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Technical Note

On steady one-dimensional diffusion in binary ideal gas mixtures

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Abstract

Steady, one-dimensional, diffusion in binary ideal gas mixtures is analyzed for both a zero mass average velocity and a zero molar average velocity, to give solutions for equimass and equimolar counterdiffusion. It is shown that the prescription of constant pressure results in equimass counterdiffusion rather than the commonly assumed equimolar counterdiffusion, and that these two situations are fundamentally different. Application to the analysis of venting processes is discussed.

Keywords: Counterdiffusion; Equimass; Equimolar; Binary; Gas mixtures

Most texts introduce steady, one-dimensional, diffusion by considering two large chambers connected by a tube, as shown in Fig. 1a, or by considering a venting problem, as shown in Fig. 1b. In both cases the temperature and total pressure are specified to be constant, and diffusion through the connecting tube is analyzed assuming equimolar counterdiffusion of species 1 and 2. The purpose of this communication is to show that the results of such analysis are incorrect, to provide the correct solution, and to illuminate the true nature of the practical venting problem.

We will start by considering two cases of steady one-dimensional diffusion in an isothermal, inert, binary gas mixture.

Case 1. On a mass basis the governing species and mass conservation equations reduce to

$$n_1 = m_1 \rho v + j_1 = \text{const.} \tag{1}$$

$$n = \rho v = \text{const.} \tag{2}$$

A solution of these equations is

$$v = 0; \quad j_1 = \text{const.}(= -j_2), \quad P = \text{const.} \tag{3}$$

Notice that a zero mass average velocity requires a constant total pressure according to Newton's second law of motion. Introducing Fick's law,

$$-\rho \mathscr{D}_{12} \frac{\mathrm{d}m_1}{\mathrm{d}z} = \text{const.} \tag{4}$$

and assuming an ideal gas mixture,

$$\rho = \frac{PM}{\mathscr{R}T}, \quad \text{where } \frac{1}{M} = \frac{m_1}{M_1} + \frac{m_2}{M_2} \tag{5}$$

$$\frac{PM_1M_2\mathscr{D}_{12}}{\mathscr{R}T(m_1(M_2 - M_1) + M_1)} \frac{\mathrm{d}m_1}{\mathrm{d}z} = \text{const.} \tag{6}$$

For convenience we will take as boundary conditions

$$z = 0, \quad m_1 = 1; \quad z = L, \quad m_1 = 0 \tag{7}$$

The resulting mass fraction distribution is then

$$m_1 = \frac{M_2(M_1/M_2)^{z/L} - M_1}{M_2 - M_1} \tag{8}$$

and the diffusion flux is

$$j_1 = -j_2 = \frac{P\mathscr{D}_{12}}{\mathscr{R}TL} \frac{M_1M_2}{(M_2 - M_1)} \ln\left(\frac{M_1}{M_2}\right) \tag{9}$$

Since $v = 0$, there is no convective flux, and $j_1 = n_1$, $j_2 = n_2$.

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Nomenclature

c	molar concentration, kmol/m^3
$\mathscr{D}_{12}$	binary diffusion coefficient, m^2/s
D	tube diameter, m
J^*	molar diffusion flux relative to v^*, kmol/m^2 s
J	mass diffusion flux relative to v, kg/m^2 s
L	tube length, m
M	molecular weight, kg/kmol
m	mass fraction
N	absolute molar flux, kmol/m^2 s
n	absolute mass flux, kg/m^2 s
P	pressure, Pa
$\mathscr{R}$	gas constant, J/kmol K
r	radial coordinate, m
T	absolute temperature, K
V	bulk velocity, m/s
v	mass average velocity, m/s
v^*	molar average velocity, m/s
x	mole fraction, spatial coordinate, m
y	spatial coordinate, m
z	spatial coordinate, m
μ	dynamic viscosity, kg/m s
ρ	density, kg/m^3
τ	characteristic diffusion time, s

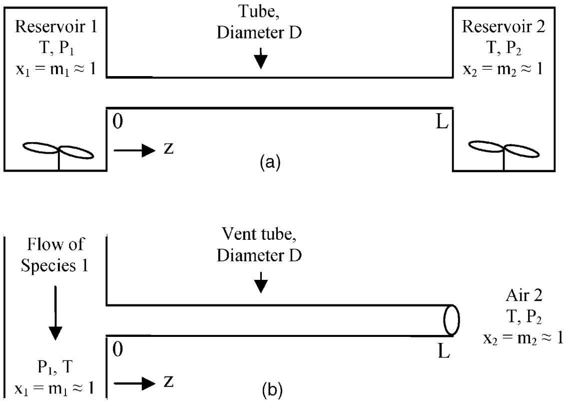

Fig. 1. Configurations used for illustrating equimolar counterdiffusion.

Case 2. On a molar basis the governing species and mole conservation equations are

$$N_1 = x_1 c v^* + J_1^* = \text{const.} \tag{10}$$

$$N = c v^* = \text{const.} \tag{11}$$

A solution of these equations is

$$v^* = 0, \quad J_1^* = -c\mathscr{D}_{12}\frac{\mathrm{d}x_1}{\mathrm{d}z} = -J_2^* = \text{const.} \tag{12}$$

We cannot deduce from this result that the pressure and molar concentration are necessarily constant (they are not constant). However, if we *assume P*, and hence c, are constant, then from Eq. (12)

$$\frac{\mathrm{d}x_1}{\mathrm{d}z} = \text{const.} \tag{13}$$

Again for convenience we take as boundary conditions

$$z = 0, \quad x_1 = 1; \quad z = L, \quad x_1 = 0 \tag{14}$$

Then $x_1 = z/L$.

And

$$J_1^* = \frac{c\mathscr{D}_{12}}{L} = -J_2^* \tag{15}$$

Since $v^* = 0$ there is no molar convective flux and $J_1^* = N_1$, $J_2^* = N_2$.

We are now in a position to discuss the diffusion problems shown in Fig. 1a and b. Standard texts e.g. [1–8] specify at the outset that the pressure in the two chambers or streams are equal and that the pressure remains constant everywhere. Then $P = \text{const.}$ in the connecting tube and the Case 1 analysis applies. Clearly we have an equimass counterdiffusion problem, and the Case 1 analysis is exact in the context of the problem specification. However, as is well known, the above referenced texts all claim that the diffusion is equimolar and hence that the Case 2 analysis is appropriate. To show that the Case 2 analysis is inappropriate, we examine the implications of equimolar counterdiffusion. Although the molar average velocity v^* is zero, the mass average velocity v is not zero, for

$$\rho v = M_1 N_1 + M_2 N_2 = J_1^*(M_1 - M_2) \tag{16}$$

$$v = J_1^* \frac{(M_1 - M_2)}{\rho} \tag{17}$$

If $M_1 < M_2$ (imagine species 1 to be helium and species 2 air, then $\rho = \rho_{\mathrm{He}}$ at $z = 0$, and $\rho = \rho_{\mathrm{air}}$ at $z = L$); correspondingly v is in the negative z-direction and increases in the direction of flow. Even in a truly one-dimensional problem where the dimensions in the x- and y-directions are imagined to be infinite, there is a pressure gradient required to accelerate the flow. But more importantly, in a connecting tube, there will be pressure gradient required to overcome viscous forces associated with the velocity profile, say $v(r)$ in a circular tube. Thus clearly the *assumption* of equimolar counterdiffusion is inconsistent with the specified constant pressure. The situation in a connecting tube is further complicated by the fact that equimolar counterdiffusion cannot be one-dimensional, for, at the walls of the tube, the mass average velocity $v \to 0$, and the diffusion there is equimass, not equimolar: thus, Eqs. (10) and (11) do not apply, and two-dimensional governing equations are required.

Of course, it is tempting to suggest that, since the pressure gradient associated with equimolar counterdiffusion is very small, Eqs. (14) and (15) are at least approximately correct, and that these simple results are preferable to the more complicated exact results, Eqs. (8) and (9). Unfortunately, this is not true, which is best demonstrated by a numerical example.

Again consider helium as species 1, air as species 2; $P = 1$ atm $= 1.0133 \times 10^5$ Pa, $T = 300$ K, $L = 1$ m, $\mathscr{D}_{12} = 0.713 \times 10^{-4}$ m^2/s [9]. Then Eq. (9) gives $n_1 = 2.66 \times 10^{-5}$ kg/m^2 s $= -n_2$ as the exact solution. The corresponding exact solution for the absolute molar fluxes is

$$N_1 = \frac{n_1}{M_1} = 2.66 \times 10^{-5}/4 = 6.66 \times 10^{-6} \text{ kmol/m}^2\text{ s}$$

$$N_2 = \frac{n_2}{M_2} = -2.66 \times 10^{-5}/29$$
$$= -0.918 \times 10^{-6} \text{ kmol/m}^2\text{ s}$$

Also, $cv^* = N_1 + N_2 = 5.74 \times 10^{-6}$ kmol/m^2 s.

This is certainly not equimolar counterdiffusion and v^* is not zero. On the other hand, the result obtained assuming equimolar counterdiffusion, Eq. (15), gives

$$N_1 = 2.896 \times 10^{-6} \text{ kmol/m}^2\text{ s} = -N_2$$

The error is very large! The source of the discrepancy is now clear. The exact solution for $P =$ const. requires that there be a convective molar flux of 5.74×10^{-6} kmol/m^2 s, which is actually about twice the diffusion fluxes obtained assuming equimolar counterdiffusion: thus the equimolar diffusion assumption is not even approximately true.

When issues such as these are raised, we often suggest that an appropriate experiment be performed. Let us examine the key issue for such an experiment, namely, how accurately we need to measure the pressure differential between the two chambers. At the very least we should be able to measure the pressure differential required to have equimolar counterdiffusion with an error of less than, say, 20%. The mass velocity is

$$n = M_1N_1 + M_2N_2 = J_1^*(M_1 - M_2) = 2.896 \times 10^{-6}(4\text{–}29)$$
$$= -7.24 \times 10^{-5} \text{ kg/m}^2\text{ s}$$

Ignoring entrance and two-dimensional effects, the pressure gradient for Poiseuille flow can be used,

$$\frac{\mathrm{d}P}{\mathrm{d}z} = \frac{32\mu V}{D^2} = \frac{32n}{D^2}\frac{\mu}{\rho} \tag{18}$$

Let us calculate $(\mathrm{d}P/\mathrm{d}z)$ at each end of a 5 mm inside diameter tube. At $z = 0$ there is pure helium and $\rho = 0.1624$ kg/m^3, $\mu = 20.1 \times 10^{-6}$ kg/m s, while at $z = L$ there is pure air with $\rho = 1.177$ kg/m^3, $\mu = 18.43 \times 10^{-6}$ kg/m s (at 1 atm, 300 K) [9]. The resulting pressure gradients are

$$\left.\frac{\mathrm{d}P}{\mathrm{d}z}\right|_0 = 1.15 \times 10^{-2} \text{ Pa/m}; \quad \left.\frac{\mathrm{d}P}{\mathrm{d}z}\right|_L = 1.45 \times 10^{-3} \text{ Pa/m}$$

The acceleration pressure drop can be calculated to be many orders of magnitude smaller and is ignored. For an approximate estimate we can use the average of the above two gradients, so that for a 1 m long tube,

$$\Delta P \approx 6.5 \times 10^{-3} \text{ Pa}$$

(a more accurate result can be obtained by numerical integration). Then with a desired error of less than 20%, the pressure differential must be measured to within $6.5 \times 10^{-3} \times 0.2 \approx 10^{-3}$ Pa (10^{-8} atm). It is also of interest to estimate the time constant for steady conditions to be obtained [10], and is $\tau \sim L^2/\mathscr{D}_{12} = 1^2/0.713 \times 10^{-4} = 1.4 \times 10^4$ s (4 h). It is surely impossible to perform such an experiment.

Of course, if an experiment is impractical, there cannot be any significance of these issues to the practical venting problem, shown in Fig. 1b. We can now see that the venting rate is controlled by the pressure differential, rather than the diffusion rates given by Eqs. (9) and (15). When venting to the atmosphere, the atmospheric pressure will vary far more than pressure differentials calculated here. The practical problem will be characterized by essentially hydrodynamic flows of either helium or air, depending on the difference in pressures, and Eq. (18) can be used to estimate the venting (or ingestion) rates. Venting is not a diffusion problem.

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