17A.6 Diffusivity and Schmidt number for chlorine-air mixtures.

(a) We begin by tabulating molecular parameters for chlorine and air from Table E.1, and estimating the binary parameters σ_{AB} and ε_{AB}/κ from Eqs. 17.3-14 and 15:

Species	M, g/g-mol	σ, Å	ε/κ, K
A: Cl_2	70.91	4.115	357.
B: Air	28.97	3.617	97.0
AB:		3.866	186.1

Equation 17.3-12 and Table E.2 then give the following prediction of $\mathcal{D}_{AB}$ for chlorine-air mixtures at $T = 75°\text{F} = 23.89°\text{C} = 297.04$ K:

$$\begin{aligned}\mathcal{D}_{AB} &= 0.0018583\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{p\sigma_{AB}^2\Omega_{\mathcal{D},AB}} \\ &= 0.0018583\sqrt{(297.04)^3\left(\frac{1}{28.97}+\frac{1}{70.91}\right)}\frac{1}{(1)(3.866)^2(1.169)} \\ &= 0.120\ \text{cm}^2/\text{s}\end{aligned}$$

(b) Equation 17.2-1 needs the following values from Table E.1:

Component	M, g/g-mol	T_c, K	p_c, atm
A: Cl_2	70.91	417.	76.1
B: Air	28.97	132.	36.4

The nonpolar version of Eq. 17.2-1 then gives the prediction

$$\begin{aligned}\mathcal{D}_{AB} &= 2.745\times 10^{-4}\left(\frac{297.04}{\sqrt{417.\times 132.}}\right)^{1.823} \\ &\quad \cdot (76.1\times 36.4)^{1/3}(417.\times 132.)^{5/12}(1/70.91+1/28.97)^{1/2}/1\ \text{atm} \\ &= 0.123\ \text{cm}^2/\text{s}\end{aligned}$$

(c) The result of **(a)**, and the ideal gas expression for c, give

$$c\mathcal{D}_{AB} = \frac{p}{RT}\mathcal{D}_{AB} = 4.92\times 10^{-6}\ \text{g-mol/cm·s}$$

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

$$\text{Sc} = \frac{\mu}{\rho\mathcal{D}_{AB}} = \frac{\mu}{Mc\mathcal{D}_{AB}} = \frac{\mu}{(x_AM_A + x_BM_B)c\mathcal{D}_{AB}}$$

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

x_{Cl_2}	0.00	0.25	0.50	0.75	1.00
μ, g/cm·s	0.000183	0.000164	0.000150	0.000139	0.000131
M, g/g-mol	28.97	39.455	49.94	60.425	70.91
Sc	1.28	0.84	0.61	0.47	0.375

We see that the Schmidt number depends strongly on the composition when M_A and M_B differ greatly. This fact is also illustrated in Table 17.3-1 and in Problem 17A.4.

18A.2 Sublimation of small iodine spheres in still air.

(a) From Table E.1 and Eqs. 17.3-14,15, we get the following values for the system I_2-air:

Species	M	σ, Å	ε/κ, K
A: I_2	253.81	4.982	550.
B: air	28.97	3.617	97.0
AB		4.2995	231.0

Thus, at $T = 40°\text{C} = 313.15\text{K}$, we get the argument value

$$\kappa T/\varepsilon_{AB} = 313.15/231.0 = 1.356,$$

at which Table E.2 gives $\Omega_{\mathcal{D},AB} = 1.251$. Equation 17.3-12 then gives

$$\begin{aligned}
\mathcal{D}_{AB} &= 0.0018583\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{p\sigma^2\Omega_{\mathcal{D},AB}} \\
&= 0.0018583\sqrt{(313.15)^3\left(\frac{1}{253.81}+\frac{1}{28.97}\right)}\frac{1}{(747/760)(4.2995)^2(1.251)} \\
&= 0.0888\ \text{cm}^2/\text{s}
\end{aligned}$$

(b) Equation 18.2-27, with $r_2 \to \infty$, gives

$$\begin{aligned}
W_A &= 4\pi r_1 c\mathcal{D}_{AB}\ln\left(\frac{1-x_{A2}}{1-x_{A1}}\right) \\
&= 4\pi r_1\frac{p\mathcal{D}_{AB}}{RT}\ln\left(\frac{p}{p-p_{A,\text{vap}}}\right) \\
&= 4\pi(0.5\ \text{cm})\frac{(747/760\ \text{atm})(0.0888\ \text{cm}^2/\text{s})}{(82.06\times 313.15\ \text{cm}^3\text{atm/g-mol})}\ln\left(\frac{747}{747-1.03}\right) \\
&= 2.95\times 10^{-8}\ \text{g-mol/s}\times 3600\ \text{s/hr} \\
&= 1.06\times 10^{-4}\ \text{g-mol/hr}
\end{aligned}$$

18B.5 Absorption of chlorine by cyclohexene

a. For a second-order reaction, Eq. 18.4-4 has to be replaced by

$$-\mathscr{D}_{AB}\frac{d^2c_A}{dz^2}+k_2'''c_A^2=0$$

with the same boundary conditions as before. Introduce the dimensionless variables $\Gamma=c_A/c_{A0}$ and $\zeta=\sqrt{k_2'''c_{A0}/6\mathscr{D}_{AB}}z$. Then the differential equation becomes

$$\frac{d^2\Gamma}{d\zeta^2}-6\Gamma^2=0$$

with boundary conditions $\Gamma(0)=1$ and $\Gamma(\infty)=0$. We now let $d\Gamma/d\zeta=p(\Gamma)$, so that $d^2\Gamma/d\zeta^2=dp/d\zeta=(dp/d\Gamma)(d\Gamma/d\zeta)=p(dp/d\Gamma)$. Then we obtain a differential equation that is first order and separable

$$p\frac{dp}{d\Gamma}=6\Gamma^2$$

This may be inegrated, and we use the boundary condition that at $\zeta=\infty$, $\Gamma=0$ and *also* that $d\Gamma/d\zeta=p(\Gamma)=0$:

$$\int_0^p p\,dp=\int_0^\Gamma 6\Gamma^2 d\Gamma$$

from which

$$\tfrac{1}{2}p^2=2\Gamma^3 \qquad \text{or} \qquad \frac{d\Gamma}{d\zeta}=\pm 2\Gamma^{3/2}$$

Here we must choose the minus sign, since the slope of the concentration vs. distance curve is negative. Then using the first boundary condition, we can integrate this equation to get:

$$\int_1^\Gamma \Gamma^{-3/2}d\Gamma=-\int_0^\zeta d\zeta \qquad \text{or} \qquad \Gamma^{-1}=(1+\zeta)^2$$

Hence the final expression for the concentration profile is

$$\frac{c_{A0}}{c_A} = \left(1 + \sqrt{\frac{k_2'''c_{A0}}{6\mathscr{D}_{AB}}}z\right)^2$$

b. From the result of (*a*) we get the absorption rate at the liquid gas interface:

$$N_{Az}\big|_{z=0} = -\mathscr{D}_{AB}\frac{dc_A}{dz}\bigg|_{z=0} = \sqrt{\tfrac{2}{3}k_2'''c_A^3\mathscr{D}_{AB}}$$

c. The equation to be solved is

$$-\mathscr{D}_{AB}\frac{d^2c_A}{dz^2} + f(c_A) = 0 \qquad \text{or} \qquad p\frac{dp}{dc_A} = \frac{f(c_A)}{\mathscr{D}_{AB}}$$

where we have introduced the variable p as before. The resulting equation is integrated, as before, to give

$$\int_0^p \bar{p}\,d\bar{p} = \frac{1}{\mathscr{D}_{AB}}\int_0^{c_A} f(\bar{c}_A)d\bar{c}_A \qquad \text{or} \qquad p = \frac{dc_A}{dz} = -\sqrt{\frac{2}{\mathscr{D}_{AB}}\int_0^{c_A} f(\bar{c}_A)d\bar{c}_A}$$

A second integration yields

$$\int_{c_{A0}}^{c_A}\frac{d\bar{c}_A}{\sqrt{(2/\mathscr{D}_{AB})\int_0^{\bar{c}_A} f(\bar{\bar{c}}_A)d\bar{\bar{c}}_A}} = -\int_0^1 dz = -z$$

Then we differentiate both sides with respect to z to get

$$\frac{1}{\sqrt{(2/\mathscr{D}_{AB})\int_0^{c_A} f(\bar{c}_A)d\bar{c}_A}}\frac{dc_A}{dz} = -1 \text{ and } \frac{dc_A}{dz}\bigg|_{z=0} = -\sqrt{(2/\mathscr{D}_{AB})\int_0^{c_{A0}} f(c_A)dc_A}$$

This together with $N_{Az}\big|_{z=0} = -\mathscr{D}_{AB}(dc_A/dz)\big|_{z=0}$ gives Eq. 18B.5-2.

18B.7 Diffusion from a suspended droplet

a. A mass balance on A over a spherical shell of thickness Δr is (in molar units)

$$4\pi r^2 \cdot N_{Ar}\big|_r - 4\pi(r+\Delta r)^2 \cdot N_{Ar}\big|_{r+\Delta r} = 0$$

or, equivalently

$$(4\pi r^2 N_{Ar})\big|_r - (4\pi r^2 N_{Ar})\big|_{r+\Delta r} = 0$$

Now divide by $4\pi\Delta r$ and take the limit as Δr goes to zero to get

$$\frac{d}{dr}(r^2 N_{Ar}) = 0$$

This may be integrated to give $r^2 N_{Ar} = C_1$. We may use the boundary condition that $N_{Ar} = N_{Ar1}$ at $r = r_1$ (the gas liquid interface) to evaluate the constant and obtain $r^2 N_{Ar} = r_1^2 N_{Ar1}$.

b . Equation 18.0-1, written for the radial component in spherical coordinates, is

$$N_{Ar} = -c\mathscr{D}_{AB}\frac{dx_A}{dr} + x_A\left(N_{Ar} + N_{Br}\right)$$

If gas B is not moving, then N_{Br} may be set equal to zero and the equation may be solved for the molar flux of A:

$$N_{Ar} = -\frac{c\mathscr{D}_{AB}}{1-x_A}\frac{dx_A}{dr}$$

Multiplying by r^2 and using the result obtained in (*a*), we get Eq. 19B.7-1:

$$r_1^2 N_{Ar1} = -\frac{c\mathscr{D}_{AB}}{1-x_A} r^2 \frac{dx_A}{dr}$$

c. Equation 19B.7-1 can be rearranged to give

$$r_1^2 N_{Ar1} \frac{dr}{r^2} = -c\mathcal{D}_{AB} \frac{dx_A}{1-x_A}$$

Integration then gives

$$r_1^2 N_{Ar1}\left(-\frac{1}{r}\right)\Bigg|_{r_1}^{r_2} = -c\mathcal{D}_{AB}\left[-\ln(1-x_A)\right]\Big|_{x_{A1}}^{x_{A2}}$$

or

$$r_1^2 N_{Ar1}\left(\frac{1}{r_1}-\frac{1}{r_2}\right) = +c\mathcal{D}_{AB}\left[\ln(1-x_{A2})-\ln(1-x_{A1})\right]$$

This may be rearranged to give

$$r_1^2 N_{Ar1}\left(\frac{r_2-r_1}{r_1 r_2}\right) = c\mathcal{D}_{AB} \ln\frac{x_{B2}}{x_{B1}}$$

or, when solved for the molar flux of A

$$N_{Ar1} = \frac{c\mathcal{D}_{AB}}{r_2-r_1}\left(\frac{r_2}{r_1}\right)\ln\frac{x_{B2}}{x_{B1}}$$

When $r_2 \to \infty$ (and presumably also $x_{A2} \to 0$), this last result gives

$$N_{Ar1} = \frac{c\mathcal{D}_{AB}}{r_1}\ln\frac{1}{x_{B1}}$$