THE PROBLEM OF NONSTEADY DIFFUSION

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A solution has been derived for the nonsteady diffusion equation for two flasks of identical volume, connected by a capillary, with consideration given to the transition process and the diffusion resistance of the flasks. This solution is compared with the approximate Ney and Armistead solution.

The two-flask method of experimentally measuring the coefficients of mutual gas diffusion has recently gained widespread acceptance. The experimental data are processed according to the following Ney and Armistead [1] formula:

$$\frac{c^{\infty}-c_2}{c^{\infty}-c_{02}} = \exp\left[-\varepsilon\frac{V_1+V_2}{V_2}\mathrm{Fo}\right]. \tag{1}$$

It was assumed in the derivation of this formula that:

1. The concentration varies linearly along the capillary length.
2. A concentration gradient exists only in the capillary.
3. The capillary volume is considerably smaller than the flask volumes containing the test gases.

Our paper is devoted to evaluating the effect of the above-cited assumptions on the two-flask method for measuring the diffusion coefficients.

Let us consider the diffusion of a gas through a capillary connecting two spherical flasks of identical volume and filled with a mixture of different gases. It is assumed that the temperature and pressure within these vessels are identical. The capillary ends are located at the flask centers and we assume that the concentrations are distributed with spherical symmetry about the vessel centers. In this formulation of the problem one end of the capillary can be replaced by a spherical surface source, and the other by a sink. Here, to preserve the conditions of balance the cross-sectional area of the capillary must be equal to the area of the surface source (sink), i.e., $\pi r_c^2 = 4\pi r_1^2$ or $r_1 = (1/2)r_c$.

With the above-indicated assumptions, the system of diffusion equations in the one-dimensional case for a capillary and the flasks can be written as follows:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2},$$

$$\frac{\partial c_{1,2}}{\partial t} = D\left(\frac{\partial^2 c_{1,2}}{\partial r^2} + \frac{2}{r}\frac{\partial c_{1,2}}{\partial r}\right)$$

with the following initial and boundary conditions: when $t = 0$, $c = c_{01}$ for $0 < x \le L$; $c_1 = c_{01}$ and $c_2 = c_{02}$ for $0 < r \le R$;

$$1.\ \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = 0 \quad \text{when } r = R;$$

$$2.\ \frac{\partial \bar{c}_1}{\partial t} = -\frac{aD}{V}\frac{\partial c}{\partial x} \quad \text{when } x = L;$$

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$$3.\ \frac{\partial \overline{c_2}}{\partial t} = \frac{aD}{V}\frac{\partial c}{\partial x} \quad \text{when } x = 0;$$

$$4.\ c(0,\ t) = c_2(r_1,\ t), \quad c(L,\ t) = c_1(r_1,\ t);$$

$$\overline{c}_{1,2} = \frac{4\pi}{V}\int\limits_0^R c_{1,2}(r,\ t)\, r^2 dr.$$

The solution of this problem can be found with the Laplace transform [2]. Omitting the extremely cumbersome calculations, we have

$$c - c^\infty = (c_{01} - c_{02}) \sum_{n=1}^{\infty} \left\{ \sin\mu_n \left[\frac{E_1}{E_2 \sin \mu_n r_C/L} \sin\mu_n \left(1 - \frac{x}{L}\right) \right.\right.$$
$$\left.\left. + \cos\mu_n \left(1 - \frac{x}{L}\right)\right] \exp\left[-\mu_n^2 \mathrm{Fo}\ \right]\right\} \left\{\mu_n + (-1)^n \alpha \sin \mu_n\right\}^{-1}, \tag{2}$$

$$c_1 - c^\infty = \frac{a(c_{01} - c_{02})}{2\pi r r_C} \sum_{n=1}^{\infty} \left\{ \frac{1}{E_2} \sin \mu_n \left[\cos \mu_n \left(\frac{R}{L}\frac{r}{L}\right) \right.\right.$$
$$\left.\left. - \frac{1}{\mu_n R/L} \sin \mu_n \left(\frac{R}{L} - \frac{r}{L}\right)\right] \exp\left[-\mu_n^2 \mathrm{Fo}\ \right]\right\} \left\{\mu_n + (-1)^n \alpha \sin \mu_n\right\}^{-1}, \tag{3}$$

$$c_2 - c^\infty = \frac{a(c_{01} - c_{02})}{2\pi r r_C} \sum_{n=1}^{\infty} \frac{\sin\mu_n \left[\frac{1}{E_2} \cos\mu_n - \frac{1}{E_1} \sin\mu_n \sin\mu_n \frac{r_C}{2L}\right]}{\mu_n + (-1)^n \alpha \sin\mu_n}$$
$$\times \left[\cos\mu_n \left(\frac{R}{L} - \frac{r}{L}\right) - \frac{1}{\mu_n R/L} \sin\mu_n \left(\frac{R}{L} - \frac{r}{L}\right)\right] \exp\left[-\mu_n^2 \mathrm{Fo}\ \right], \tag{4}$$

where

$$c^\infty = \frac{c_{01}(aL + V) + c_{02} V}{2V + aL}, \quad E_1 = \cos\mu_n \frac{R}{L} - \frac{1}{\mu_n R/L} \sin\mu_n \frac{R}{L},$$

$$E_2 = \cos\mu_n \left(\frac{R}{L} - \frac{r_C}{2L}\right) - \frac{1}{\mu_n R/L} \sin\mu_n \left(\frac{R}{L} - \frac{r_C}{2L}\right),$$

$$\alpha = \mu_n \frac{r_K}{2L} \operatorname{ctg} \mu_n \frac{r_C}{2L} + \frac{1}{E_1} \mu_n \frac{R}{L} \sin \mu_n \frac{R}{L}$$
$$+ \frac{1}{E_2}\left[\frac{r_C}{2R} \cos\mu_n \left(\frac{R}{L} - \frac{r_C}{2L}\right) - \mu_n \left(\frac{R}{L} - \frac{r_C}{2L}\right) \sin\mu_n \left(\frac{R}{L} - \frac{r_C}{2L}\right)\right];$$

μ_n is determined from the characteristic equation

$$\operatorname{tg}\mu_n = \frac{2E_1E_2 \sin\mu_n \frac{r_C}{2L}}{E_2^2 \sin^2\mu_n \frac{r_C}{2L} - E_1^2}. \tag{5}$$

These solutions describe the concentration distribution of the gas over the capillary length and along the flask radii. The investigator is most interested in the time relationship that applies to the average concentration in the vessels. After integration of (3) and (4) in limits from 0 to R we find the following expressions for the average concentrations:

$$\overline{c}_1 - c^\infty = -2\varepsilon \frac{L}{r_C}(c_{01} - c_{02}) \sum_{n=1}^{\infty} \frac{\frac{E_1}{E_2} \sin\mu_n \exp\left[-\mu_n^2 \mathrm{Fo}\right]}{\mu_n^2 \left[\mu_n + (-1)^n \alpha \sin\mu_n\right]}, \tag{6}$$

$$\overline{c}_2 - c^\infty = 2\varepsilon \frac{L}{r_C}(c_{01} - c_{02}) \sum_{n=1}^{\infty} \frac{\sin\mu_n \left[\frac{E_1}{E_2} \cos\mu_n - \sin\mu_n \sin\mu_n \frac{r_C}{2L}\right] \exp\left[-\mu_n^2 \mathrm{Fo}\right]}{\mu_n^2 \left[\mu_n + (-1)^n \alpha \sin\mu_n\right]}. \tag{7}$$

TABLE 1. Roots of the Characteristic Equation (5)

$R/L,\ r_c/L,\ \varepsilon$	μ_1	μ_2	μ_3
0,5; 0,01; $6\cdot10^{-4}$	0,03447	3,1113	6,2215
0,5; 0,05; 0,015	0,1692	3,0126	5,9830

TABLE 2. Time to Reach a Quasisteady State for Various Capillary Geometries

ε	Fo	t
$6\cdot10^{-4}$	0,15 (0,14)	30 (28)
0,015	0,51 (0,49)	102 (98)

Note: We have calculated t for $D = 0.5\cdot10^{-4}$ m^2/sec and $L^2 = 1$ m^2.

We bring (5) to a form convenient for analysis. It is simple to demonstrate that when $\varepsilon \ll 1$ even $\mu_1 \ll 1$. Expanding the right-hand member of (5) in powers of μ_1 and limiting ourselves to terms of the first order of smallness, we find

$$\operatorname{tg}\mu_1 \approx \frac{2\varepsilon}{\mu_1\left(1+\frac{r_c}{L}+\ldots\right)}. \tag{8}$$

It follows directly from (8) that for $\varepsilon \ll 1$

$$\mu_1^2 \approx \frac{2\varepsilon}{1+r_c/L}.$$

The remaining values of μ_n will be close to $(n-1)\pi$, $n = 2, 3, \ldots, \infty$.

It will be interesting to evaluate the magnitude of the average gas concentration in the flask as a ratio of the concentration at the end of the capillary. From (2) and (6) for the quasisteady state we find

$$\frac{\bar{c}_1-c^\infty}{c_L-c^\infty} = -\frac{E_1}{E_2}\,\frac{2\varepsilon}{\mu_1 r_c/L} \approx 1+\frac{r_c}{L}+\ldots.$$

If the geometric dimensions of the installation are known, the resulting expression thus makes it possible immediately to evaluate the error which we introduce into the concentration by neglecting the diffusion resistance of the flasks.

In order to carry out certain numerical calculations we found the three first roots of the characteristic equation (5) (see Table 1) for two values of the parameter ε.

With (2) we calculated the time to establish the quasisteady state in the assumption that the concentration in the middle of the capillary differs from the linear distribution by 1%. The results are shown in Table 2. The values of the Fourier number virtually coincide with the values (shown in parenthesis) calculated earlier from a formula derived without consideration of the concentration gradient in the vessels, and this formula [3], when $V_1 = V_2$, has the form

$$c-c^\infty = (c_{01}-c_{02})\sum_{n=1}^{\infty}\left\{\sin\alpha_n\left[\cos\alpha_n\left(1-\frac{x}{L}\right)-\frac{\alpha_n}{\varepsilon}\sin\alpha_n\left(1-\frac{x}{L}\right)\right]\exp[-\alpha_n^2\,\mathrm{Fo}]\right\}$$

$$\times\left\{\alpha_n+\sin\alpha_n\cos\alpha_n+\frac{\varepsilon}{\alpha_n}\sin^2\alpha_n\right\}^{-1}, \tag{9}$$

$$\operatorname{tg}\alpha_n = \frac{2\varepsilon\alpha_n}{\alpha_n^2-\varepsilon^2}. \tag{10}$$

Formula (9) can thus be used to evaluate the time needed to reach the quasisteady state in a given experimental installation. Moreover, it can be demonstrated that (9) can be reduced to solutions (6) and (7) (when $x = L$ and 0, respectively), if the roots derived from the characteristic equation (10) are replaced by the expression $\alpha_n^2/(1 + r_c/L)$. The average concentrations calculated from (9), with the corrected values of the roots, are in very good agreement with the quantities calculated according to the rigorous formula (7) for all of the values of the Fourier number (see Table 3). This markedly reduces the volume of calculation.

TABLE 3. The Average Concentration as a Function of the Dimensionless Time for Various Values of the Parameter ε

Fo	$\varepsilon = 6 \cdot 10^{-4}$, $c^{\infty} = 0{,}5002$			$\varepsilon = 0{,}015$, $c^{\infty} = 0{,}5037$		
	I	II	III	IV	V	VI
0,5	0,000517	0,000518	0,000295	0,0119	0,0120	0,0069
1	0,000774	0,000775	0,000591	0,0189	0,0190	0,0138
5	0,00315	0,00315	0,00295	0,0714	0,0712	0,0652
10	0,00608	0,00607	0,0587	0,1290	0,1287	0,1220
50	0,0290	0,0290	0,0287	0,3835	0,3833	0,3778
100	0,0561	0,0560	0,0557	0,4752	0,4750	0,4728
200	0,1059	0,1058	0,1052	0,5037	0,5037	0,5037
300	0,1501	0,1501	0,1492	0,5037	0,5037	0,5037
500	0,2242	0,2241	0,2230	0,5037	0,5037	0,5037

Note: I, IV) The value of c_2 from formula (7); II, V) from (9) ; III, VI) from (1).

The concentration values in columns 4 and 7 of Table 3 were calculated from (1) with consideration of the Maxwell–Rayleigh [4] end correction which reduces to the replacement of the actual length L by $L_{eff} = L + 1.64\, r_c$.

We see from the cited data that the transition process has a marked effect on the concentration distribution for times comparable to the time needed to establish the quasisteady state. The effect of the transition process on the accuracy with which the diffusion coefficients are measured will be a function, in the final analysis, of the relationship between the duration of the experiment and the time at which the quasisteady state sets in.

It also follows from these data that the correction for the end effect is quite substantial (see Table 3). The resulting solutions are therefore quite necessary for an exact analysis of the experimental data. The Maxwell–Rayleigh end correction apparently is not sufficiently correct, since in its calculation the finiteness of the volumes was not taken into consideration, nor the approximate spherical symmetry of the diffusion flux within the volumes. The importance of the correction factor for the diffusion in the volumes can be demonstrated with a specific example. Thus, when $\varepsilon = 6 \cdot 10^{-4}$ the diffusion coefficient must be reduced by approximately 1%, whereas when $\varepsilon = 0.015$ it must be reduced by ~10%, when the contents of the volumes are analyzed following a 10% change in their concentration.

These calculations also show that the Maxwell–Rayleigh correction is somewhat larger than necessary.

NOTATION

c_{01}, c_{02}, c_1, c_2, c^{∞}	are the molar concentrations of the gas in the flasks at the initial instant, at the instant t, in sec, and after complete mixing;
R, V_1, V_2	are, respectively, the radius and volumes of the flasks;
D	is the diffusion coefficient;
r_c, L, a	are, respectively, the radius, the length, and the area of the capillary cross section;
$\varepsilon = aL/V_1$	is the ratio of the capillary volume to the volume of flask 1;
$\mathrm{Fo} = Dt/L^2$	is the Fourier diffusion number.

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