# A SOLUTION OF THE DIFFUSION EQUATION

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A nonstationary solution is obtained for the diffusion equation in the case of two gas containers of arbitrary volume, connected by a capillary. If the volume of the capillary is regarded as negligibly small in comparison with the flask volumes, the solution turns into the formula derived by Ney and Armsteady, and as the volume of one of the flasks approaches infinity, the solution turns into the one derived by Frank-Kamenetskii.

To measure the coefficients of mutual diffusion in gases, we make extensive use of the method in which two pistons are connected to each other by means of a wide capillary. The experimental data are processed according to theoretical formulas in whose derivation it is assumed that the volume of the capillary is substantially smaller than the volumes containing the subject gases, while a concentration gradient exists only within the capillary and is a function exclusively of time. However, to evaluate the accuracy of the experimental data, as well as for experimental installations exhibiting a volume ratio that is none too small, it is desirable to have an exact solution to the problem. Such a solution would make it possible also to evaluate the time required to establish a quasi-steady state in these or similar experimental installations.

Let us examine the process of diffusion through a capillary connecting two vessels of volumes $V_1$ and $V_2$, which have been filled with a mixture of gases of differing composition at identical temperatures and pressures. As a result of diffusion, the concentrations of the gases in the flasks will even out with the passage of time. This problem was solved by Ney and Armstead [1] under the above-cited assumptions. Their solution has the form

$$\frac{c^\infty - c_2(t)}{c^\infty - c_{02}} = \exp\left[-\frac{Ds}{L}\,\frac{V_1+V_2}{V_1V_2}\,t\right]. \quad (1)$$

Assuming that the diffusion factor is independent of concentration, and that the diffusion is not complicated by hydrodynamic transport, the solution of the stated problem in the one-dimensional case reduces to the solution of the equation

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

having the following initial and boundary conditions:

1. $c = c_{01}$ when $t = 0$ and $0 < x \leqslant L$,

$c = c_{02}$ when $t = 0$ and $x = 0$;

2. $\dfrac{\partial c}{\partial t} = -\dfrac{Ds}{V_1}\,\dfrac{\partial c}{\partial x}$ when $x = L$;

3. $\dfrac{\partial c}{\partial t} = \dfrac{Ds}{V_2}\,\dfrac{\partial c}{\partial x}$ when $x = 0$.

Conditions 2 and 3 correspond to the fact that the concentration of the gas at the end of the tube is equal to the concentration in the flask. We will solve the problem by means of an operator. It has the form

$$c(x,\ t) - c^\infty = 2(c_{01} - c_{02}) \times$$
$$\times \sum_{n=1}^{\infty}\left(\sin\mu_n\left[\frac{V_2}{V_1+V_2}\cos\mu_n\left(1-\frac{x}{L}\right) - \frac{\mu_n V_2}{\varepsilon(V_1+V_2)}\sin\mu_n\left(1-\frac{x}{L}\right)\right]\right)\times$$
$$\times\left[\mu_n + \sin\mu_n\cos\mu_n + \frac{2\varepsilon V_1}{\mu_n(V_1+V_2)}\sin^2\mu_n\right]^{-1}$$
$$\times \exp\left[-(\mu_n/L)^2 Dt\right], \quad (3)$$

where

$$c^\infty = \frac{c_{01}(sL+V_1) + c_{02}V_2}{V_1+V_2+sL};$$

$\mu_n$ are the roots of the characteristic equation,

$$\operatorname{tg}\mu_n = \frac{\varepsilon\mu_n\,\dfrac{V_1+V_2}{V_2}}{\mu_n^2 - \varepsilon^2\,\dfrac{V_1}{V_2}}. \quad (4)$$

It would be interesting to investigate the case in which $V_2 \to \infty$, while the concentration of the subject gas when $x = 0$ is equal to zero at any instant of time. Under these conditions, solution (3) is written in the form

$$c(x,\ t) = 2c_{01}\sum_{n=1}^{\infty}\frac{\sin\mu_n\,\dfrac{x}{L}}{\mu_n + \sin\mu_n\cos\mu_n}\times$$
$$\times\exp\left[-\left(\frac{\mu_n}{L}\right)^2 Dt\right], \quad (5)$$

where

$$\operatorname{tg}\mu_n = \frac{\varepsilon}{\mu_n}.$$

Formula (5) may be used to analyze the experimental data for the diffusion of a gas from some volume through capillaries into an unbounded medium filled with another gas.

We will reduce the derived solution (3) to a form convenient for practical utilization. For this purpose we will assume that the volume of the capillary is considerably smaller than the volume of flask 1, i.e., $\varepsilon \ll 1$. Under this condition, neglecting terms with $\varepsilon^2$, we can write relation (4) in the form

$$\operatorname{tg}\mu_n \approx \frac{\varepsilon}{\mu_n}\,\frac{V_1+V_2}{V_2}. \tag{6}$$

For small values of $\varepsilon$, $\operatorname{tg}\mu_1$ can be replaced by $\mu_1$ so that from expression (6) we obtain

$$\mu_1^2 \approx \varepsilon\,\frac{V_1+V_2}{V_2}.$$

The remaining approximate values of $\mu_n$ can be found from the relationship

$$\mu_n = (n-1)\pi + \frac{\varepsilon}{\mu_n}\,\frac{V_1+V_2}{V_2} + \ldots \quad n = 2, 3 \ldots \infty.$$

The expression being summed in Eq. (3) is expanded into a series in powers of $\varepsilon$ and we will limit ourselves to terms of the first order of smallness. Having carried out the necessary calculations and having isolated the term with n = 1, we obtain

$$c(x,t) - c^\infty = (c_{01}-c_{02}) \times \left[\frac{x}{L} + \frac{1}{3}\,\frac{x}{L}\,\varepsilon\,\frac{V_1+V_2}{V_2} - \frac{x}{L}\,\varepsilon\,\frac{V_1}{V_2} + \left(\frac{x}{L}\right)^2 \frac{\varepsilon}{2}\,\frac{V_1}{V_2} - \left(\frac{x}{L}\right)^3 \frac{\varepsilon}{6}\,\frac{V_1+V_2}{V_2} + \frac{1}{3}\,\varepsilon\,\frac{V_1}{V_2} - \frac{V_1}{V_1+V_2}\right] \times$$
$$\times \exp\left[-\frac{Ds}{L}\,\frac{V_1+V_2}{V_1V_2}\,t\right] + (c_{01}-c_{02}) \times \sum_{k=1}^{\infty} \frac{2}{k\pi}\left[\sin k\pi\,\frac{x}{L} + \frac{\varepsilon}{k\pi}\left(\frac{x}{L}\,\frac{V_1+V_2}{V_2} - \frac{V_1}{V_2}\right) \times \cos k\pi\,\frac{x}{L} - \frac{2\varepsilon}{(k\pi)^2}\sin k\pi\,\frac{x}{L}\right] \times$$
$$\times \exp\left[-\left(\frac{k\pi}{L}\right)^2 Dt\right], \tag{7}$$

where k = n − 1.

If the concentration of the subject gas in flask 2 (when x = 0) is denoted $c_2(t)$, solution (7) assumes the form

$$c_2(t) - c^\infty = (c_{01}-c_{02})\left(\frac{1}{3}\,\varepsilon\,\frac{V_1}{V_2} - \frac{V_1}{V_1+V_2}\right) \times \exp\left[-\frac{Ds}{L}\,\frac{V_1+V_2}{V_1V_2}\,t\right] - (c_{01}-c_{02}) \times \sum_{k=1}^{\infty} \frac{2\varepsilon}{(k\pi)^2}\,\frac{V_1}{V_2} \exp\left[-\left(\frac{k\pi}{L}\right)^2 Dt\right]. \tag{8}$$

The first term in this equation describes the quasi-steady process, while all of the remaining terms after the summation sign are significant only at the initial instant of time and are associated with the establishment of the quasi-steady state in the capillary. If we treat the volume of the capillary as negligibly small in comparison with the volumes of the flasks and if we exclude those terms describing the transfer process, we obtain the familiar solution (1). Equation (2) makes it possible to evaluate the correction factors which can subsequently be used to refine the data derived from formula (1).

For the case in which $V_2 \to \infty$, while the concentration of the gas at the end of the capillary (when x = = 0) is equal to zero, for any instant of time from Eq. (7) we obtain

$$\frac{c_1(t)}{c_{01}} = \left(1 + \frac{\varepsilon}{6}\right)\exp\left[-\frac{Ds}{LV_1}\,t\right] + \sum_{k=1}^{\infty} (-1)^k \frac{2\varepsilon}{(k\pi)^2} \exp\left[-\left(\frac{k\pi}{L}\right)^2 Dt\right], \tag{9}$$

where $c_1(t)$ is the concentration of the subject gas in flask 1 (when x = L).

Solution (9) (approximate method) was derived by Frank-Kamenetskii [2] and is used to analyze the diffusion of one gas through a capillary into a volume filled with another gas. This solution is easily derived from the exact solution (5) by expansion into series in powers of $\varepsilon$, limiting ourselves to terms of the first order of smallness.

## NOTATION

$c_{02}$, $c_2(t)$, and $c^\infty$ are the concentrations of the gas under study in bulb 2 at time t and after final mixing; D is the diffusion coefficient; s is the capillary cross-section; L is the capillary length; $\varepsilon$ is the ratio of the volume of the capillary to the volume of bulb 1.

## REFERENCES

1. E. P. Ney and F. C. Armstead, Phys. Rev., **71**, no. 1, 14–19, 1947.

2. Ts. M. Kalibanova, P. V. Pomerantsev, and D. A. Frank Kamenetskii, ZhTF, vol. XII, no. 1, 1942.

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