} = (CD_{AB} / y) \ln (1 - x_{A,y}) / (1 - x_{A,0}).$$

With $C = p / \Re T$, $x_{B,y} = 1 - x_{A,y}$ and $x_{B,0} = 1 - x_{A,0}$, recognizing that $x_B = p_B/p$, find

$$p_B (y) = p_{B,0} \cdot \exp \left(N''_{A,y} \frac{\Re T}{p D_{AB}} y \right)$$

$$p_{B,0} = p - p_{A,0} = p_{sat} (28°C) - p_{sat} (24°C) = (0.03767 - 0.02983) \, bar = 0.00784 \, bar.$$

With $N''_{A,y} = -(0.020/2) kg/m^2 \cdot s / 28 kg/kmol = 3.57 \times 10^{-4} kmol/m^2 \cdot s,$

$$p_B (y) = 0.0784 \, bar \times \exp \left(3.57 \times 10^{-4} kmol/m^2 \cdot s \frac{8.314 \times 10^{-2} m^3 \cdot bar/kmol \cdot K \times 299 \, K}{0.03767 \, bar \times 6.902 \times 10^{-4} m^2 / s} \right)$$

$$p_B (y) = 784 \, kPa \times \exp (-0.3415y)$$

with p_B in [kPa] and y in [mm], where T = 26°C = 299 K, the average temperature of the air-steam mixture, and $D_{AB} \approx p^{-1} T^{3/2} = 0.26 \times 10^{-4}$ m²/s (1/0.03767) (299/298)$^{3/2}$ = 6.902 × 10^{-4} m²/s. Selected values for the pressure are shown below and the distribution is shown above:

| y (mm)	0	5	10	15
p_B(y) (kPa)	784	142	25.8	4.7

COMMENTS: To minimize inert gas effects, the usual practice is to pass vapor over the surfaces so that the inerts are eventually collected near the outlet region of the condenser. Our estimate shows that the effective region to be swept is approximately 10 mm thick.

PROBLEM 14.32

KNOWN: Column containing liquid phase of water (A) evaporates into the air (B) flowing over the mouth of the column.

FIND: Evaporation rate of water $(kg/h \cdot m^2)$ using the known value of the binary diffusion coefficient for the water vapor - air mixture.

SCHEMATIC:
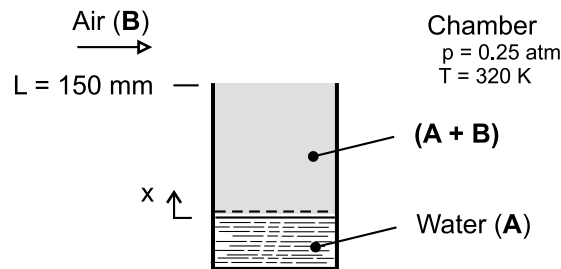
ASSUMPTIONS: (1) Steady-state, one-dimensional diffusion in the column, (2) Constant properties, (3) Uniform temperature and pressure throughout the column, (4) Water vapor exhibits ideal gas behavior, and (5) Negligible water vapor in the chamber air.

PROPERTIES: *Table A-6, water* (T = 320 K): $p_{sat} = 0.1053$ bar; *Table A-8, water vapor-air* (0.25 atm, 320 K): Since $D_{AB} \sim p^{-1} T^{3/2}$ find

$$D_{AB} = 0.26 \times 10^{-4} \text{ m}^2/\text{s } (1.00/0.25)(320/298)^{3/2} = 1.157 \times 10^{-4} \text{ m}^2/\text{s}$$

ANALYSIS: Equimolar counter diffusion occurs in the vertical column as water vapor, evaporating at the liquid-vapor interface (x = 0), diffuses up the column through air out into the chamber. From Eq. 14.7, the molar flow rate per unit area is

$$N''_{A,x} = \frac{C D_{AB}}{L} \ln \frac{1-x_{A,L}}{1-x_{A,0}}$$

where C is the mixture concentration determined from the ideal gas law as

$$C = \frac{p}{R_u T} = \frac{0.25 \text{ atm}}{8.205 \times 10^{-2} \text{ m}^3 \cdot \text{atm/kmol} \cdot \text{K} \times 320 \text{ K}} = 0.009397 \text{ kmol/m}^3$$

where $R_u = 8.205 \times 10^{-2} \text{ m}^3 \cdot \text{atm/kmol} \cdot \text{K}$. The mole fractions at x = 0 and x = L are

$$x_{A,L} = 0 \qquad \text{(no water vapor in air above column)}$$

$$x_{A,0} = p_A / p = 0.1053/0.25 = 0.4212$$

where p_A is the saturation pressure for water at T = 320 K. Substituting numerical values

$$N''_{A,x} = \frac{0.009397 \text{ kmol}/\text{m}^3 \times 1.157 \times 10^{-4} \text{ m}^2/\text{s}}{0.150 \text{ m}} \ln \frac{(1-0)}{(1-0.4212)}$$

$$N''_{A,x} = 3.964 \times 10^{-6} \text{ kmol}/\text{m}^2 \cdot \text{s}$$

or, on a mass basis,

$$m''_{A,x} = N''_{A,x} M_A$$

$$m''_{A,x} = 3.964 \times 10^{-6} \text{ kmol}/\text{m}^2 \cdot \text{s} \times 3600 \text{ s/h} \times 18 \text{ kg/kmol}$$
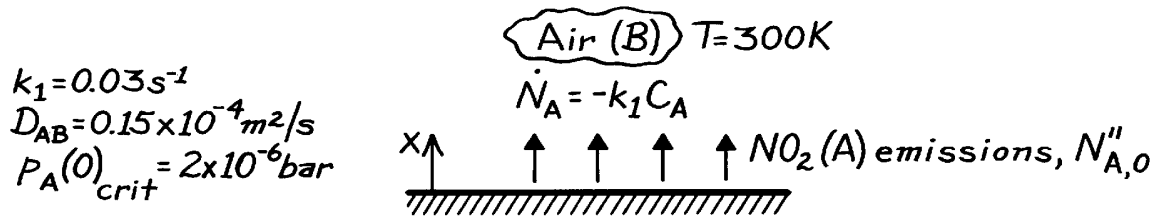
$$m''_{A,x} = 0.257 \text{ kg/m}^2 \cdot \text{h} \qquad\qquad <$$

PROBLEM 14.33

KNOWN: Ground level flux of NO_2 in a stagnant urban atmosphere.

FIND: (a) Vertical distribution of NO_2 molar concentration, (b) Critical ground level flux of NO_2, $N''_{A,0,crit}$.

SCHEMATIC:

ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion in a stationary medium, (3) Total molar concentration C is uniform, (4) Perfect gas behavior.

ANALYSIS: (a) For the prescribed conditions the molar concentration of NO_2 is given by Eq. 14.80, subject to the following boundary conditions.

$$C_A(\infty) = 0, \qquad \left.\frac{dC_A}{dx}\right)_{x=0} = -\frac{N''_{A,0}}{D_{AB}}.$$

From the first condition, $C_1 = 0$. From the second condition,

$$-mC_2 = -N''_{A,0}/D_{AB}.$$

Hence

$$C_A(x) = \frac{N''_{A,0}}{mD_{AB}}e^{-mx} \qquad\qquad <$$

where $m = (k_1/D_{AB})^{1/2}$.

(b) At ground level, $C_A(0) = \dfrac{N''_{A,0}}{mD_{AB}}$. Hence, from the perfect gas law,

$$p_A(0) = C_A(0)\Re T = \frac{\Re T N''_{A,0}}{mD_{AB}}.$$

Hence, with $m = (0.03/0.15 \times 10^{-4})^{1/2}\ m^{-1} = 44.7\ m^{-1}$.

$$N''_{A,0,crit} = \frac{mD_{AB}p_A(0)_{crit}}{\Re T} = \frac{44.7 m^{-1} \times 0.15 \times 10^{-4} m^2/s \times 2 \times 10^{-6}\ bar}{8.314 \times 10^{-2} m^3 \cdot bar/kmol \cdot K \times 300\ K}$$

$$N''_{A,0,crit} = 5.38 \times 10^{-11}\ kmol/s \cdot m^2. \qquad\qquad <$$
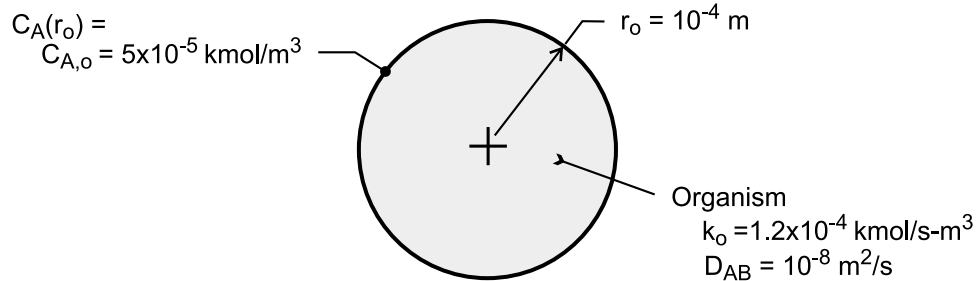
COMMENTS: Because the dispersion of pollutants in the atmosphere is governed strongly by convection effects, the above model should be viewed as a first approximation which describes a worst case condition.

PROBLEM 14.34

KNOWN: Radius of a spherical organism and molar concentration of oxygen at surface. Diffusion and reaction rate coefficients.

FIND: (a) Radial distribution of O_2 concentration, (b) Rate of O_2 consumption, (c) Molar concentration at $r = 0$.

SCHEMATIC:

$C_A(r_o) =$
$C_{A,o} = 5 \times 10^{-5}$ kmol/m^3

$r_o = 10^{-4}$ m

Organism
$k_o = 1.2 \times 10^{-4}$ kmol/s-m^3
$D_{AB} = 10^{-8}$ m^2/s

ASSUMPTIONS: (1) Steady-state, one-dimensional diffusion, (2) Stationary medium, (3) Uniform total molar concentration, (4) Constant properties (k_0, D_{AB}).

ANALYSIS: (a) For the prescribed conditions and assumptions, Eq. (14.40) reduces to

$$\frac{D_{AB}}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_A}{dr}\right) - k_0 = 0$$

$$r^2 \frac{dC_A}{dr} = \frac{k_0 r^3}{3D_{AB}} + C_1$$

$$C_A = \frac{k_0 r^2}{6D_{AB}} - \frac{C_1}{r} + C_2$$

With the requirement that $C_A(r)$ remain finite at $r = 0$, $C_1 = 0$. With $C_A(r_o) = C_{A,o}$

$$C_2 = C_{A,o} - \frac{k_0 r_o^2}{6D_{AB}}$$

$$C_A = C_{A,o} - (k_0/6D_{AB})(r_o^2 - r^2) \qquad <$$

Because C_A cannot be less than zero at any location within the organism, the right-hand side of the foregoing equation must always exceed zero, thereby placing limits on the value of $C_{A,o}$. The smallest possible value of $C_{A,o}$ is determined from the requirement that $C_A(0) \geq 0$, in which case

$$C_{A,o} \geq \left(k_0 r_o^2/6D_{AB}\right) \qquad <$$

(b) Since oxygen consumption occurs at a uniform volumetric rate of k_0, the total respiration rate is $\dot{R} = \forall k_0$, or

$$\dot{R} = (4/3)\pi r_o^3 k_0 \qquad <$$

Continued …..

(c) With $r = 0$,

$$C_A(0) = C_{A,o} - k_0 \, r_o^2 / 6 D_{AB}$$

$$C_A(0) = 5 \times 10^{-5} \, \text{kmol}/\text{m}^3 - 1.2 \times 10^{-4} \, \text{kmol}/\text{s} \cdot \text{m}^3 \left(10^{-4} \, \text{m}\right)^2 / 6 \times 10^{-8} \, \text{m}^2 / \text{s}$$

$$C_A(0) = 3 \times 10^{-5} \, \text{kmol}/\text{m}^3 \qquad\qquad <$$

COMMENTS: (1) The minimum value of $C_{A,o}$ for which a physically realistic solution is possible is $C_{A,o} = k_0 \, r_o^2 / 6 D_{AB} = 2 \times 10^{-5} \, \text{kmol}/\text{m}^3$.
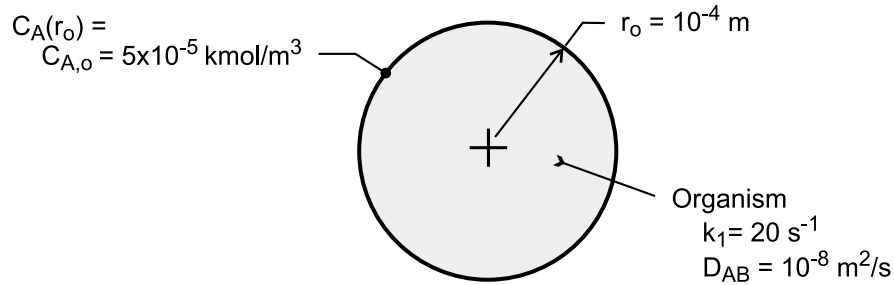
(2) The total respiration rate may also be obtained by applying Fick's law at $r = r_o$, in which case
$$\dot{R} = -N_A(r_o) = +D_{AB}\left(4\pi \, r_o^2\right) d C_A / dr \Big|_{r=r_o} = D_{AB}\left(4\pi \, R_o^2\right)\left(k_o / 6 D_{AB}\right) 2 r_o = (4/3)\pi \, r_o^3 k_0.$$
The result agrees with that of part (b).

PROBLEM 14.35

KNOWN: Radius of a spherical organism and molar concentration of oxygen at its surface. Diffusion and reaction rate coefficients.

FIND: (a) Radial distribution of O_2 concentration, (b) Expression for rate of O_2 consumption, (c) Molar concentration at $r = 0$ and rate of oxygen consumption for prescribed conditions.

SCHEMATIC:

$C_A(r_o) =$
$C_{A,o} = 5 \times 10^{-5}$ kmol/m^3

$r_o = 10^{-4}$ m

Organism
$k_1 = 20$ s^{-1}
$D_{AB} = 10^{-8}$ m^2/s

ASSUMPTIONS: (1) Steady-state, one-dimensional diffusion, (2) Stationary medium, (3) Uniform total molar concentration, (4) Constant properties (k_1, D_{AB}).

ANALYSIS: (a) For the prescribed conditions and assumptions, Eq. (14.40) reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(D_{AB}\, r^2\, \frac{dC_A}{dr}\right) - k_1 C_A = 0$$

With $y \equiv r\, C_A$, $d\, C_A/dr = (1/r)\, dy/dr - y/r^2$ and

$$\frac{1}{r^2}\frac{d}{dr}\left(D_{AB}\, r^2\, \frac{dC_A}{dr}\right) = \frac{D_{AB}}{r^2}\frac{d}{dr}\left(r\frac{dy}{dr} - y\right) = \frac{D_{AB}}{r^2}\left(r\frac{d^2 y}{dr^2}\right)$$

The species equation is then

$$\frac{d^2 y}{dr^2} - \frac{k_1}{D_{AB}}\, y = 0$$

The general solution is of the form

$$y = C_1 \sinh\left(k_1/D_{AB}\right)^{1/2} r + C_2 \cosh\left(k_1/D_{AB}\right)^{1/2} r$$

or

$$C_A = \frac{C_1}{r}\sinh\left(k_1/D_{AB}\right)^{1/2} r + \frac{C_2}{r}\cosh\left(k_1/D_{AB}\right)^{1/2} r$$

Because C_A must remain finite at $r = 0$, $C_2 = 0$. Hence, with $C_A(r_o) = C_{A,o}$,

$$C_1 = \frac{C_{A,o}\, r_o}{\sinh\left(k_1/D_{AB}\right)^{1/2} r_o}$$

and

Continued .....

$$C_A = C_{A,o}\left(\frac{r_o}{r}\right)\frac{\sinh\left(k_1/D_{AB}\right)^{1/2}r}{\sinh\left(k_1/D_{AB}\right)^{1/2}r_o} \qquad <$$

(b) The total O_2 consumption rate corresponds to the rate of diffusion at the surface of the organism.

$$\dot{R} = -N_A\left(r_o\right) = +D_{AB}\left(4\pi r_o^2\right)dC_A/dr\big|_{r_o}$$

$$\dot{R} = 4\pi r_o^2 D_{AB}\,C_{A,o}\,r_o\left[-\frac{1}{r_o^2}+\frac{1}{r_o}\left(k_1/D_{AB}\right)^{1/2}\cot\left(k_1/D_{AB}\right)^{1/2}r_o\right]$$

$$\dot{R} = 4\pi r_o\,D_{AB}\,C_{A,o}\left(\alpha\coth\alpha-1\right) \qquad <$$

where $\alpha \equiv \left(k_1\,r_o^2/D_{AB}\right)^{1/2}$.

(c) For the prescribed conditions, $(k_1/D_{AB})^{1/2} = (20\text{ s}^{-1} \div 10^{-8}\text{ m}^2/\text{s})^{1/2} = 44{,}720\text{ m}^{-1}$ and $\alpha = 4.472$.

$$C_A = \frac{5\times10^{-5}\text{kmol}/\text{m}^3\times10^{-4}\text{m}}{\sinh\left(4.472\right)}\times\frac{\sinh\left(k_1/D_{AB}\right)^{1/2}r}{r} = 1.136\times10^{-10}\frac{\text{kmol}}{\text{m}^3}\times\frac{\sinh\left(k_1/D_{AB}\right)^{1/2}r}{r}$$

In the limit of $r \rightarrow 0$, the foregoing expression yields

$$C_A\left(r\rightarrow0\right) = 5.11\times10^{-6}\text{kmol}/\text{m}^3 \qquad <$$

$$\dot{R} = 4\pi\times10^{-4}\text{m}\times10^{-8}\text{m}^2/\text{s}\times5\times10^{-5}\text{kmol}/\text{m}^3\left(4.472\coth4.472-1\right)$$

$$= 2.18\times10^{-15}\text{kmol}/\text{s}$$

COMMENTS: The total respiration rate may also be obtained by integrating the volumetric rate of consumption over the volume of the organism. That is, $\dot{R} = -\int\dot{N}_A\,d\forall = \int_0^{r_o}k_1\,C_A\left(r\right)4\pi r^2 dr$.

PROBLEM 14.36

KNOWN: Radius and catalytic reaction rate of a porous spherical pellet. Surface mole fraction of reactant and effective diffusion coefficient.

FIND: (a) Radial distribution of reactant concentration in pellet, total reactant consumption rate, and pellet effectiveness, (b) CO consumption rate and effectiveness for prescribed conditions.

SCHEMATIC:
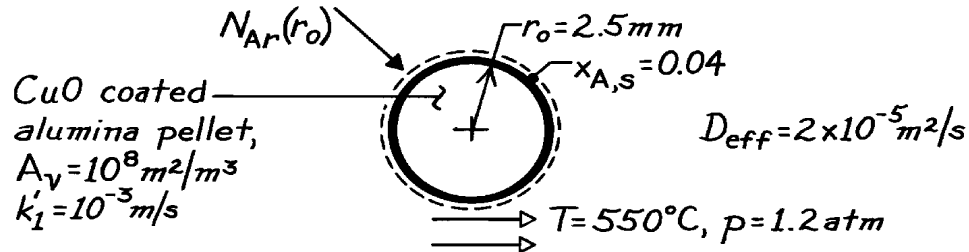
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional radial diffusion, (3) Constant properties, (4) Homogeneous chemical reactions, (5) Isothermal, constant pressure conditions within pellet, (6) Stationary medium.

ANALYSIS: (a) In spherical coordinates, the mass diffusion equation is given by

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(CD_{AB}r^2\frac{\partial x_A}{\partial r}\right)+\dot{N}_A=0$$

where C, D_{AB} are constant and $\dot{N}_A=-k_1' A_v C_A$. Hence

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dx_A}{dr}\right)-\frac{k_1'A_v}{D_{eff}}x_A=0.$$

The boundary conditions are $x_A(r_o)=x_{A,s}$ and $x_A(0)$ is finite. Transform the dependent variable, $y\equiv rx_A$, with

$$\frac{dx_A}{dr}=\frac{1}{r}\frac{dy}{dr}-\frac{y}{r^2}\qquad\text{or}\qquad\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dx_A}{dr}\right)=\frac{1}{r^2}\frac{d}{dr}\left(r\frac{dy}{dr}-y\right)=\frac{1}{r^2}\left(r\frac{d^2y}{dr^2}\right).$$

Hence

$$\frac{d^2y}{dr^2}-\frac{k_1'A_v}{D_{eff}}y=0.$$

The general solution is of the form

$$y=C_1\,\sinh(ar)+C_2\,\cosh(ar)$$

where $a\equiv\left(k_1'A_v/D_{eff}\right)^{1/2}$ giving

$$x_A=\frac{C_1}{r}\sinh(ar)+\frac{C_2}{r}\cosh(ar)$$

and using the boundary conditions,

$$x_A(0)\text{ finite}\to C_2=0\qquad\qquad x_A(r_o)=x_{A,s}\to C_1=x_{A,s}r_o/\sinh(ar_o).$$

Continued …..

Hence

$$x_A(r) = x_{A,s}(r_o/r)\frac{\sinh(ar)}{\sinh(ar_o)}. \qquad <$$

Applying conservation of species to a control volume about the pellet, $\dot{N}_{A,in} + \dot{N}_{A,g} = 0$, the total rate of consumption of A in the pellet is

$$-\dot{N}_{A,g} = \dot{N}_{A,in} = N_{A,r}(r_o) = 4pr_o^2 J_{A,r}^*(r_o).$$

Hence

$$N_{A,r}(r_o) = \left(4pr_o^2\right)\left(-CD_{eff}\frac{dx_A}{dr}\right)_{r=r_o} = \frac{4pr_o^3}{\sinh(ar_o)}CD_{eff}x_{A,s}\left[\frac{\sinh(ar)}{r^2} - \frac{\cosh(ar)}{r^2}\right]_{r=r_o}$$

$$N_{A,r}(r_o) = 4pr_oCD_{eff}x_{A,s}\left[1 - \frac{ar_o}{\tanh(ar_o)}\right]. \qquad <$$

The pellet effectiveness ε is defined as $\varepsilon \equiv N_{A,r}(r_o)/[N_{A,r}(r_o)]_{max}$ and the maximum consumption occurs if $x_A(r) = x_{A,s}$ for all $0 \le r \le r_o$. Hence

$$\left[N_{A,r}(r_o)\right]_{max} = \dot{N}_A V_p = -k_1' A_v C x_{A,s}\frac{4}{3}pr_o^3$$

$$e = -\frac{3}{a^2 r_o^2}\left[1 - \frac{ar_o}{\tanh(ar_o)}\right]. \qquad <$$

(b) To evaluate the rate, first determine values for these parameters:

$$C = \frac{p}{\Re T} = \frac{1.2\,atm}{0.08205\,m^3 \cdot atm/kmol \cdot K \times 823\,K} = 0.0178\,kmol/m^3$$

$$a = \left(\frac{k_1' A_v}{D_{eff}}\right)^{1/2} = \left(\frac{10^{-3}\,m/s \times 10^8\,m^2/m^3}{2\times 10^{-5}\,m^2/s}\right)^{1/2} = 7.07\times 10^4 m^{-1}$$

$$ar_o = 176.8 \qquad\qquad \tanh(ar_o) = 1.$$

Hence the consumption rate is

$$N_{A,r}(r_o) = 4p(0.0025\,m)0.0178\,kmol/m^3 \times 2\times 10^{-5}\,m^2/s \times 0.04(1-176.8)$$

$$N_{A,r}(r_o) = -7.86\times 10^{-8}\,kmol/s \qquad <$$

and the effectiveness is

$$e = -\frac{3}{\left(7.07\times 10^4\,m^{-1}\right)^2(0.0025\,m)^2}[1-176.8] = 0.0169 \qquad <$$

COMMENTS: For the range of conditions of interest, $\varepsilon \approx 3/ar_o$. Hence ε may be increased by $\downarrow r_o, \downarrow k_1', \downarrow A_v$ and $\uparrow D_{eff}$. However, $N_{A,r}(r_o)$ would decrease with $\downarrow r_o, \downarrow k_1'$ and $\downarrow A_v$.

PROBLEM 14.37

KNOWN: Molar concentrations of oxygen at inner and outer surfaces of lung tissue. Volumetric rate of oxygen consumption within the tissue.

FIND: (a) Variation of oxygen molar concentration with position in the tissue, (b) Rate of oxygen transfer to the blood per unit tissue surface area.

SCHEMATIC:
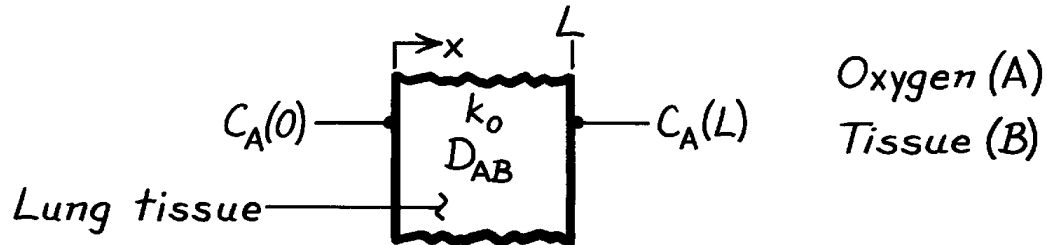
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional species transfer by diffusion through a plane wall, (3) Homogeneous, stationary medium with uniform total molar concentration and constant diffusion coefficient.

ANALYSIS: (a) From Eq. 14.78 the appropriate form of the species diffusion equation is

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_o = 0.$$

Integrating,

$$dC_A / dx = (k_o / D_{AB}) x + C_1 \qquad C_A = \frac{k_o}{2 D_{AB}} x^2 + C_1 x + C_2.$$

With $C_A = C_A(0)$ at $x = 0$ and $C_A = C_A(L)$ at $x = L$,

$$C_2 = C_A(0) \qquad C_1 = \frac{C_A(L) - C_A(0)}{L} - \frac{k_o L}{2 D_{AB}}.$$

Hence

$$C_A(x) = \frac{k_o}{2 D_{AB}} x (x - L) + \left[C_A(L) - C_A(0) \right] \frac{x}{L} + C_A(0). \qquad <$$

(b) The oxygen assimilation rate per unit area is

$$N''_{A,x}(L) = -D_{AB} \left(dC_A / dx \right)_{x=L}$$

$$N''_{A,x}(L) = -D_{AB} \left(\frac{k_o L}{D_{AB}} - \frac{k_o L}{2 D_{AB}} \right) - \frac{D_{AB}}{L} \left[C_A(L) - C_A(0) \right]$$

$$N''_{A,x} = -\frac{k_o L}{2} + \frac{D_{AB}}{L} \left[C_A(0) - C_A(L) \right]. \qquad <$$

COMMENTS: The above model provides a highly approximate and simplified treatment of a complicated problem. The lung tissue is actually heterogeneous and conditions are transient.

PROBLEM 14.38

KNOWN: Combustion at constant temperature and pressure of a hydrogen-oxygen mixture adjacent to a metal wall according to the reaction $2H_2 + O_2 \rightarrow 2H_2O$. Molar concentrations of hydrogen, oxygen, and water vapor are 0.10, 0.10 and 0.20 $kmol/m^3$, respectively. Generation rate of water vapor is 0.96×10^{-2} $kmol/m^3 \cdot s$.

FIND: (a) Expression for C_{H_2} as function of distance from wall, plot qualitatively, (b) C_{H_2} at the wall, (c) Sketch also curves for $C_{O_2}(x)$ and $C_{H_2O}(x)$, and (d) Molar flux of water at x = 10mm.

SCHEMATIC:
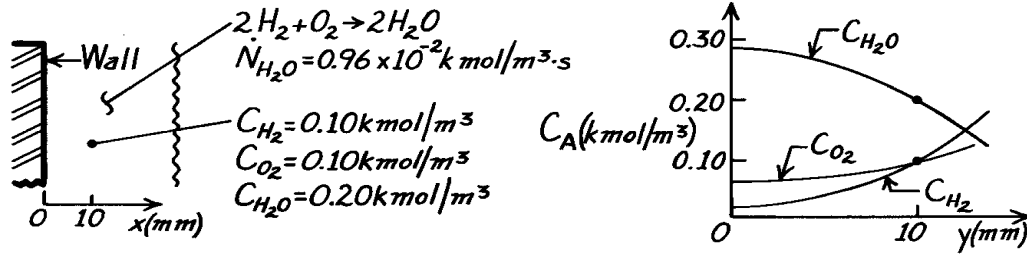
ASSUMPTIONS: (1) Steady-state conditions, (2) One-dimensional diffusion, (3) Stationary mixture, (4) Constant properties including pressure and temperature.

PROPERTIES: Species binary diffusion coefficient (given, for H_2, O_2 and H_2O): $D_{AB} = 0.6 \times 10^{-5}$ m^2/s.

ANALYSIS: (a) The species conservation equation, Eq. 14.38b, and its general solution are

$$\frac{d^2C_A}{dx^2} + \frac{\dot{N}_A}{D_{AB}} = 0 \qquad\qquad C_A(x) = -\frac{\dot{N}_A}{2D_{AB}}x + C_1 x + C_2. \qquad (1,2)$$

The boundary condition at the wall must be $dC_A(0)/dx = 0$, such that $C_1 = 0$. For the species hydrogen, evaluate C_2 from knowledge of $C_{H_2}(10\ mm) = 0.10\ kmol/m^3$ and $\dot{N}_{H_2} = -\dot{N}_{H_2O}$, according to the chemical reaction. Hence,

$$0.10\ kmol/m^3 = -\frac{\left(-0.96 \times 10^{-2} kmol/m^3 \cdot s\right)}{2 \times 0.6 \times 10^{-5} m^2/s}(0.010\ m)^2 + 0 + C_2$$

$$C_2 = 0.02\ kmol/m^3.$$

Hence, the hydrogen species concentration distribution is

$$C_{H_2}(x) = -\frac{\dot{N}_{H_2}}{2D_{AB}}x^2 + 0.02 = 800x^2 + 0.02 \qquad\qquad <$$

which is parabolic with zero slope at the wall; see sketch above.

(b) The value of C_{H_2} at the wall is,

$$C_{H_2}(0) = (0 + 0.02)kmol/m^3 = 0.02\ kmol/m^3. \qquad\qquad <$$

Continued …..

(c) The concentration distribution for water vapor species will be of the same form,

$$C_{H_2O}(x) = -\frac{\dot{N}_{H_2O}}{2D_{AB}}x^2 + C_1 x + C_2 \tag{3}$$

With $C_1 = 0$ for the wall condition, find C_2 from $C_{H_2O}(10 \text{ mm})$,

$$0.20 \text{ kmol/m}^3 = -\frac{\left(0.96\times10^{-2} \text{ kmol/m}^3\right)}{2\times0.6\times10^{-5} \text{ m}^2/s}(0.010 \text{ m})^2 + C_2 \qquad C_2 = 0.28 \text{ kmol/m}^3.$$

Hence, C_{H_2O} at the wall is,

$$C_{H_2O}(0) = 0 + 0 + C_2 = 0.28 \text{ kmol/m}^3$$

and its distribution appears as above. Recognizing that $\dot{N}_{O_2} = -0.5\dot{N}_{H_2O}$, by the same analysis, find

$$C_{O_2}(0) = 0.06 \text{ kmol/m}^3$$

and its shape, also parabolic with zero slope at the wall is shown above.

(d) The molar flux of water vapor at x = 10 mm is given by Fick's law

$$N''_{H_2O,x} = -D_{AB}\frac{dC_{H_2O}}{dx}$$

and using the concentration distribution of Eq. (3), find

$$N''_{H_2O,x} = -D_{AB}\frac{d}{dx}\left(-\frac{\dot{N}_{H_2O}}{2D_{AB}}x^2\right) = +\dot{N}_{H_2O}x$$

and evaluation at the location x = 10 mm, the species flux is

$$N''_{H_2O,x}(10 \text{ mm}) = +\left(0.96\times10^{-2} \text{ kmol/m}^3\cdot s\right)\times0.010 \text{ m} = 9.60\times10^{-5} \text{ kmol/m}^2\cdot s. \qquad <$$

**COMMENTS:** Note that the generation rate of water vapor is a positive quantity. Whereas for H_2 and O_2, species are consumed and hence $\dot{N}_{H_2}$ and $\dot{N}_{O_2}$ are negative. According to the chemical reaction one mole of H_2 and 0.5 mole of O_2 are consumed to generate one mole of H_2O. Therefore, $\dot{N}_{H_2} = -\dot{N}_{H_2O}$ and $\dot{N}_{O_2} = -0.5 \dot{N}_{H_2O}$.

KNOWN: Ground level flux of NO_2 in a stagnant urban atmosphere.

FIND: (a) Governing differential equation and boundary conditions for the molar concentration of NO_2, (b) Concentration of NO_2 at ground level three hours after the beginning of emissions.

SCHEMATIC:
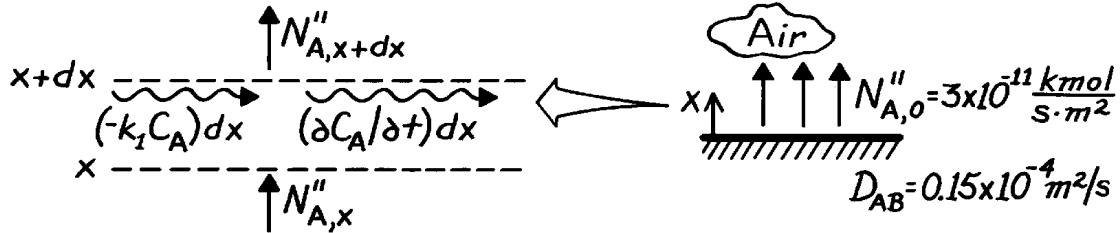
ASSUMPTIONS: (1) One-dimensional diffusion in a stationary medium, (2) Uniform total molar concentration, (3) Constant properties.

ANALYSIS: (a) Applying the species conservation requirement, Eq. 14.33, on a molar basis to a unit area of the control volume,

$$N''_{A,x} - (k_1 C_A) dx - N''_{A,x+dx} = \frac{\partial C_A}{\partial t} dx.$$

With $N''_{A,x+dx} = N''_{A,x} + (\partial N''_{A,x} / \partial x) dx$ and $N''_{A,x} = -D_{AB}(\partial C_A / \partial x)$, it follows that

$$D_{AB} \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A = \frac{\partial C_A}{\partial t}. \qquad <$$

Initial Condition: $C_A(x,0) = 0$. $\qquad <$

Boundary Conditions: $\quad -D_{AB} \frac{\partial C_A}{\partial x}\Bigg)_{x=0} = N''_{A,0}, \qquad C_A(\infty, t) = 0. \qquad <$

(b) The present problem is analogous to Case (2) of Fig. 5.7 for heat conduction in a semi-infinite medium. Hence by analogy to Eq. 5.59, with $k \leftrightarrow D_{AB}$ and $a \leftrightarrow D_{AB}$,

$$C_A(x,t) = 2N''_{A,0}\left(\frac{t}{p D_{AB}}\right)^{1/2} \exp\left(-\frac{x^2}{4 D_{AB} t}\right) - \frac{N''_{A,0} x}{D_{AB}} \text{erfc}\left(\frac{x}{2(D_{AB} t)^{1/2}}\right)$$

At ground level (x = 0) and 3h,

$$C_A(0,3h) = 2N''_{A,0}\left(\frac{t}{p D_{AB}}\right)^{1/2}$$

$$C_A(0,3h) = 2\left(3 \times 10^{-11} \text{kmol/s} \cdot \text{m}^2\right)\left(10,800 \text{s}/p \times 0.15 \times 10^{-4} \text{m}^2 / \text{s}\right)^{1/2} = 9.08 \times 10^{-7} \text{kmol/m}^3. \qquad <$$

COMMENTS: The concentration decays rapidly to zero with increasing x, and at x = 100 m it is, for all practical purposes, equal to zero.

KNOWN: Carbon dioxide concentration at water surface and reaction rate constant.

FIND: (a) Differential equation which governs variation with position and time of CO_2 concentration in water, (b) Appropriate boundary conditions and solution for a deep body of water with negligible chemical reactions.

SCHEMATIC:
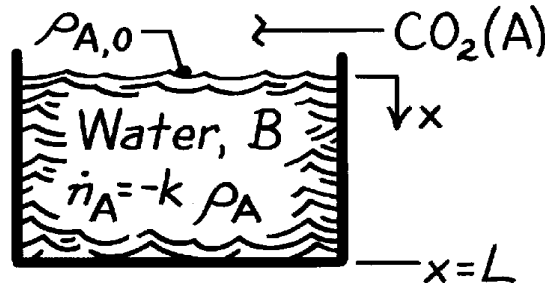
ASSUMPTIONS: (1) One-dimensional diffusion in x, (2) Constant properties, including total density ρ, (3) Water is stagnant.

ANALYSIS: (a) From Eq. 14.37b, it follows that, for the prescribed conditions,

$$D_{AB} \frac{\partial^2 r_A}{\partial x^2} - k_1 r_A = \frac{\partial r_A}{\partial t}. \qquad <$$

The first term on the left-hand side represents the *net* transport of CO_2 into a differential control volume by diffusion. The second term represents the rate of CO_2 consumption due to chemical reactions. The term on the right-hand side represents the rate of increase of CO_2 storage within the control volume.

(b) For a deep body of water, appropriate boundary conditions are

$$r_A(0,t) = r_{A,0}$$

$$r_A(\infty,t) = 0$$

and, with negligible chemical reactions, the species diffusion equation reduces to

$$\frac{\partial^2 r_A}{\partial x^2} = \frac{1}{D_{AB}} \frac{\partial r_A}{\partial t}.$$

With an initial condition, $\rho_A(x,0) \equiv \rho_{A,i} = 0$, the problem is analogous to that involving heat transfer in a semi-infinite medium with constant surface temperature. By analogy to Eq. 5.57, the species concentration is then

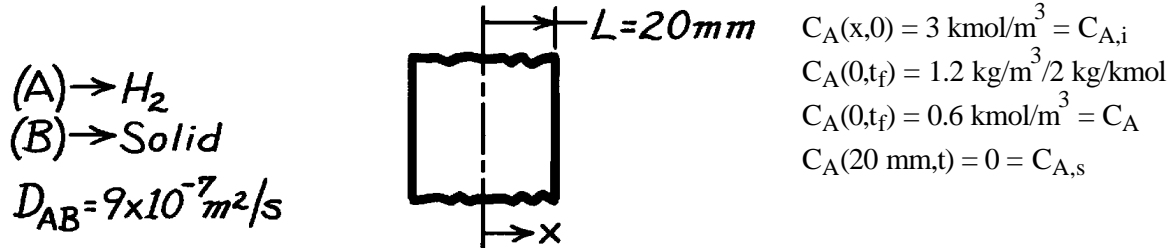$$\frac{r_A(x,t) - r_{A,0}}{-r_{A,0}} = \mathrm{erf}\left(\frac{x}{2(D_{AB}t)^{1/2}}\right)$$

$$r_A(x,t) = r_{A,0}\,\mathrm{erfc}\left(\frac{x}{2(D_{AB}t)^{1/2}}\right). \qquad <$$

PROBLEM 14.41

KNOWN: Initial concentration of hydrogen in a sheet of prescribed thickness. Surface concentrations for time $t > 0$.

FIND: Time required for density of hydrogen to reach prescribed value at midplane of sheet.

SCHEMATIC:

$\vdash L = 20mm$ $C_A(x,0) = 3 \text{ kmol/m}^3 = C_{A,i}$

(A) → H_2 $C_A(0,t_f) = 1.2 \text{ kg/m}^3/2 \text{ kg/kmol}$

(B) → Solid $C_A(0,t_f) = 0.6 \text{ kmol/m}^3 = C_A$

$D_{AB} = 9 \times 10^{-7} m^2/s$ $C_A(20 \text{ mm,t}) = 0 = C_{A,s}$

ASSUMPTIONS: (1) One-dimensional diffusion in x, (2) Constant D_{AB}, (3) No internal chemical reactions, (4) Uniform total molar concentration.

ANALYSIS: Using Heisler chart with heat and mass transfer analogy

$$g^* = \frac{C_A - C_{A,s}}{C_{A,i} - C_{A,s}} = \frac{0.6 - 0}{3.0 - 0} = 0.2 = g_o^*$$

With $Bi_m = \infty$, Fig. D.1 may be used with

$$q_o^* = 0.2, \qquad\qquad Bi^{-1} = 0$$
$$Fo \approx 0.75.$$

Hence

$$Fo_m = \frac{D_{AB}t_f}{L^2} = 0.75$$

$$t_f = 0.75(0.02 \text{ m})^2 / 9 \times 10^{-7} m^2 / s$$

$$t_f = 333s. \qquad\qquad\qquad <$$

COMMENTS: If the one-term approximation to the infinite series solution

$$q^* = \sum_{n=1}^{\infty} C_n \exp\left(-V_n^2 Fo\right) \cos\left(V_n x^*\right)$$

is used, it follows that

$$g_o^* \approx C_1 \exp\left(-V_1^2 Fo_m\right) = 0.2$$

Using values of $V_1 = 1.56$ and $C_1 = 1.27$, it follows that

$$\exp\left[-(1.56)^2 Fo_m\right] = 0.157$$

$$Fo_m = 0.76$$

which is in excellent agreement with the result from the chart.

PROBLEM 14.42

KNOWN: Sheet material has high, uniform concentration of hydrogen at the end of a process, and is then subjected to an air stream with a specified, low concentration of hydrogen. Mass transfer parameters specified include: convection mass transfer coefficient, h_m, and the mass diffusivity and solubility of hydrogen (A) in the sheet material (B), D_{AB} and S_{AB}, respectively.

FIND: (a) The final mass density of hydrogen in the material if the sheet is exposed to the air stream for a very long time, $\rho_{A,f}$, (b) Identify and evaluate the parameter that can be used to determine whether the transient mass diffusion process in the sheet can be characterized by a uniform concentration at any time; *Hint*: this situation is analogous to the lumped capacitance method for a transient heat transfer process; (c) Determine the time required to reduce the hydrogen concentration to twice the limiting value calculated in part (a).

SCHEMATIC:
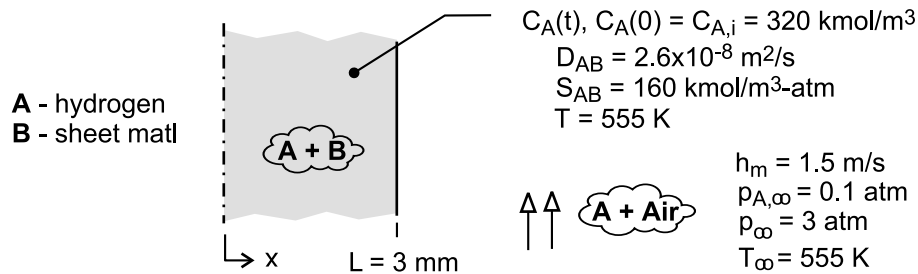
ASSUMPTIONS: (1) One-dimensional diffusion, (2) Material B is stationary medium, (3) Constant properties, (4) Uniform temperature in air stream and material, and (5) Ideal gas behavior.

ANALYSIS: (a) The final content of H_2 in the material will depend upon the solubility of H_2 (A) in the material (B) and its partial pressure in the free stream. From Eq. 14.44,

$$C_{A,f} = S_{AB}\, p_{A,\infty} = 160 \text{ kmol} / \text{m}^3 \cdot \text{atm} \times 0.1 \text{ atm} = 16 \text{ kmol} / \text{m}^3$$

$$\rho_f = M_A\, C_{A,f} = 2 \text{ kg} / \text{kmol} \times 16 \text{ kmol} / \text{m}^3 = 32 \text{ kg} / \text{m}^3 \qquad <$$

(b) The parameters associated with transient diffusion in the material follow from the analogous treatment of Section 5.2 (Fig. 5.3) and are represented in the schematic.
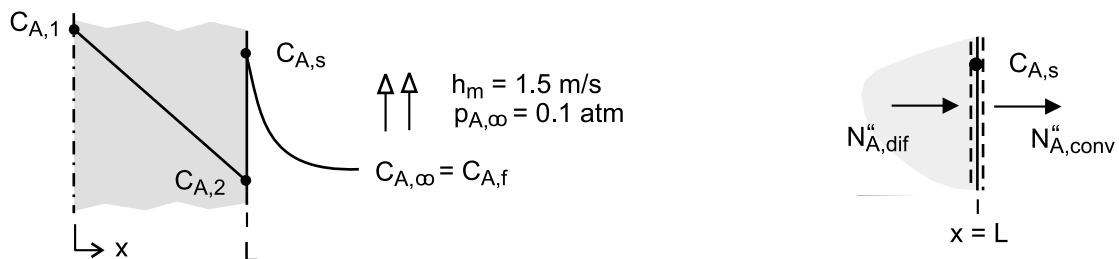
In the material, from Fick's law, the diffusive flux is

$$N''_{A,dif} = D_{AB} \left(C_{A,1} - C_{A,2} \right) / L \qquad (1)$$

At the surface, $x = L$, the rate equation, Eq. 6.8, convective flux of species A is

$$N''_{A,conv} = h_m \left(C_{A,s} - C_{A,\infty} \right)$$

Continued …..

and substituting the ideal gas law, Eq. 14.9, and introducing the solubility relation, Eq. 14.44,

$$N''_{A,conv} = \frac{h_m}{S_{AB}\, R_u\, T_\infty} \left(S_{AB}\, p_{A,s} - S_{AB}\, p_{A,\infty} \right)$$

$$N''_{A,conv} = \frac{h_m}{S_{AB}\, R_u\, T_\infty} \left(C_{2,s} - C_{A,\infty} \right) \tag{2}$$

where $C_{A,\infty} = C_{A,f}$, the final concentration in the material after exposure to the air stream a long time. Considering a surface species flux balance, as shown in the schematic above, with the rate equations (1) and (2),

$$\frac{D_{AB}\left(C_{A,1} - C_{A,2}\right)}{L} = \frac{h_m}{S_{AB}\, R_u\, T_\infty} \left(C_{A,s} - C_{A,f} \right)$$

$$\frac{C_{A,1} - C_{A,2}}{C_{A,s} - C_{A,f}} = \frac{h_m / S_{AB}\, R_u\, T_\infty}{D_{AB} / L} = \frac{R''_{m,dif}}{R''_{m,conv}} = Bi_m \tag{3}$$

and introducing resistances to species transfer by diffusion, Eq. 14.51, and convection. Recognize from the analogy to heat transfer, Eq. 5.10 and Table 14.2, that when $Bi_m < 0.1$, the concentration can be characterized as uniform during the transient process. That is, the diffusion resistance is negligible compared to the convection resistance,

$$Bi_m = \frac{h_m L}{S_{AB}\, R_u\, T_\infty\, D_{AB}} < 0.1 \tag{4}$$

$$Bi_m = \frac{\left(1.5 \text{ m/h} \times 3600 \text{ s/h}\right) \times 0.003 \text{ m}}{160 \text{ kmol/m}^3 \cdot \text{atm} \times 8.205 \times 10^{-2}\, \text{m}^3 \cdot \text{atm/kmol} \cdot \text{K} \times 555 \text{ K} \times 2.68 \times 10^{-8}\, \text{m}^2/\text{s}}$$

$$Bi_m = 6.60 \times 10^{-3} \quad < \quad 0.1$$

Hence, the mass transfer process can be treated as a nearly uniform concentration situation. From conservation of species on the material with uniform concentration,

$$-N''_{A,conv} = \dot{N}''_{A,st}$$

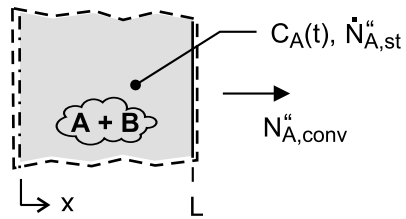$$-\frac{h_m}{S_{AB}\, R_u\, T_\infty} \left(C_A - C_{A,f} \right) = L \frac{d\, C_A}{dt}$$

Integrating, with the initial condition $C_A(0) = C_{A,i}$, find

$$\frac{C_A - C_{A,f}}{C_{A,i} - C_{A,f}} = \exp\left(-\frac{h_m\, t}{L\, S_{AB}\, R_u\, T_\infty} \right) \tag{5} \quad <$$

which is similar to the analogous heat transfer relation for the lumped capacitance analysis, Eq. 5.6.

(c) The time, t_o, required for the material to reach a concentration twice that of the limiting value, $C_A(T_o) = 2 C_{A,f}$, can be calculated from Eq. (5).

$$\frac{(2-1) \times 16 \text{ kmol}/\text{m}^3}{(320\text{-}16) \text{ kmol}/\text{m}^3} = \exp\left(-\frac{1.5 \text{ m}/\text{h} \times t_o}{0.003 \text{ m} \times 160 \text{ kmol}/\text{m}^3 \cdot \text{atm} \times 8.205 \times 10^{-2} \text{ m}^3 \cdot \text{atm}/\text{kmol} \cdot \text{K} \times 555 \text{ K}}\right)$$
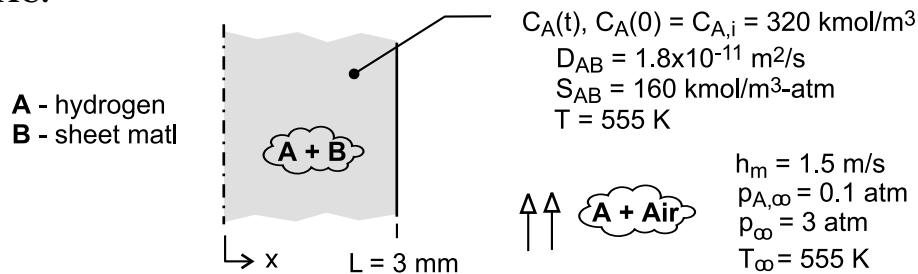
$$t_o = 42.9 \text{ hour} \qquad <$$

PROBLEM 14.43

KNOWN: Hydrogen-removal process described in Problem 14.3 (S), but under conditions for which the mass diffusivity of hydrogen gas (A) in the sheet (B) is $D_{AB} = 1.8 \times 10^{-11}$ m^2/s (instead of 2.6×10^{-8} m^2/s). With a smaller D_{AB}, a uniform concentration condition may no longer be assumed to exist in the material during the removal process.

FIND: (a) The final mass density of hydrogen in the material if the sheet is exposed to the air stream for a very long time, $\rho_{A,f}$, (b) Identify and evaluate the parameters that describe the transient mass transfer process in the sheet; *Hint*: this situation is analogous to that of transient heat conduction in a plane wall; (c) Assuming a uniform concentration in the sheet at any time during the removal process, determine the time required to reach twice the limiting mass density calculated in part (a); (d) Using the analogy developed in part (b), determine the time required to reduce the hydrogen concentration to twice the limiting value calculated in part (a); Compare the result with that from part (c).

SCHEMATIC:

$C_A(t)$, $C_A(0) = C_{A,i} = 320$ kmol/m3
$D_{AB} = 1.8 \times 10^{-11}$ m2/s
$S_{AB} = 160$ kmol/m3-atm
$T = 555$ K

A - hydrogen
B - sheet matl

⟨A + B⟩

⟨A + Air⟩

$h_m = 1.5$ m/s
$p_{A,\infty} = 0.1$ atm
$p_\infty = 3$ atm
$T_\infty = 555$ K

$\rightarrow$ x   L = 3 mm

ASSUMPTIONS: (1) One-dimensional diffusion, (2) Material B is a stationary medium, (3) Constant properties, (4) Uniform temperature in air stream and material, and (5) Ideal gas behavior.

ANALYSIS: (a) The final content of H$_2$ in the material will depend upon the solubility of H$_2$ (A) in the material (B) at its partial pressure in the free stream. From Eq. 14.44,

$$C_{A,f} = S_{AB}\, p_{A,\infty} = 160 \text{ kmol/m}^3 \cdot \text{atm} \times 0.1 \text{ atm} = 16 \text{ kmol/m}^3$$

$$\rho_f = M_A\, C_{A,f} = 2 \text{ kg/kmol} \times 16 \text{ kmol/m}^3 = 32 \text{ kg/m}^3 \qquad\qquad <$$

(b) For the plane wall shown in the schematic below, the heat and mass transfer conservation equations and their initial and boundary conditions are

Heat transfer

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

$$T(x,0) = T_i$$

$$\frac{\partial T}{\partial x}(0,t) = 0$$

$$-k\frac{\partial T}{\partial x}(L,t) = h\big[T(L,t) - T_\infty\big]$$

Mass (Species A) transfer

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial x^2}$$

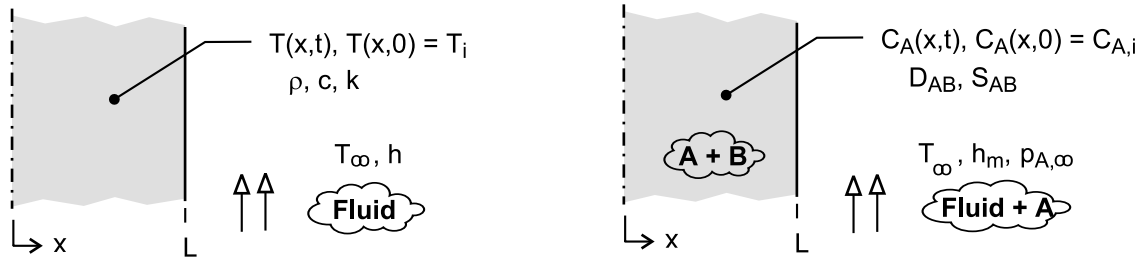$$C_A(x,0) = C_{A,i}$$

$$\frac{\partial C_A}{\partial x}(0,t) = 0$$

$$-D_{AB}\frac{\partial C_A}{\partial x}(L,t) = \frac{h_m}{S_{AB}\, R_u\, T}\big[C_A(x,t) - C_f\big]$$

Continued …..

The derivation for the species transport surface boundary condition is developed in the solution for Problem 14.3 (S). The solution to the mass transfer problem is identical to the analogous heat transfer problem provided the transport coefficients are represented as

$$\frac{h}{k} \quad <=> \quad \frac{h_m / S_{AB} \, R_u \, T}{D_{AB}} \tag{1}$$

(c) The uniform concentration transient diffusion process is analogous to the heat transfer lumped-capacitance process. From the solution of Problem 14.3 (S), the time to reach twice the limiting concentration, $C_A(t_o) = 2\, C_{A,f}$, can be calculated as

$$\frac{C_A(t_o) - C_{A,f}}{C_{A,i} - C_{A,f}} = \exp\left(-\frac{h_m \, t_o}{L \, S_{AB} \, R_u \, T}\right) \tag{2}$$

$$t_o = 42.9 \text{ hour} \qquad\qquad <$$

For the present situation, the mass transfer Biot number is

$$Bi_m = \frac{h_m \, L}{S_{AB} \, R_u \, T \, D_{AB}}$$

$$Bi_m = \frac{(1.5 \text{ m}/\text{h}/3600 \text{ s}/\text{h}) \times 0.003 \text{ m}}{160 \text{ kmol}/\text{m}^3 \cdot \text{atm} \times 8.205 \times 10^{-2}\, \text{m}^3 \cdot \text{atm}/\text{kmol} \cdot \text{K} \times 555 \text{ K} \times 1.8 \times 10^{-11}\, \text{m}^2/\text{s}}$$

$$Bi_m = 9.5 \gg 0.1$$

and hence the concentration of A within B is not uniform

(d) Invoking the analogy with the heat transfer situation, we can use the one-term series solution, Eq. 5.40, with $Bi_m <=> Bi$ and

$$Fo_m <=> Fo \qquad\qquad Fo_m = \frac{D_{AB}\, t}{L^2} \tag{3}$$

With $Bi_m = 9.5$, find $\zeta_1 = 1.4219$ rad and $C_1 = 1.2609$ from Table 5.1, so that Eq. 5.41 becomes

$$\frac{C_A(t_o) - C_{A,f}}{C_{A,i} - C_{A,f}} = C_1 \exp\left(-\zeta_1^2 \, Fo_m\right)$$

$$\frac{(2-1) \times 16 \, kmol/m^3}{(320-16)kmol/m^3} = 1.2609 \, \exp\left(-1.4219^2 \, Fo_m\right)$$

$$Fo_m = \frac{1.8 \times 10^{-11} \, m^2/s \times t_o}{(0.003 \, m)^2} = 1.571$$

$$t_o = 218 \text{ hour} \qquad <$$

COMMENTS: (1) Since $Bi_m = 9.5$, the uniform concentration assumption is not valid, and we expect the analysis to provide a longer time estimate to reach $C_A(t_o) = 2 \, C_{A,f}$.
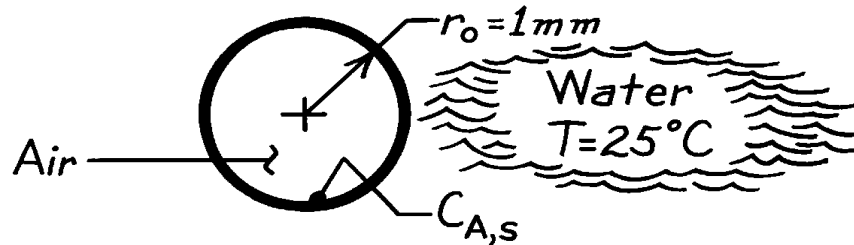
(2) Note that the uniform concentration analysis model of part (c) does not include D_{AB}. Why is this so?

PROBLEM 14.44

KNOWN: Radius and temperature of air bubble in water.

FIND: Time to reach 99% of saturated vapor concentration at center.

SCHEMATIC:

ASSUMPTIONS: (1) One-dimensional radial diffusion of vapor in air, (2) Constant properties, (3) Air is initially dry.

PROPERTIES: *Table A-8*, Water vapor-air (300 K): $D_{AB} = 0.26 \times 10^{-4}$ m²/s.

ANALYSIS: Use Heisler charts with heat and mass transfer analogy,

$$g^* \equiv \frac{C_A - C_{A,s}}{C_{A,i} - C_{A,s}} = 1 - \frac{C_A}{C_{A,s}}.$$

For $g_o^* = 1 - 0.99 = 0.01$ and $Bi_m^{-1} = 0$, from Fig. D.7 find $Fo_m \approx 0.52$. Hence with

$$Fo_m = \frac{D_{AB}t}{r_o^2} = 0.52$$

$$t = 0.52\left(10^{-6}\, m^2\right)/0.26 \times 10^{-4}\, m^2/s = 0.02\,s. \qquad <$$

COMMENTS: (1) This estimate is likely to be conservative, since shear driven motion of air within the bubble would enhance vapor transport from the surface to the center.

(2) If the one-term approximation to the infinite series solution,

$$q^* = \sum_{n=1}^{\infty} C_n \exp\left(-V_n^2 Fo\right) \frac{\sin\left(V_n r^*\right)}{V_n r^*}$$

is used, it follows that with sin 0/0 = 1,

$$g_o^* \approx C_1 \exp\left(-z_1^2 Fo_m\right) = 0.1.$$

Using values of $C_1 = 2.0$ and $V_1 = 3.11$ for $Bi_m = 100$, it follows that

$$0.01 = 2.0 \exp\left[-(3.11)^2 Fo_m\right] \qquad \text{or} \qquad Fo_m = 0.55$$
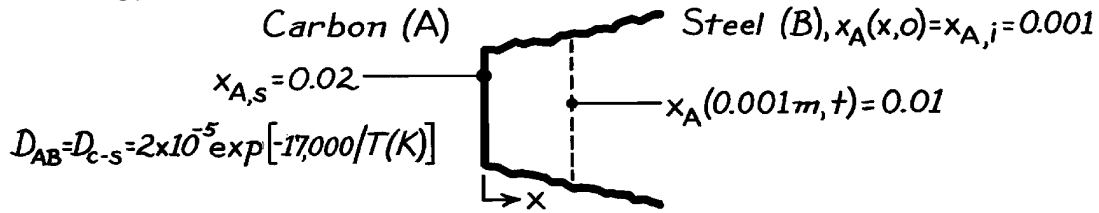
which is in reasonable agreement with the Heisler chart result.

KNOWN: Initial carbon content and prescribed surface content for heated steel.

FIND: Time required for carbon mole fraction to reach 0.01 at a distance of 1 mm from the surface.

SCHEMATIC:

ASSUMPTIONS: (1) Steel may be approximated as a semi-infinite medium, (2) One-dimensional diffusion in x, (3) Isothermal conditions, (4) No internal chemical reactions, (5) Uniform total molar concentration.

ANALYSIS: Conditions within the steel are governed by the species diffusion equation of the form

$$\frac{\partial^2 C_A}{\partial x^2} = \frac{1}{D_{AB}} \frac{\partial C_A}{\partial t}$$

or, in molar form,

$$\frac{\partial^2 x_A}{\partial x^2} = \frac{1}{D_{AB}} \frac{\partial x_A}{\partial t}.$$

The initial and boundary conditions are of the form

$$x_A(x,0) = 0.001$$

$$x_A(0,t) = x_{A,s} = 0.02 \qquad x_A(\infty,t) = 0.001.$$

The problem is analogous to that of heat transfer in a semi-infinite medium with constant surface temperature, and by analogy to Eq. 5.57, the solution is

$$\frac{x_A(x,t) - x_{A,s}}{x_{A,i} - x_{A,s}} = \mathrm{erf}\left(\frac{x}{2(D_{AB}t)^{1/2}}\right)$$

where

$$D_{AB} = 2\times10^{-5}\exp\left[-17,000/1273\right] = 3.17\times10^{-11}\,\mathrm{m}^2\,/\mathrm{s}.$$

Hence

$$\frac{0.01 - 0.02}{0.001 - 0.02} = 0.526 = \mathrm{erf}\left(\frac{0.001\,\mathrm{m}}{2\left(3.17\times10^{-11}t\right)^{1/2}}\right)$$

where $\mathrm{erf}\,w = 0.526 \to w \approx 0.51$,

$$0.51 = 0.001/2\left(3.17\times10^{-11}t\right)^{1/2} \qquad\qquad \text{or} \qquad\qquad t = 30,321\,\mathrm{s} = 8.42\ \mathrm{h.} \ <$$

PROBLEM 14.46

KNOWN: Thick plate of pure iron at 1000°C subjected to a carburizing process with sudden exposure to a carbon concentration $C_{C,s}$ at the surface.

FIND: (a) Consider the heat transfer analog to the carburization process; sketch the mass and heat transfer systems; explain correspondence between variables; provide analytical solutions to the mass and heat transfer situation; (b) Determine the carbon concentration ratio, $C_C(x, t)/C_{C,s}$, at a depth of 1 mm after 1 hour of carburization; and (c) From the analogy, show that the time dependence of the mass flux of carbon into the plate can be expressed as $n''_C = \rho_{C,s}(D_{C-Fe}/\pi t)^{1/2}$; also, obtain an expression for the mass of carbon per unit area entering the iron plate over the time period t.

SCHEMATIC:
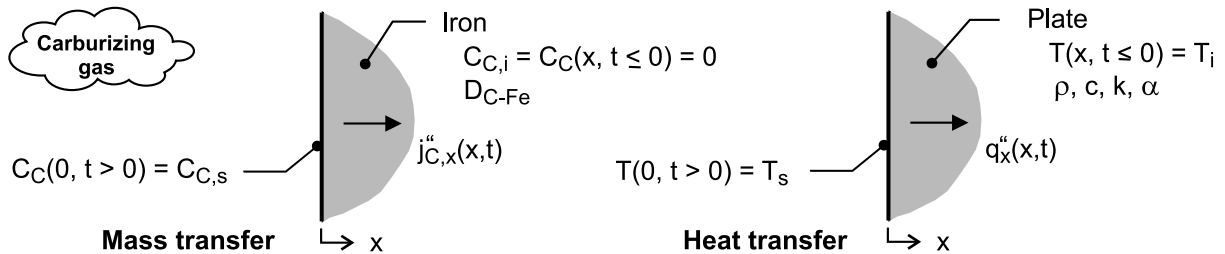
ASSUMPTIONS: (1) One-dimensional transient diffusion, (2) Thick plate approximates a semi-infinite medium for the transient mass and heat transfer processes, and (3) Constant properties.

ANALYSIS: (a) The analogy between the carburizing mass transfer process in the plate and the heat transfer process is illustrated in the schematic above. The basis for the mass - heat transfer analogy stems from the similarity of the conservation of species and energy equations, the general solution to the equations, and their initial and boundary conditions. For both processes, the plate is a semi-infinite medium with initial distributions, $C_C(x, t \le 0) = C_{C,i} = 0$ and $T(x, t \le 0) = T_i$, suddenly subjected to a surface potential, $C_C(0, t > 0) = C_{C,s}$ and $T(0, t > 0) = T_s$. The heat transfer situation corresponds to Case 1, Section 5.7, from which the following relations were obtained.

Mass transfer	*Heat transfer*

Rate equation

$$j''_C = -D_{AB}\frac{\partial C_c}{\partial x} \qquad\qquad q''_x = -k\frac{\partial T}{\partial x}$$

Diffusion equation

$$\frac{\partial}{\partial x}\left(\frac{\partial C_C}{\partial x}\right) = \frac{1}{D_{AB}}\frac{\partial C_C}{\partial t} \quad [14.84] \qquad\qquad \frac{\partial}{\partial x}\left(\frac{\partial T}{\partial x}\right) = \frac{1}{\alpha}\frac{\partial T}{\partial t} \quad [2.15]$$

Potential distribution

$$\frac{C_C(x,\ t) - C_{C,s}}{0 - C_{C,s}} = \qquad\qquad \frac{T(x,\ t) - T_s}{T_i - T_s} = \operatorname{erf}\left(\frac{x}{2(\alpha t)^{1/2}}\right) \quad [5.58]$$

$$\frac{C_C(x,\ t)}{C_{C,s}} = \operatorname{erfc}\left(\frac{x}{2(D_{AB}\ t)^{1/2}}\right)$$

Continued …..

Flux

See Part (c)

$$q_s''(t) = \frac{k\,(T_s - T_i)}{(\pi \alpha t)^{1/2}} \quad [5.58]$$

(b) Using the concentration distribution expression above, with $L = 1$ mm, $t = 1$ h and $D_{AB} = 3 \times 10^{-11}$ m^2/s, find the concentration ratio,

$$\frac{C_C\,(1\text{ mm, }1\text{ h})}{C_{C,s}} = \text{erfc}\left(\frac{0.001\text{ m}}{2\left(3\times10^{-11}\text{ m}^2/\text{s}\times3600\text{ s}\right)^{1/2}} \right) = 0.0314 \qquad <$$

(c) From the heat flux expression above, the mass flux of carbon can be written as

$$n_{C,s}'' = \frac{D_{C-Fe}\,\left(\rho_{C,s} - 0\right)}{\left(\pi\,D_{C-Fe}\,t\right)^{1/2}} = \rho_{c,s}\,\left(D_{C-Fe}/\pi\,t\right)^{1/2} \qquad <$$

The mass per unit area entering the plate over the time period follows from the integration of the rate expression

$$m_C''\,(t) = \int_0^t n_{C,s}''\,dt = \rho_{C,s}\,\left(D_{AB}/\pi\right)^{1/2} \int_0^t t^{-1/2}\,dt = 2\,\rho_{C,s}\,\left(D_{C-Fe}\,t/\pi\right)^{1/2}$$

PROBLEM 14.47

KNOWN: Thickness, initial condition and bottom surface condition of a water layer.

FIND: (a) Time to reach 25% of saturation at top, (b) Amount of salt transfer in that time, (c) Final concentration of salt solution at top and bottom.

SCHEMATIC:
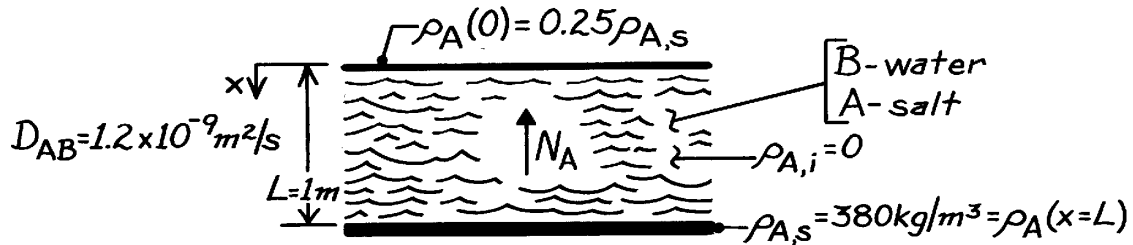
ASSUMPTIONS: (1) One-dimensional diffusion, (2) Uniform total mass density, (3) Constant D_{AB}.

ANALYSIS: (a) With constant ρ and D_{AB} and no homogeneous chemical reactions, Eq. 14.37b reduces to

$$\frac{\partial^2 r_A}{\partial x^2} = \frac{1}{D_{AB}} \frac{\partial r_A}{\partial t}.$$

with the origin of coordinates placed at the top of the layer, the dimensionless mass density is

$$g^*\left(x^*, Fo_m\right) = \frac{g}{g_i} = \frac{r_A - r_{A,s}}{r_{A,i} - r_{A,s}} = 1 - \frac{r_A}{r_{A,s}}$$

Hence, $g^*\left(0,\ Fo_{m,1}\right) = 1 - 0.25 = 0.75$. The initial condition is $g^*\left(x^*, 0\right) = 1$, and the boundary conditions are

$$\left. \frac{\partial g^*}{\partial x^*} \right|_{x^*=0} = 0 \qquad g^*\left(1,\ Fo_m\right) = 0$$

where the condition at $x^* = 1$ corresponds to $Bi_m = \infty$. Hence, the mass transfer problem is analogous to the heat transfer problem governed by Eq. 5.34 to 5.37. Assuming applicability of a one-term approximation ($Fo_m > 0.2$), the solution is analogous to Eq. 5.40.

$$g^* = C_1 \exp\left(-V_1^2 Fo_m\right) \cos\left(V_1 x^*\right).$$

With $Bi_m = \infty$, $V_1 = p / 2 = 1.571$ rad and, from Table 5.1, $C_1 \approx 1.274$. Hence, for $x^* = 0$,

$$0.75 = 1.274 \exp\left[-(1.571)^2 Fo_{m,1}\right]$$

$$Fo_{m,1} = -\ln\left(0.75/1.274\right) / \left(1.571\right)^2 = 0.215.$$

Hence,

$$t_1 = \frac{L^2}{D_{AB}} Fo_{m,1} = \frac{(1\ m)^2}{1.2 \times 10^{-9}\ m^2/s} \, 0.215 = 1.79 \times 10^8\ s = 2071\,days. \qquad <$$

(b) The change in the salt mass within the water is

$$\Delta M_A = M_A(t_1) - M_{A,i} = \int (r_A - r_{A,i}) dV = A \int_0^L r_A dx$$

Hence,

$$\Delta M_A'' = r_{A,s} \int_0^L (r_A / r_{A,s}) dx$$

$$\Delta M_A'' = r_{A,s} L \int_0^1 (1 - g^*) dx^*$$

$$\Delta M_A'' = r_{A,s} L \int_0^1 \left[1 - C_1 \exp\left(-V_1^2 Fo_m\right) \cos\left(V_1 x^*\right) \right] dx^*$$

$$\Delta M_A'' = r_{A,s} L \left[1 - C_1 \exp\left(-V_1^2 Fo_m\right) \sin V_1 / V_1 \right].$$

Substituting numerical values,

$$\Delta M_A'' = 380 \ kg/m^3 (1 \ m) \left[1 - \frac{1.274 \exp\left[-(1.571)^2 \, 0.215 \right] 1}{1.571 \mathrm{rad}} \right]$$

$$\Delta M_A'' = 198.7 \ kg/m^2. \qquad <$$

(c) Steady-state conditions correspond to a uniform mass density in the water. Hence,

$$r_A(0,\infty) = r_A(L,\infty) = \Delta M_A'' / L = 198.7 \ kg/m^3. \qquad <$$

COMMENTS: (1) The assumption of constant ρ is weak, since the density of salt water depends strongly on the salt composition.

(2) The requirement of $Fo_m > 0.2$ for the one-term approximation to be valid is barely satisfied.

KNOWN: Temperature distribution expression for a semi-infinite medium, initially at a uniform temperature, that is suddenly exposed to an instantaneous amount of energy, $Q_o'' \ (J / m^2)$.

Analogous situation of a silicon (Si) wafer with a 1-μm layer of phosphorous (P) that is placed in a furnace suddenly initiating diffusion of P into Si.

FIND: (a) Explain the correspondence between the variables in the analogous temperature and concentration distribution expressions, and (b) Determine the mole fraction of P at a depth of 0.1 mm in the Si after 30 s.

SCHEMATIC:
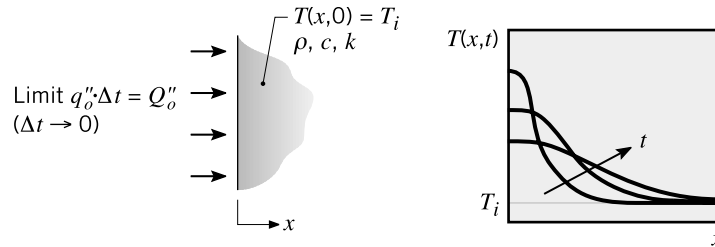
ASSUMPTIONS: (1) One-dimensional, transient diffusion, (2) Wafer approximates a semi-infinite medium, (3) Uniform properties, and (4) Diffusion process for Si and P is initiated when the wafer reaches the elevated temperature as a consequence of the large temperature dependence of the diffusion coefficient.

PROPERTIES: *Given in statement*: $D_{P-Si} = 1.2 \times 10^{-17} \ m^2/s$; Mass densities of Si and P: 2000 and 2300 kg/m^3; Molecular weights of Si and P: 30.97 and 28.09 kg/kmol.

ANALYSIS: (a) For the thermal process illustrated in the schematic, the temperature distribution is

$$T(x, \ t) - T_i = \frac{Q_o''}{\rho c (\pi \alpha t)^{1/2}} \exp\left(-x^2 / 4\alpha t\right) \qquad \text{(HT)}$$

where T_i is the initial, uniform temperature of the medium. For the mass transfer process, the P concentration has the form

$$C_P(x, \ t) = \frac{M_{P,o}''}{(\pi \, D_{P-Si} \, t)^{1/2}} \exp\left(-x^2 / 4 \, D_{P-Si} \, t\right) \qquad \text{(MT)}$$

where $M_{P,o}''$ is the molar area density (kmol/m^2) of P represented by the film of concentration C_P and thickness d_o.

The correspondence between mass and heat transfer variables in the equations HT and MT involves the following conditions. The LHS represents the increase with time of the temperature or concentration above the initial uniform distribution. The initial concentration is zero, so only the C_P (x, t) appears. On the RHS note the correspondence of the terms in the exponential parenthesis and in the denominator. The thermal diffusivity and diffusion coefficient are directly analogous; this can be seen by comparing the MT and HT diffusion equations, Eq. 2.15 and 14.84. The terms $Q_o'' / \rho c$ and $M_{P,o}''$ for HT and MT represent the energy and mass instantaneously appearing at the surface. The product ρc is the thermal capacity per unit area and appears in the storage term of the HT diffusion equation. For MT, the "capacity" term is the volume itself.

(b) The molar area density (kmol/m^2) of P associated with the film of thickness $d_o = 1 \ \mu m$ and concentration $C_{P,o}$ is

$$M''_{P,o} = C_{P,o} \cdot d_o = (\rho_P / M_P)d_o$$

$$M''_{P,o} = \left(2000 \ kg / m^3 / 30.97 \ kmol / kg\right) \times 1 \times 10^{-6} \ m$$

$$M''_{P,o} = 6.458 \times 10^{-5} \ kmol / m^2$$

Substituting numerical values into the MT equation, find

$$C_p(0.1 \ mm, \ 30 \ s) = \frac{6.458 \times 10^{-5} \ kmol / m^2}{\left(\pi \times 1.2 \times 10^{-17} \ m^2 / s \times 30 \ s\right)} \exp - (0.0001 \ m)^2 / \left(4 \times 1.2 \times 10^{-7} \ m^2 / s \times 30 \ s\right)\Bigg]$$

$$C_p = 0.08188 \ kmol / m^3$$

The mole fraction of P in the Si wafer is

$$x_P = C_P / C_{Si} = C_P / (\rho_{Si} / M_{Si})$$

$$x_P = 0.08188 \ kmol / m^3 / \left(2300 \ kg / m^3 / 28.09 \ kmol / kg\right)$$

$$x_P = 2.435 \times 10^{-5} \qquad\qquad <$$