300. *The Application of the Frictional-coefficient Formalism to Diffusion in Binary Mixtures of Neutral Substances.*

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The relation between the three diffusion coefficients of a binary mixture is shown to take the simple form, often termed the Hartley–Crank equation, if the frictional coefficients ζ_{11}, ζ_{22}, and ζ_{12} obey the relation $\zeta_{12}^2 = \zeta_{11}\zeta_{22}$. The statistical-mechanical theory of Kirkwood and Bearman is discussed in the light of this conclusion, and it is shown that the " Hartley–Crank " equation *may* be obeyed even when the excess volume of the mixture is non-zero. Some recent experimental results on diffusion in binary mixtures of gases and of liquids are reviewed, and the practical difficulties of obtaining satisfactory numerical values of frictional coefficients are discussed in the light of these.

TRANSPORT of material by diffusion in a binary non-electrolyte system is usually described in terms of three coefficients which can be derived directly from experimental measurements. They are the differential mutual diffusion coefficient D_{12}, which is a measure of the rate of interdiffusion of components 1 and 2, and the self-diffusion coefficients $D_1{}^*$ and $D_2{}^*$. Much effort has been spent on the analysis of the magnitudes of these coefficients and a number of more or less simplified models proposed. This diffusion-coefficient formalism, however, though the oldest, is by no means the only possible one; material flows can, for example, be expressed as linear combinations of the gradients of chemical potential in the system multiplied by Onsager coefficients, as in the usual form of non-equilibrium thermodynamics. Alternatively, the chemical potential gradients (grad μ_i) can be written as linear combinations of relative matter flows multiplied by " frictional coefficients." [1]

Several slightly different definitions have been used for these, *e.g.*, Klemm's coefficients [1c] (r_{ik}), and Laity's [1d] (ζ_{ik}), are defined as:

$$\text{grad}\ \mu_i = \sum_k r_{ik} N_k(\vec{v}_k - \vec{v}_i) = \sum_k \zeta_{ik} c_k(\vec{v}_k - \vec{v}_i), \tag{1}$$

where N_k, c_k, and $\vec{v}_k$ are, respectively, the molar fraction, the molarity, and the absolute velocity of component k. The differences between these definitions are slight and the choice of which to use in any instance is determined by convenience. Laity's formulation is used here. Symmetry arguments suggest that $\zeta_{ik} = \zeta_{ki}$, and, if this is so, there are $\frac{1}{2}j(j+1)$ independent coefficients in a j-component system. For a mixture of two neutral components it can be shown [1d] that

$$D_{12} = \frac{v\boldsymbol{R}T}{\zeta_{12}}\left(\frac{\partial \ln a_1}{\partial \ln N_1}\right)_{T,P}, \tag{2a}$$

$$D_1{}^* = \frac{v\boldsymbol{R}T}{(N_1\zeta_{11} + N_2\zeta_{12})}, \tag{2b}$$

and

$$D_2{}^* = \frac{v\boldsymbol{R}T}{(N_2\zeta_{22} + N_1\zeta_{12})}, \tag{2c}$$

where v is the mean molar volume. ζ_{11} is, strictly, the frictional coefficient between normal and labelled molecules of component 1. These equations do not involve any assumptions about the change in volume on mixing of the two components, except insofar as the coefficient D_{12} of (2a) requires to be identified with the experimental diffusion coefficient.[2]

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[1] (*a*) Onsager, *Ann. N.Y. Acad. Sci.*, 1945, **46**, 241; (*b*) Lamm, *J. Phys. Chem.*, 1957, **61**, 948; (*c*) Klemm, *Z. Naturforsch.*, 1953, **8a**, 397; (*d*) Laity, *J. Phys. Chem.*, 1959, **63**, 80; *J. Chem. Phys.*, 1959, **30**, 682.

[2] Tyrrell, " Diffusion and Heat Flow in Liquids," Butterworths Scientific Publns., London, 1961, Chap. 3.

If we write

$$D_{12}^{\mathrm{id.}} \equiv D_{12}\left(\frac{\partial \ln a_1}{\partial \ln N_1}\right)_{T,P}^{-1},$$

then equation (2) can be transformed into

$$D_{12}^{\mathrm{id.}}\left(2 - \frac{N_1\zeta_{11}D_1{}^* + N_2\zeta_{22}D_2{}^*}{\boldsymbol{R}T}\right) = N_2D_1{}^* + N_1D_2{}^*. \tag{3}$$

The question of the relation between the three diffusion coefficients of a binary system has had much attention, and a number of derivations of the following equation, frequently but not quite correctly referred to as the Hartley–Crank equation, have been proposed:[3]

$$D_{12}^{\mathrm{id.}} = N_2D_1{}^* + N_1D_2{}^*. \tag{4}$$

All these derivations involve unstated or physically obscure assumptions.[4] From the purely phenomenological point of view, (3) reduces to (4) if

$$N_2\zeta_{22}D_2{}^* + N_1\zeta_{11}D_1{}^* = v\boldsymbol{R}T,$$

a condition which, it is easy to show, is equivalent to the requirement that

$$\zeta_{11}\zeta_{22} = \zeta_{12}^2. \tag{5}$$

If $\zeta_{11}\zeta_{22} > \zeta_{12}^2$, then $D_{12}^{\mathrm{id.}} > N_2D_1{}^* + N_1D_2{}^*$, and *vice-versa.*

The statistical-mechanical theory of transport processes, developed by Kirkwood, employs frictional coefficients of the above form, defining them in terms of the equilibrium radial distribution function $g_{ij}^{2,0}$, and the variation of the pair-wise potential V_{ij} between molecules i and j with the magnitude r of the vector distance $\vec{r}$ separating them, as

$$\zeta_{ij} = \frac{1}{6}\int g_{ij}^{2,0}\frac{\mathrm{d}V_{ij}}{\mathrm{d}r}[\psi_{ij}^{(1)} + \psi_{ji}^{(1)}]\mathrm{d}^3\vec{r}$$

$\psi_{ij}^{(1)}$, $\psi_{ij}^{(1)}$ are scalar coefficients in a first-order expansion in spherical harmonics of the pair correlation function $g_{ij}^{2,1}$. With certain assumptions, Bearman[4,5] has shown that ratios of frictional coefficients can be expressed in terms of integrals which are, in principle, calculable, *e.g.*:

$$\frac{\zeta_{11}v\boldsymbol{R}T}{N_1\zeta_{11} + N_2\zeta_{12}} = \zeta_{11}D_1{}^* = \frac{1}{3}\int\frac{\mathrm{d}V_{11}}{\mathrm{d}r}(\psi_{11}^{(1)}D_1{}^*)g_{11}^{2,0}\mathrm{d}^3\vec{r} \equiv I_1. \tag{6}$$

A similar equation applies for $\zeta_{22}D_2{}^*$, and, from these, it follows that

$$\frac{\zeta_{11}\zeta_{22}}{\zeta_{12}^2} = \frac{1}{N_1N_2}\left[\frac{v\boldsymbol{R}T}{I_1} - N_1\right]\left[\frac{v\boldsymbol{R}T}{I_2} - N_2\right].$$

If equation (4) is to hold, the left-hand side of this equation must be unity, and hence

$$N_1(I_1 - v_1\boldsymbol{R}T) + N_2(I_2 - v_2\boldsymbol{R}T) = 0$$

or

$$\left.\begin{aligned} I_1 &= v_1\boldsymbol{R}T \\ I_2 &= v_2\boldsymbol{R}T \end{aligned}\right\} \tag{7}$$

and

v_1 and v_2 are the partial molar volumes of the components in the mixture. In general the integrals I_1 and I_2 are dependent on composition, but equation (7) limits their dependence to a particular form. Combination of (6) and (7) gives

$$\zeta_{12}/\zeta_{11} = \zeta_{22}/\zeta_{12} = v_2/v_1. \tag{8}$$

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[3] (*a*) Darkén, *Trans. Amer. Inst. Min.* (*Metall.*) *Engrs.*, 1948, **175**, 184; (*b*) Prager, *J. Chem. Phys.*, 1953, **21**, 1344; (*c*) Barrer, *J. Phys. Chem.*, 1957, **61**, 178; (*d*) Carman and Stein, *Trans. Faraday Soc.*, 1956, **52**, 619.

[4] See, *e.g.*, Bearman, *J. Phys. Chem.*, 1961, **65**, 1961.

[5] Bearman, *J. Chem. Phys.*, 1960, **32**, 1308.

This is consistent with condition (5) but cannot be deduced from a purely phenomenological theory. Furthermore, from (2) and (8),

$$D_1^*/D_2^* = v_2/v_1. \tag{9}$$

Equations (8) and (9) were derived by Bearman[5] who showed that I_1 and I_2 are independent of composition if (i) the radial distribution functions are independent of mole fraction at constant temperature and pressure and (ii) if there is no volume change on mixing. Expressions (8) and (9) then follow at once from (6). The present argument shows that equations such as (4), (8), and (9) *may* be obeyed even when a volume change does occur on mixing, provided that the appropriate partial molar volumes are used instead of molar volumes. Horrocks and McLaughlin[6] have calculated mutual diffusion coefficients for the system carbon tetrachloride–cyclohexane, using Bearman's equations, and claim that better agreement with experiment is obtained if partial molar volumes are used, though it must be admitted that the improvement in this particular case is small.

Frictional coefficients are also helpful in considering the recent data of Miller and Carman on gaseous mixtures.[7] They have shown that, for binary mixtures of krypton, carbon dioxide, and dichlorodifluoromethane with hydrogen, the heavier component being denoted by suffix 1, $1/D_1^*$ is a linear function of N_1. This confirmed the equation, based on kinetic theory,

$$1/D_1^* = N_1/(D_1^*)^\circ + N_2/D_{12}, \tag{10}$$

where $(D_1^*)^\circ$ is the self-diffusion coefficient in the pure component, since D_{12} is virtually independent of composition for gaseous mixtures. Since such mixtures are almost ideal, it follows from equation (2) that

$$1/D_1^* = N_1\zeta_{11}/v_1\boldsymbol{R}T + N_2/D_{12}$$

and

$$(D_1^*)^\circ = v_1^\circ\boldsymbol{R}T/\zeta_{11}^\circ. \tag{11}$$

If ζ_{11}/v_1 is independent of composition, equation (10) follows from equation (11); for these mixtures, this is almost equivalent to saying that ζ_{11} should be independent of composition. Miller and Carman have obtained self-diffusion coefficients for the heavier components and the mutual diffusion coefficients, but self-diffusion coefficients for hydrogen have not yet been obtained. There seems no reason why these should not also obey equation (10), and, if this proves to be so, ζ_{22} should be independent of concentration also. If both equations (4) and (10) are also to be obeyed simultaneously it is necessary that

$$(D_1^*)^\circ(D_2^*)^\circ = D_{12}^2. \tag{12}$$

This would permit the calculation of the self-diffusion of pure hydrogen from the existing data on mixtures. The results are shown:

CO_2 —H_2: 3·16 cm.^{2} sec.$^{-1}$
Kr —H_2: 4·55 cm.^{2} sec.$^{-1}$
CF_2Cl_2 —H_2: 3·62 cm.^{2} sec.$^{-1}$

and are much too high. At 288°K the diffusion coefficient of deuterium in hydrogen is 1·24 cm.^{2} sec.$^{-1}$, and at 273°K that of ortho- in para-hydrogen is 1·285 cm.^{2} sec.$^{-1}$.[8] Apparently equation (12), and hence also (4), cannot apply to these mixtures. This conclusion was reached by Miller and Carman, apparently solely on the grounds that equations (10) and (4) must always be incompatible, which is not the case.

These examples show the usefulness of the frictional-coefficient concept in the discussion of general questions. However, their numerical calculation for real systems is beset with difficulties. The most suitable liquid mixtures to test equations (4), (8), and (9) would be

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[6] Horrocks and McLaughlin, *Trans. Faraday Soc.*, 1962, **58**, 1357.
[7] Miller and Carman, *Trans. Faraday Soc.*, 1961, **57**, 2143.
[8] Jost, "Diffusion," Academic Press, New York, 1952, p. 430.

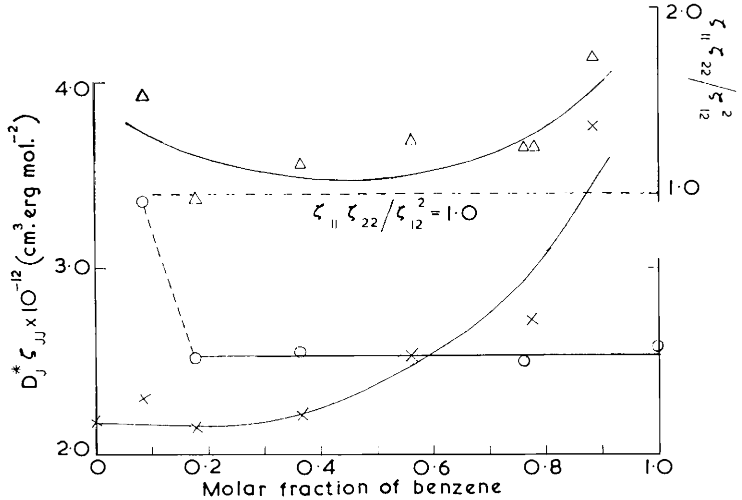
mixtures of liquefied rare gases, but data on these are only beginning to become available.[9] Complete diffusion studies have been carried out by Miller and Carman [10] on three mixtures, namely, bromobenzene–benzene, nitromethane–benzene, and nitromethane–carbon tetrachloride. The first of these obeys Raoult's law closely, though there is a small contraction in volume on mixing, while the other pairs are non-ideal. To judge from the graphs in the original papers these careful diffusion measurements show a variation on replicate experiments of never less than ±2%, and sometimes as much as ±8%. If the proportional errors in $D_{12}^{\mathrm{id.}}$ and D^* (that is, the ratio of the standard deviation to the mean magnitude) are assumed to be the same, and are denoted by P, the usual rule for combination of errors gives

$$(\sigma_{11}/\zeta_{11})^2 = \frac{(D_{12}^{\mathrm{id.}})^2 + (D_1^*)^2 N_2^2}{(D_{12}^{\mathrm{id.}} - D_1^* N_2)^2} \cdot P^2.$$

σ_{11}^2 is the variance of ζ_{11}. Since $D_{12}^{\mathrm{d.}}$ and D_1^* are of the same order of magnitude, a suitable approximate form of this is:

$$(\sigma_{11}/\zeta_{11})^2 = P^2(1 + N_2^2)/N_1^2.$$

This tends to infinity as N_1 approaches zero and, even at $N_1 = 0{\cdot}5$, (σ_{11}/ζ_{11}) is $5^{\frac{1}{2}}P$. It is tempting to adopt the variation of the ratio $(\zeta_{11}\zeta_{22}/\zeta_{12}^2)$ from unity as a measure of the departure of the system from the norm represented by equations (4), (8), and (9). However, the ratio of the standard deviation of this quantity to the magnitude of the ratio itself is, with the above assumptions,



System benzene (1)–bromobenzene (2) at 25°. Variation of certain frictional coefficient functions with concentration.

○, $D_1^*\zeta_{11}$ ×, $D_2^*\zeta_{22}$ (left-hand scale) △, $\zeta_{11}/\zeta_{22}/\zeta_{12}^2$ (right-hand scale).

$$\left[\frac{1 + N_2^2}{N_1^2} + \frac{1 + N_1^2}{N_2^2} + 4\right]^{\frac{1}{2}} P;$$

this reaches a minimum value of $3{\cdot}74P$ at $N = 0{\cdot}5$ and increases to infinity at either end of the concentration range. Thus, to obtain a satisfactory set of frictional coefficients it is essential to achieve a very high standard of precision in the measurement of the three diffusion coefficients. There is no doubt that such data are not at present available for any system. The Figure shows values of $D_1^*\zeta_{11}$, $D_2^*\zeta_{22}$, and $(\zeta_{11}\zeta_{22}/\zeta_{12}^2)$ calculated for benzene

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[9] Bearman, *J. Phys. Chem.*, 1962, **66**, 379.

[10] Miller and Carman, *Trans. Faraday Soc.*, 1959, **55**, 1831, 1838.

(1)-bromobenzene (2) mixtures from the graphs given in reference 10. The last quantity should be unity if equation (4) is obeyed strictly; over the region round $N = 0{\cdot}5$ where experimental errors have least influence it seems to be a little greater than this. $D_1{}^*\zeta_{11}$ is very constant except at $N_1 = 0{\cdot}1$ (the influence of experimental error is very large in this region), while $D_2{}^*\zeta_{22}$ seems to show a distinct rise as the bromobenzene becomes more dilute. Similar curves for the other systems studied by Miller and Carman have been calculated but show no very striking differences. The only possible conclusion is that, with existing data, the calculation of frictional coefficients is not a very profitable exercise. On the other hand, the examples in the earlier sections of this paper show that they can be of considerable use in general discussions of diffusion.

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