Equations for Calculations of Liquid Diffusivities from Measurements in Diaphragm Cells

BY F. A. L. DULLIEN * AND L. W. SHEMILT †

From the general equation for diffusion in a liquid binary system, new formulae have been derived which apply, regardless of volume change on mixing, to diffusion in a porous diaphragm cell. Calculations of differential diffusivities from integral values based on measurements from experiments using wide initial concentration differences may be made rigorously. Errors involved through the use of the traditional logarithmic or simple formula in the general case are computed. It is also shown that where the density of the solution is linear in the volume concentration, the general equation of diffusion reduces to Fick's first law, and the various formulae based upon the general equation reduce to the corresponding simple formulae.

NOTATION

a	constant coefficient in eqn. (3),
b	effective cross-sectional area for diffusion,
A	constant coefficient in eqn. (3),
D_A	apparent diffusivity obtained by applying the formulas (eqn. (38) and (40)) valid only for no volume changes on mixing to systems where volume changes occur on mixing,
$\bar{D}_{AB}$	space average diffusivity, defined in eqn. (16),
D_{AB}	true binary diffusivity (based on concentration as driving force),
$\bar{D}_{AB}^{*}$	apparent integral diffusivity obtained by using eqn. (40) in cases where volume changes occur on mixing,
I	quantity defined by eqn. (25),
K	quantity defined by eqn. (23),
L	effective pore length for diffusion in porous diaphragm,
n_A	unidirectional net mass flux of species A in binary system with respect to stationary axes (per unit area),
n_A^V	unidirectional pure mass diffusion flux of species A in binary system with respect to the volume centre of the system as frame of reference (per unit area)
r_{AB}	ratio of the magnitude of fluxes n_A and n_B,
R	quantity defined by eqn. (26),
V	total volume,
v_A	partial specific volume of species A in a binary system.
β	cell constant defined by eqn. (22),
$\bar{\beta}$	mean cell constant,
θ	time,
ρ	total mass density,
ρ_A	mass density (component concentration) of species A in binary system,
ρ_A^0	mass density of pure species A
ω_A	mass fraction of species A in binary system,
o, f (subscript)	quantities evaluated at the initial and final conditions, respectively,
', " (superscript)	quantities pertaining to the closed and the open half-cell, respectively,

* School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, U.S.A.
† Department of Chemical Engineering, University of New Brunswick, Fredericton, Canada.

† (superscript)   mean of the values of the quantity evaluated in the two cell-halves,

—— (above symbol)   mean of the values of the quantity evaluated at initial and final conditions,

—— (above symbol)   referring to diffusivity: space and time average of the quantity,

~ (above symbol)   referring to diffusivity: space average of the quantity,

A, B (subscript)   components A and B respectively.

1. INTRODUCTION

The diaphragm cell technique, first introduced by Northrop and Anson,[1] has been widely used as an experimental method utilizing Fick's first law to obtain diffusion coefficients in liquids.   The procedure is fundamentally a simple one whereby diffusion takes place through a porous diaphragm separating two cells in which the respective liquid concentrations are different to provide a driving force or potential difference.   The method has been discussed by several authors but most thoroughly by Gordon.[2]   Subsequently, among others, Stokes [3-5] has contributed substantially towards perfecting this technique.   However, the method has lacked a convenient and general procedure for computing the true differential diffusivities from the experimental integral values.   Although the use of small concentration differences can offset this difficulty to a large extent, it has often been pointed out (e.g., ref. (2), (6)), that for a given analytical error, the relative error in the value of the calculated diffusivity increases rapidly with decreasing initial concentration differences in the diffusion experiment.   A further difficulty in the way of using large concentration differences has been the accompanying volume changes which, if appreciable, as in a number of systems, introduce an unknown error in the value of the diffusivity.

These difficulties have been eliminated by the use of the general formulae announced by a preliminary report [9] and here derived and discussed in full.   The general formulae apply rigorously to binary liquid systems regardless of volume changes on diffusion.   Experimental work involving improved cell design and measurements on a non-ideal system is being published elsewhere.[10]

2. DERIVATION OF FICK'S FIRST LAW FROM THE MORE GENERAL EQUATION OF DIFFUSION

It has been shown [11] that for a binary system with components A and B, the flux of component A through a fixed plane (in a diffusion cell) can be given as

$$\eta_A = -\rho D_{AB}\frac{\partial \omega_A}{\partial x}+\omega_A(n_A+n_B). \tag{1}$$

The first term on the right-hand side of eqn. (1) gives the pure diffusional flux of A with the centre of mass as the frame of reference for diffusion.   The second member on the right gives the flux of A by bulk mass flow with respect to fixed axes as frame of reference.   The algebraic sum of the two fluxes gives the net flux of A with respect to fixed axes as frame of reference, even though the frame of reference for *diffusion* is the centre of mass movement.

Considering condensed systems only, if the mass density is constant,

$$n_A = -D_{AB}\frac{\partial \rho_A}{\partial x}. \tag{2}$$

Eqn. (2) is, of course, recognizable as Fick's first law.

The general eqn. (1) will also reduce to eqn. (2) if the restriction imposed is less

rigorous than above, and is simply that the overall mass density be linear in the component concentration ρ_A:

$$\rho = a + b\rho_A. \tag{3}$$

This restriction is identical to the condition of no volume change on mixing.[8]

The reduction of eqn. (1) to eqn. (2) with this restriction is facilitated by transforming eqn. (1) into a product form:

$$n_A\left[\frac{n_A - \omega_A(n_A + n_B)}{n_A}\right] = -\rho D_{AB}\frac{\partial \omega_A}{\partial x} \tag{4}$$

Using

$$\omega_A + \omega_B = 1, \tag{5}$$

and introducing

$$r_{BA} = \left|\frac{n_B}{n_A}\right| \overset{!}{=} -\frac{n_B}{n_A}, \tag{6}$$

into eqn. (4) gives the transformed form of eqn. (1):

$$n_A = -\rho D_{AB}(\omega_A r_{BA} + \omega_B)^{-1}\frac{\partial \omega_A}{\partial x}. \tag{7}$$

Eqn. (7) can be derived also from the same fundamental laws as provide the basis of eqn. (1).[8]

For the restriction of no volume change on mixing, it may be noted from an inspection of the physical situation that

$$r_{BA} = -\frac{d\rho_B}{d\rho_A} = 1 - \frac{d\rho}{d\rho_A}. \tag{8}$$

Also,

$$\rho d\omega_A = d\rho_A\left(1 - \omega_A\frac{d\rho}{d\rho_A}\right). \tag{9}$$

Introducing eqn. (8) and (9) into eqn. (7) gives eqn. (2) as desired.

It should be noted that, if the centre of mass movement is maintained as the frame of reference for diffusion, then eqn. (2) will give the pure diffusion flux of A only if ρ is constant, because, on diffusion, the centre of mass will move with respect to the fixed co-ordinate system whenever ρ varies with the composition. Eqn. (2) will rigorously, and also conveniently, give the pure diffusional flux of A in the fixed co-ordinate system as frame of reference.

This may be proved by introduction of the average volumetric flow rate (or, the volume centre of the system) as frame of reference for diffusion, when the pure diffusional flux of A with respect to this frame of reference can be shown [8] to be given by the following equation:

$$n_A^V = \frac{-v_B\rho^2}{v_A\rho_A + v_B\rho_B}D_{AB}\frac{\partial \omega_A}{\partial x}. \tag{10}$$

Eqn. (10) also reduces to Fick's first law, for the case of additive volumes, in the form of eqn. (2), by introduction of the following consistent equations:

$$v_A\rho_A + v_B\rho_B = 1, \tag{11}$$

$$v_B = 1/\rho_B^0, \tag{12}$$

and

$$d\omega_A = \frac{\left(1 - \dfrac{\rho_A^0 - \rho_B^0}{\rho_A^0}\right)\omega_A}{\rho}\, d\rho_A. \tag{13}$$

For no volume change on mixing, the volumetric flow rate as frame of reference will, of course, be identical with the fixed co-ordinate system.

3. DERIVATION OF EQUATIONS FOR LIQUID DIFFUSION COEFFICIENTS IN DIAPHRAGM CELLS

In this section, a formula based on eqn. (7) is derived for the purpose of computing diffusivities from diaphragm cell experiments based on a treatment similar to that given by Gordon,[2] who limited himself, however, to the additive volume case.

The schematic model of a diaphragm diffusion cell consists of two compartments, each containing a homogeneous mixture of different compositions, and a small section (the porous diaphragm) separating the two compartments. It is assumed that inside this section diffusion occurs by a molecular mechanism only. The boundaries between the small diffusion section of continuously varying composition and the bulk of the homogeneous solutions on both sides of it are assumed to be sharp. Either of the two compartments can be open while the other one is closed. All volume changes, if any, occurring on diffusion will be observable in the volume of the solution in the open compartment.

In order to facilitate the mathematical treatment, the assumption of space-constant diffusion fluxes is introduced. Barnes [12] has investigated the validity of this assumption under certain simplifying conditions. In the present work, this assumption was checked once more under more general conditions, necessitating numerical solution of the set of partial differential equations describing the physical situation. The results showed that under the usual working conditions this assumption does not introduce an error exceeding $0 \cdot 02\ \%$ in the value of D_{AB}.

The definition of uniform flux means that

$$n_A' = n_A'' = n_A. \tag{14}$$

Hence the right-hand side of eqn. (7) may be replaced by another expression equally constant but more convenient :

$$\rho D_{AB}(\omega_A r_{BA} + \omega_B)^{-1}\frac{\partial \omega_A}{\partial x} = {}^\dagger\rho\tilde{D}_{AB}(\omega_A^\dagger r_{BA} + \omega_B^\dagger)^{-1}\left(\frac{\omega_A'' - \omega_A'}{L}\right). \tag{15}$$

$\tilde{D}_{AB}$ is a space average diffusivity, the value of which is found by integrating eqn. (15) between the limits as defined by the conditions at the two faces of the diaphragm :

$$\tilde{D}_{AB} = \frac{\omega_A^\dagger r_{AB} + \omega_B^\dagger}{{}^\dagger\rho\,(\omega_A'' - \omega_A')}\int_{\omega_A'}^{\omega_A''}\frac{\rho D_{AB}}{\omega_A r_{BA} \cdot \,\,_B}d\omega_A. \tag{16}$$

Eqn. (16) is then the defining equation for $\tilde{D}_{AB}$.

Material balances are set up on the two compartments with allowance for the possibility of changing volume in the open compartment :

$$[-A{}^\dagger\rho\tilde{D}_{AB}(\omega_A^\dagger r_{BA} + \omega_B^\dagger)^{-1}]\frac{\omega_A'' - \omega_A'}{L} = \frac{d\rho_A'}{d\theta}V', \tag{17}$$

$$[A{}^\dagger\rho\tilde{D}_{AB}(\omega_A^\dagger r_{BA} + \omega_B^\dagger)^{-1}]\frac{\omega_A'' - \omega_A'}{L} = \frac{d(\rho_A''V'')}{d\theta}. \tag{18}$$

Adding eqn. (17) and (18),

$$-A\overset{\dagger}{\rho}\tilde{D}_{AB}(\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger})^{-1}\frac{\omega_A''-\omega_A'}{L}\left(\frac{1}{V''}+\frac{1}{V'}\right)d\theta - \rho_A''\frac{dV''}{V''}=d(\rho_A''-\rho_A')=d\Delta\rho_A. \tag{19}$$

From elementary definitions,

$$\overset{\dagger}{\rho}(\omega_A''-\omega_A') = \tfrac{1}{2}\Delta\rho_A + \tfrac{1}{2}(\rho'\omega_A''-\rho''\omega_A'). \tag{20}$$

Combining eqn. (19) and (20) and, after some rearrangements, dividing the resulting equation by $\Delta\rho_A$:

$$\frac{-\tilde{D}_{AB}A(\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger})^{-1}}{2L}\left[1+\frac{\rho'\omega_A''-\rho''\omega_A'}{\Delta\rho_A}\right]\left(\frac{1}{V''}+\frac{1}{V'}\right)d\theta + \frac{\rho_A''}{\Delta\rho_A}\frac{dV''}{V''} =$$
$$-d\ln(\Delta\rho_A). \tag{21}$$

Letting

$$\beta = \frac{A}{L}\left(\frac{1}{V'}+\frac{1}{V''}\right), \tag{22}$$

where β is usually referred to as the " cell factor " or the " cell constant ", and

$$K = \frac{\rho'\omega_A''-\rho''\omega_A'}{\Delta\rho_A}, \tag{23}$$

on integration from $\theta = 0$ to $\theta = \theta$, eqn. (21) becomes

$$\int_0^{\theta} \frac{-\tilde{D}_{AB}}{2}(\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger})^{-1}(1+K)d\theta = \frac{\ln R+I}{\beta}, \tag{24}$$

where

$$I = \int_{V_f''}^{V_0''} \frac{\rho_A''dV''}{\Delta\rho_A V''} \tag{25}$$

$$R = \frac{(\Delta\rho_A)_0}{(\Delta\rho_A)_f}, \tag{26}$$

and

$$\bar{\beta} = \frac{\beta_0+\beta_f}{2}. \tag{27}$$

It is convenient to define a space and time average diffusivity

$$\bar{D}_{AB}\left(\overline{\frac{1+K}{\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger}}}\right)\theta = \int_0^{\theta} \tilde{D}_{AB}\frac{1+K}{\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger}}d\theta. \tag{28}$$

Using eqn. (28), eqn. (24) can be rewritten as

$$\bar{D}_{AB} = -2\frac{\ln I+R}{\bar{\beta}\theta}\left(\frac{\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger}}{1+K}\right). \tag{29}$$

Eqn. (29) is the formula for computing D_{AB} from the experimental results.

For a relationship between $\tilde{D}_{AB}$ and $\bar{D}_{AB}$ that does not contain time, eqn. (21) can be rearranged and integrated:

$$\bar{\beta}\theta = \int_0^{f} \frac{d\ln(\Delta\rho_A)+\dfrac{\rho_A''dV''}{\Delta\rho_A V''}}{\dfrac{\tilde{D}_{AB}}{2}(\omega_A^{\dagger}r_{BA}+\omega_B^{\dagger})^{-1}(1+K)}. \tag{3 }$$

Comparing eqn. (30) with eqn. (29) gives the desired relationship:

$$\bar{D}_{AB} = -\int_0^f \left(d\ln(\Delta\rho_A) + \frac{\rho_A'' dV''}{\Delta\rho_A V''} \right) \frac{\overline{(\ln R + I)}}{\bar{D}_{AB}(1+K)} \frac{\overline{(\omega_A^\dagger r_{BA} + \omega_B^\dagger)/(1+K)}}{\bar{D}_{AB}(1+K)}. \tag{31}$$

For simplification, the term

$$\frac{\omega_A^\dagger r_{BA} + \omega_B^\dagger}{\bar{D}_{AB}(1+K)}$$

can be adequately approximated by its arithmetic mean.   Hence,

$$\bar{D}_{AB} = \left(\frac{\overline{\omega_A^\dagger r_{BA} + \omega_B^\dagger}}{\rho(\omega_A'' - \omega_A')} \right) \int_{\omega_A'}^{\omega_A''} \frac{\rho D_{AB}}{\omega_A r_{BA} + \omega_B} d\omega_A. \tag{32}$$

A more convenient alternative form of eqn. (31) is obtained by rearrangement along with use of eqn. (16):

$$\bar{D}_{AB} = \frac{2(\ln R + I)\left(\frac{\overline{\omega_A^\dagger r_{BA} + \omega_B^\dagger}}{1+K} \right)}{-\int_0^f \frac{\rho_A'' dV''}{F(\omega_A'',\omega_A')V''} - \int_0^f \frac{d(\Delta\rho_A)}{F(\omega_A'', \omega_A')}}, \tag{33}$$

where

$$F(\omega_A'', \omega_A') = \int_{\omega_A'}^{\omega_A''} \frac{\rho D_{AB}}{(\omega_A r_{BA} + \omega_B)} d\omega_A. \tag{34}$$

Either the rigorous eqn. (33) or the approximate eqn. (32) which saves computation time, can be used to compute $\bar{D}_{AB}$, if D_{AB} and ρ are known as functions of the composition.   The more usual problem of calculating D_{AB} from a series of values of $\bar{D}_{AB}$, involves some trial and error.

As shown earlier, for no volume change on mixing, the general equation, eqn. (7), reduces to Fick's first law.   It must follow that, in the same special case, eqn. (29) reduces to the simple logarithmic formula generally used for diaphragm-cell calculations.   For the condition of no volume change,

$$r_{BA} = -\rho_B^\circ/\rho_A^\circ, \tag{35}$$

and

$$\frac{\rho_B^\circ - \rho_A^\circ}{\rho_A^\circ} = \frac{\rho' - \rho''}{\Delta\rho_A}. \tag{36}$$

By elementary transformations and using eqn. (23) it can be shown that

$$(\omega_A^\dagger r_{BA} + \omega_B^\dagger) = (1+K)/2. \tag{37}$$

Since $dV'' = 0$ in this case, on comparing eqn. (37) with eqn. (24), (25), (28) and (29) we have

$$\ln R = -\beta \bar{D}_{AB}\theta, \tag{38}$$

which is the simple logarithmic formula.

Further, for the same imposition of the condition of no volume change on mixing, the general eqn. (32) should reduce to the well-known expression for integral diffusivity, based on Fick's law.   The condition by which eqn. (7) was reduced to eqn. (2) is equivalent to replacing the term under the integral sign in eqn. (32) by $D_{AB}d\rho_A$.

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By elementary transformation, using eqn. (23) and (37) it can be shown that

$$\frac{\omega_A^\dagger r_{BA} + \omega_B^\dagger}{\overset{\dagger}{\rho}(\omega_A'' - \omega_A')} = \frac{1}{\rho_A'' - \rho_A'}. \tag{39}$$

By virtue of eqn. (39), for the case of additive volumes, eqn. (32) finally can be written as follows:

$$\bar{D}_{AB} = \frac{1}{\bar{\rho}_A'' - \bar{\rho}_A'} \int_{\bar{\rho}_A'}^{\bar{\rho}_A''} D_{AB} d\rho_A. \tag{40}$$

Eqn. (40) is recognizable as the formula generally used to compute the differential diffusivities from the measured diaphragm-cell integral values.

4. DISCUSSION

The equations as derived in the previous section rigorously provide the true differential diffusivities from diaphragm-cell experiments regardless of the presence of volume changes on diffusion, i.e., in the general case. Under such conditions the simpler formulae in common use do not yield values for the diffusivity that are consistent with the requirements of theory. These inconsistencies may give rise to apparent differences between the values obtained for the differential diffusivities, depending on the concentration differences used in the diaphragm-cell experiments, on whether or not the concentrations of the one or the other component are used in the formulae, and on whether or not the compartment containing the more or the less concentrated solution is the one which is open during the diffusion experiment.

To estimate the correction introduced in a diffusion experiment involving a considerable concentration difference, calculations were made based on data obtained for the ethanol + water system. In a hypothetical diffusion experiment, pure water on one side of the diaphragm was considered to diffuse into a solution containing about 0·6 g/ml ethanol until the concentration difference dropped to about 75 % of the original value. Since in this experiment there is an appreciable volume change, eqn. (38) does not yield a true integral diffusivity $\overline{D}_{AB}$ but an apparent value which may be denoted by $\overline{D}_A$ (alcohol taken as component A). Similarly, eqn. (40) is not rigorously applicable and if used consistently with eqn. (38) to compute the differential diffusivities, the latter will be apparent values which may be denoted by D_A, or

$$\overline{D}_A = \frac{1}{\bar{\rho}_A'' - \bar{\rho}_A'} \int_{\bar{\rho}_A'}^{\bar{\rho}_A''} D_A d\rho_A. \tag{41}$$

Consistent use of eqn. (29) and (32) will, of course, give the true differential diffusivities D_{AB}.

Using available D_{AB} data,[10] and the known densities of the ethanol + water mixtures, the magnitudes of D_{AB} and D_A may be compared. The following quantities were calculated for the above hypothetical experiment:

$$\overline{D}_A \cdot \beta \cdot \theta = 0\cdot4355 \text{ (using eqn. (38))},$$
$$\overline{D}_{AB} \cdot \overline{\beta} \cdot \theta = 0\cdot4775 \text{ (using eqn. (29))},$$
$$\overline{D}_{AB} = 0\cdot632 \text{ (using eqn. (32))},$$
$$\overline{D}_{AB} = 0\cdot638 \text{ (using eqn. (33))},$$
$$\overline{D}_{AB} = 0\cdot588 \text{ (using eqn. (42))},$$
$$\Delta V'' = -0\cdot69 \text{ ml (using material balances)},$$
$$\beta/\bar{\beta} = 0\cdot9965.$$

The function D_{AB}^* is a quantity defined for this case of volume changes on mixing, but in terms of the special limited eqn. (40), as

$$\bar{D}_{AB}^{\bullet} = \frac{1}{\bar{\rho}_A'' - \bar{\rho}_A'} \int_{\bar{\rho}_A'}^{\bar{\rho}_A''} D_{AB} d\rho_A. \tag{42}$$

Relative values are obtained from the above data as

$$r = \bar{D}_{AB}/\bar{D}_A = 1 \cdot 092$$

and

$$q = \bar{D}_{AB}/\bar{D}_{AB}^{\bullet} = 1 \cdot 075$$

Hence

$$r/q = \bar{D}_{AB}^{\bullet}/\bar{D}_A = 1 \cdot 016.$$

A comparison of eqn. (41) and (42) then gives

$$1 \cdot 016 \int_{\bar{\rho}_A'}^{\bar{\rho}_A''} D_A d\rho_A = \int_{\bar{\rho}_A'}^{\bar{\rho}_A''} D_{AB} d\rho_A. \tag{43}$$

Differentiating eqn. (43) on both sides with respect to the upper limit of integration,

$$1 \cdot 016 \, D_A(\bar{\rho}_A'') = D_{AB}(\bar{\rho}_A''). \tag{44}$$

The correction introduced for this particular case is thus less than 2 % in the value of the differential diffusivity at $\bar{\rho}_A''$.

Denoting by D_B the apparent value obtained by eqn. (38) for the diffusivity of component B where there are volume changes on mixing, it may similarly be calculated that

$$\bar{D}_B/\bar{D}_A = 1 \cdot 023. \tag{45}$$

It is also of some interest to note that the difference between the values obtained for $\bar{D}_{AB}$ by eqn. (32) and (33) amounts to almost 1 % in the example considered here. Although this can be considered a rather extreme case owing to the very strong lack of symmetry in the D_{AB} against concentration relationship, Gordon's claim [2] that this type of an approximation should not involve an error exceeding 0·02 % in most practical cases seems incorrect.

The conclusion may now be drawn that no reason seems to exist for not using large concentration differences in diaphragm diffusion-cell experiments through fear of the errors introduced by volume changes on diffusion.* In the first place, general but rigorous equations can be used to compute diffusivities under such conditions. Further, the possible error introduced into these calculations if the traditional simple equations are used was found to be small. Partial self-cancellation of the various correction terms in the more general equations derived above, make the net correction in the value of the differential diffusivity very much less than one would expect on the basis of the change in volume in the open compartment only.

Diaphragm diffusion-cell experiments aimed at obtaining diffusivity data extending over an entire range of concentrations can therefore be adequately conducted by allowing pure component A mutually to diffuse with a series of solutions ranging

* Hammond and Stokes [7] made a step in this direction in their work on the ethanol+water system but, to avoid what they considered excessive volume changes, they divided the complete concentration range into three parts. This resulted in an unnecessary magnification of their analytical errors and in added complications in fitting the adjacent regions.

in composition from pure component B to some intermediate value, and, in a second series, pure component B mutually to diffuse with a series of solutions the compositions of which cover the remaining portion of the concentration range. From the integral diffusivities obtained in these experiments, the corresponding differential values can be obtained by a modification of the graphical procedure introduced by Stokes,[3] which is discussed elsewhere in a report on actual experimental results.[10] An alternative procedure might use differentiation of the integrals appearing in the expressions for the integral diffusivities with respect to the upper limit of integration. In that case, small corrections would have to be made at the " pure component end " so as to adjust the integrals to the same lower limit of integration.

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