THEORY OF THE DETERMINATION OF DIFFUSION COEFFICIENTS BY THE ONE-COMPARTMENT DIAFRAGM CELL METHOD

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The problem of diffusion in a one-compartment cell, where a horizontal diafragm separates a solution of known concentration from one whose concentration is kept constant, was solved under the assumption of a pseudostationary state. Approximate equations were obtained for the calculation of the mean concentration at which the experimental value of the diffusion coefficient is equal to the actual one. By solving the second Fick's law for this case it was shown that the time of attainment of the pseudostationary state need not be considered in the calculations, especially when the duration of the diffusion measurement and calibration is inversely proportional to the corresponding diffusion coefficients.

The diafragm method is most often used in the determination of diffusion coefficients in binary liquid systems[1,2].

In the classical setup according to Stokes[3], the diffusion takes place in a diafragm which separates the diffusion cell into two parts filled with solutions differing in their concentration. The diffusion coefficient can be calculated from the time changes of the concentrations if the so-called constant of the diffusion cell is known. This geometric parameter is obtained by calibration with a solution of a known diffusion coefficient. Substantial contributions to the theory of the diafragm method were made by Barnes[4] (general solution for diffusion in the diafragm at a constant diffusion coefficient and zero volume changes during mixing), Gordon[5] (solution for diffusion in the diafragm assuming a pseudostationary state, the diffusion coefficient depending on the concentration, and zero volume changes during mixing), and Robinson and coworkers[6] (general solution for diffusion through the diafragm assuming only a pseudostationary state). The latter two methods of calculation are used in the determination of diffusion coefficients depending on concentration. Mills and coworkers[7] showed on the basis of the results of Barnes[4] and Holmes[8] that the preliminary period necessary to attain a pseudostationary state can be neglected in the calculations if the same procedure is used both in calibrating the diffusion cell, and in the diffusion measurement proper.

For the determination of diffusion coefficients, also a diffusion cell with one compartment can be used, where a horizontal diafragm separates the solution of a known concentration from one whose concentration is kept constant. In this setup, the classical procedure with a preliminary period cannot be used[9] unless the diafragm is very thin or the concentration changes are recorded continually[10-13].

The subject of the present work is the theory of the diafragm method with a one--compartment diffusion cell. After introducing general equations, the problem

of diffusion in the diafragm is solved for the most general case under the only assumption of a pseudostationary state and the results following from additional assumptions are discussed. The theory of a simplified diafragm method applied to a diffusion cell with one compartment is derived in another chapter.

THEORETICAL

General Equations

The mathematical model of the one-compartment diffusion cell is based on similar assumptions as with the classical Stokes' two-compartment cell[3,5,6]. The first Fick's law for one-dimensional binary diffusion in liquids[14] (subscript 1 refers to the solvent, 2 to the solute) reads

$$J_i = -D \, \partial c_i / \partial z , \quad i = 1, 2 , \qquad (1)$$

where D denotes binary diffusion coefficient, which depends generally on the solute concentration c_2. The molar diffusion flux of species i is defined as

$$J_i = c_i(v_i - v), \quad i = 1, 2 , \qquad (2)$$

where v_i is the velocity of species i of molar concentration c_i and v means volume average velocity defined as

$$v = c_1 \overline{V}_1 v_1 + c_2 \overline{V}_2 v_2 , \qquad (3)$$

$\overline{V}_1$ and $\overline{V}_2$ are partial molar volumes of species 1 and 2. We have obviously

$$c_1 \overline{V}_1 + c_2 \overline{V}_2 = 1 \qquad (4)$$

and by using the Gibbs-Duhem relation ($c_1 \, d\overline{V}_1 + c_2 \, d\overline{V}_2 = 0$)

$$\overline{V}_1 \, dc_1 + \overline{V}_2 \, dc_2 = 0 , \qquad (5)$$

whence

$$J_1 \overline{V}_1 + J_2 \overline{V}_2 = 0 . \qquad (6)$$

From the above equations we obtain the flux of species 2 in the diafragm:

$$c_2 v_2 = -\{D/[1 - c_2 \overline{V}_1 (\overline{V}_2/\overline{V}_1 + c_1 v_1/c_2 v_2)]\} \, \partial c_2 / \partial z . \qquad (7)$$

The diafragm has an effective cross section s, effective thickness l and volume

$$V''' = sl. \tag{8}$$

The diafragm closes the compartment (') of constant volume V' with concentrations c_1' and c_2' which are functions only of time and separates it from the external solution of volume V'' (compartment ('')) with constant concentrations c_1'' and c_2''. This can be achieved, e.g., by choosing $V'' \gg V'$ so that the time changes of c_1'' and c_2'' are negligible. The positive z coordinate is oriented from the compartment (') toward ('') perpendicular to the diafragm. The mass balance of species 1 and 2 in the compartment (') leads to the relation

$$-\mathrm{d}(c_i' V')/\mathrm{d}t = s\, c_i' v_i', \quad i = 1, 2, \tag{9}$$

where t denotes time and v_i' velocities of the components on the interface between the diafragm and the compartment (').

The general solution of this problem, i.e., of the differential equations obtained by introducing the constitutive equations (1) and (7) into the continuity equations for species in the diafragm

$$\partial c_i/\partial t + \partial(v_i c_i)/\partial z = 0, \quad i = 1, 2, \tag{10}$$

is not known. Therefore, we restrict ourselves to two special cases discussed below.

Theory Assuming a Pseudostationary State

This assumption enables to find a solution for the most general case, where the diffusion coefficients are dependent on the concentration and the volume changes during mixing are accounted for[5,6].

The diafragm and the compartment (') are filled with a solution of an equal concentration and during a preliminary period a pseudostationary state is reached in the diafragm, i.e., the concentration distribution in the diafragm is practically independent of time. A rapid attainment of this state is facilitated by a suitable construction of the diffusion cell as will be shown later. According to Eq. (10), the fluxes $c_i v_i$ with respect to the cell are practically independent of the coordinate z in the diafragm and the pseudostationary state can be defined so that the species fluxes $c_i v_i$ ($i = 1, 2$) are independent of the position, z, in the diafragm[6]. Since the volume of the compartment (') is constant,

$$\mathrm{d}V'/\mathrm{d}t = 0, \tag{11}$$

Eq. (5) for this compartment takes the form

$$\overline{V}_1' \, dc_1'/dt + V_2' \, dc_2'/dt = 0 \,, \tag{12}$$

where $\overline{V}_1'$ and $\overline{V}_2'$ are partial molar volumes of species 1 and 2 in the compartment (').

By combining Eqs (9), (11) and (12) we obtain

$$c_1' v_1'/c_2' v_2' = -\overline{V}_2'/\overline{V}_1' = c_1 v_1/c_2 v_2 \,, \tag{13}$$

where the second equality follows from the definition of the pseudostationary state for an arbitrary position in the diafragm. By combining Eqs (7) and (13) for the solute $(i = 2)$ we obtain

$$c_2 v_2 = -D(c_2)/[1 - G(c_2, c_2')] \, \partial c_2/\partial z \,, \tag{14}$$

where the function G is defined as

$$G(c_2, c_2') = c_2 \overline{V}_1 (\overline{V}_2/\overline{V}_1 - \overline{V}_2'/\overline{V}_1') \tag{15}$$

and can be obtained from the known dependence of the partial molar volumes on the concentration.

For a pseudostationary state, we can define the following function independent of the coordinate:

$$\overline{D} = -c_2 v_2 l/(c_2'' - c_2') \,. \tag{16}$$

On introducing Eq. (16) into (14) we obtain a differential equation which can be after separation of variables integrated from $z = 0$ to $z = 1$ to give

$$\overline{D} = (c_2'' - c_2')^{-1} \int_{c_1'}^{c_2''} D(c_2)/[1 - G(c_2, c_2')] \, dc_2 \,. \tag{17}$$

On the other hand, introducing Eq. (16) into (9) for $i = 2$ and considering V' and c_2'' constant we obtain after rearrangement the so-called logarithmic formula of the diafragm method in the differential form:

$$-d \ln (c_2' - c_2'')/dt = \beta \overline{D} \,, \tag{18}$$

where the cell constant β is defined by

$$\beta = s/lV' \tag{19}$$

and it depends only on the geometry of the diffusion cell with one compartment. It should be noted that with a two-compartment diffusion cell β is not constant since it depends also on V'' which can change during the measurement[6].

The resulting Eqs (17) and (18) can be used in determining diffusion coefficients in a one-compartment diffusion cell in a pseudostationary state. The dependence of c_2' on time is obtained by continual analysis, c_2'' is known, and from Eq. (18) the function $\bar{D}(c_2', c_2'')$ is found, from which, e.g., by solving integral Eq. (17) numerically the values of $D(c_2)$ are obtained (provided that the function (15) is known for the system under study, or an iteration method can be used which will be described below. The necessary constant β can be determined analogously by an inverse procedure from the measurement of a system for which the diffusion coefficient as a function of the concentration, $D(c_2)$, and the function (15) are known.

It is, however, a more common case that the continual analysis cannot be used and only the concentrations $(c_2')_0$ at the beginning of the measurement at time t_0 and $(c_2')_f$ at the end at time t_f together with $c_2'' = $ const. are known. From these data the value of $\bar{D}$ defined as

$$\bar{D} = [1/\beta(t_f - t_0)] \ln [(\Delta c')_0/(\Delta c')_f] \tag{20}$$

can be obtained, where

$$(\Delta c')_0 = (c_2')_0 - c_2'', \quad (\Delta c')_f = (c_2')_f - c_2''. \tag{21), (22)}$$

To obtain a relation between $\bar{D}$ and the diffusion coefficient $D(c_2)$, we define

$$\Delta c = c_2 - c_2'' \tag{23}$$

analogously to the preceding equations, and the dependence of D on the concentration can be written in the form

$$D(c_2) = D(c_2'') [(1 + f(\Delta c)] , \tag{24}$$

where $f(0) = 0$. We now define a function, $F(\Delta c', c_2'')$ as

$$1/[1 + F(\Delta c', c_2'')] = (1/\Delta c') \int_{c_2''}^{c_2'} \{[1 + f(c_2 - c_2'')]/[1 - G(c_2, c_2')]\} \, dc_2 \tag{25}$$

where, analogously to Eq. (23)

$$\Delta c' = c_2' - c_2'' . \tag{26}$$

From Eqs (25), (24) and (17) follows

$$D(c_2'')/\bar{D} = 1 + F(\Delta c', c_2''), \tag{27}$$

which we introduce into Eq. (18) and after separation of variables and integration from $(\Delta c')_0$ to $(\Delta c')_f$ with respect to Eq. (20) obtain

$$\tilde{D} = D(c_2'') + [1/\beta(t_f - t_0)] \int_{(\Delta c')_0}^{(\Delta c')_f} [F(\Delta c', c_2'')/\Delta c'] \, \mathrm{d} \, \Delta c' . \tag{28}$$

From the measurement of the dependence of $\tilde{D}$ on $(c_2'')_0$ and $(c_2'')_f$ at $c_2'' = \mathrm{const.}$ according to Eq. (20) the dependence of D on c_2 can be obtained by an iteration method[5,6] consisting in the determination of such values of c_2 at which $D = \tilde{D}$. The constant β can be found from the measurement of a system where the dependence of D on c_2 together with the function G is known, since $\tilde{D}$ can be calculated from Eqs (24), (25) and (28), and $\tilde{D}\beta$ can be found experimentally with the aid of Eq. (20).

The given problem is simplified if the volume changes during mixing are negligible. In this case the partial molar volumes of the components are independent of the concentration and according to Eq. (15) $G = 0$. In the case of a pseudostationary state, even a weaker assumption is sufficient, namely that the ratio of partial molar volumes of both components is independent of their concentration in the studied interval $\langle c_2''; (c_2'')_0 \rangle$. Then $\bar{D}$ is the integral diffusion coefficient and can be determined directly from Eq. (18) on the basis of a diffusion measurement with continual analysis.

Another simplification of the calculation is an approximation of Eq. (26) proposed by Gordon[5], namely (compare Eqs (21) and (22))

$$\Delta c' = \Delta c_m' = \tfrac{1}{2}[(\Delta c')_f + (\Delta c')_0] . \tag{29}$$

In this case, $F = F(\Delta c_m') = \mathrm{const.}$ and we obtain from Eqs (20), (25), (27), and (28)

$$\tilde{D} = D(c_2'') \left[1 + (1/\Delta c_m') \int_0^{\Delta c'_m} f(\Delta c) \, \mathrm{d} \, \Delta c \right], \tag{30}$$

whereby the iteration process is considerably simplified.

However, we shall show how the iteration process can be eliminated and still useful results obtained. First we shall neglect the volume changes during mixing ($G = 0$).

If the diffusion coefficient does not depend on the concentration, then

$$D = \bar{D} = \tilde{D} , \tag{31}$$

since the functions f and F are identically equal to zero.

If we assume that in the concentration interval $\langle c_2''; (c_2')_0 \rangle$ $D(c_2)$ is a linear function of c_2

$$D(c_2) = D'' + b(c_2 - c_2''),\tag{32}$$

where $D'' = D(c_2'')$ and b is a constant, then (with $G = 0$) it follows from Eq. (17) that

$$\bar{D}(c_2', c_2'') = \tfrac{1}{2} D(c_2' + c_2'').\tag{33}$$

This means that by the measurement with a continual analysis we obtain with the use of Eq. (18) the diffusion coefficient corresponding to a mean concentration $\tfrac{1}{2}(c_2' + c_2'')$. In this case we obtain from Eqs (25) and (28)

$$\bar{D} = D'' - [1/\beta(t_f - t_0)] \ln \{[1 + (\Delta c')_f \, b/2D'']/[1 + (\Delta c')_0 \, b/2D'']\}.\tag{34}$$

From this equation we obtain an approximate expression for the calculation of the mean concentration, c_s, at which the experimental $\bar{D}$ value is equal to D:

$$\bar{D} = D(c_s) = D'' + b(c_s - c_2'').\tag{35}$$

On introducing Eq. (35) into (34) and considering (20) we obtain after rearrangement

$$c_s = c_2'' + (D''/b) \ln (D_f/D_0) \{\ln [(\Delta c')_f/(\Delta c')_0] - \ln (D_f/D_0)\}^{-1},\tag{36}$$

where

$$D_f = \tfrac{1}{2} D[(c_2')_f + c_2''], \quad D_0 = \tfrac{1}{2} D[(c_2')_0 + c_2''].\tag{37}$$

Assuming that D_0 does not differ too much from D_f, we can use the following approximation:

$$\ln (D_f/D_0) \approx (b/2D'') [(c_2')_f - (c_2')_0] [1 - (b/D'')(c_M - c_2'')],\tag{38}$$

where

$$c_M = \tfrac{1}{2}(D_f + D_0).\tag{39}$$

On introducing Eq. (38) into (36) we obtain the result

$$c_s \approx c_2'' + [(c_2')_f - (c_2')_0]/2 \ln ([\Delta c_f']/(\Delta c')_0),\tag{40}$$

which approximates the sought concentration c_s at which the value of $\bar{D}$ is equal to

to the diffusion coefficient D. If the diffusion measurement does not last too long, we can expand the logarithm in Eq. (40) into series to obtain

$$c_s \approx c_M . \tag{41}$$

It should be noted that with the use of Eq. (30) we obtain for the case of the linear dependence of D on concentration (32) also Eq. (41).

The mentioned relations were derived under the assumption that a pseudostationary state is attained, to which the values of t_0 and $(c_2')_0$ are assigned. The determination of these quantities is difficult especially in a one-compartment diffusion cell. As mentioned in the introductory part, this difficulty can be overcome by using the simplified diafragm method[7].

Theory of the Simplified Diafragm Method

We shall apply the idea of the simplified diafragm method[7] to a one-compartment diffusion cell. As will be apparent from what follows, we need not consider the time of attainment of the pseudostationary state since we compensate the error thus formed by the same manner of filling the diffusion cell during both the calibration and the measurement proper. To this end we need to know the exact solution of the problem of diffusion through the diafragm, which is possible only for a constant diffusion coefficient and zero reference velocity by the method according to Barnes[4]. This will obviously be a good approximation if the diffusion coefficient is only little variable in the concentration range under study and the volume changes during mixing are small.

At the beginning of the measurement or calibration at $t = 0$, the diffusion cell of volume V' with a fritted glass disc of volume V''' is filled with the solution of concentration $(c_2')_{00}$ and dipped in a bath of volume V'' with a constant concentration c_2''. First we shall show that the assumption of zero reference velocity is practically fulfilled. On deriving Eq. (9), multiplying by $\overline{V}_i$, summing over $i = 1, 2$ and using Eqs (3), (4) and (12) we obtain

$$dV'/dt = sv' , \tag{42}$$

where v' is the volume average velocity v, defined by Eq. (3), at a volume V'.

With respect to Eq. (11) we have

$$v' = 0 , \tag{43}$$

i.e., the reference velocity at the surface of the diafragm connected with a closed volume V' is equal to zero.

The change of the reference velocity with height can be found by differentiating Eq. (3) with respect to z and using Eqs (1)–(6):

$$\partial v/\partial z = -(D/c_1\overline{V}_1)(\partial c_2/\partial z)^2 \, \partial \overline{V}_2/\partial c_2 . \qquad (44)$$

It is apparent from this equation that the reference velocity does not change with height as long as the partial molar volumes of the components are independent of the concentration (no volume changes during mixing), and with this assumption the volume average velocity is according to Eq. (43) equal to zero throughout in the diafragm.

The diffusion flux (2) is thereby reduced to the flux with respect to the apparatus, $c_i v_i$, and we have

$$c_2 v_2 = -D \, \partial c_2/\partial z . \qquad (45)$$

By introducing this equation into (10) with the assumption of a constant diffusion coefficient, the given problem is reduced to the second Fick's law

$$\partial c_2/\partial t = D \, \partial^2 c_2/\partial z^2 , \qquad (46)$$

which with regard to the mentioned manner of filling the diffusion cell is to be solved with the following boundary and initial conditions:

$$t \geqq 0 \quad c_2(0, t) = c_2'(t), \quad c_2(1, t) = c_2'' = \text{const.} ,$$

$$0 \leqq z \leqq 1 : \quad c_2(z, 0) = (c_2')_{00} . \qquad (47)$$

The diafragm surface contacting the volume V' corresponds to $z = 0$, that contacting V'' to $z = 1$; the measurement (or calibration) begins at $t = 0$.

The obtained solution $c_2(z, t)$ is introduced into the balance equation obtained from Eqs (9) and (46):

$$\mathrm{d}c_2'/\mathrm{d}t = D(s/V')(\partial c_2/\partial z)_{z=0} , \qquad (48)$$

whereby the following equation is obtained, which expresses the molar concentration c_2' in the diffusion cell as a function of time and the cell geometry:

$$c_2' = c_2'' + [(c_2')_{00} - c_2''] \{(1 + \lambda/6 - 7\lambda^2/120 + \ldots) \exp[-\beta D t(1 - \lambda/3 +$$
$$+ 4\lambda^2/45 + \ldots)] + \sum_{i=1}^{\infty} [(-1)^i \, 2\lambda/i^2\pi^2] \, (1 - 3\lambda/i^2\pi^2 + \ldots) .$$
$$. \exp[-\beta D t(i^2\pi^2 + 2\lambda - (\lambda^2/i^2\pi^2) + \ldots)/\lambda] \} . \qquad (49)$$

Here the quantity β is defined by Eq. (19), and

$$\lambda = V'''/V' \tag{50}$$

is a parameter whose value is small owing to the common condition of the cell construction, $V' \gg V'''$. The derivation of the above equation, analogous to the Barnes' work[4], was given in detail elsewhere[9].

The sum in Eq. (49) converges rapidly to zero, so that its value becomes negligible at a time t_0 which corresponds to the attainment of the pseudostationary state. At this state, indeed, Eq. (49) takes after neglecting the terms with λ^2 and rearrangement the form

$$\ln\left[(\Delta c')_0/(\Delta c')_f\right] = \bar{\beta}D(t_f - t_0), \tag{51}$$

where

$$\bar{\beta} = \beta(1 - \lambda/3) \tag{52}$$

and β is defined by Eq. (19). The time values of t_0 and t_f correspond to the concentrations $(c_2')_0$ and $(c_2')_f$; $(\Delta c')_0$ and $(\Delta c')_f$ are defined by Eqs (21) and (22). Eq. (51) is practically identical with (20) for a constant diffusion coefficient and zero reference velocity. The difference due to the factor of $(1 - \lambda/3)$ in (52) is not important since $\bar{\beta}$ or β is determined experimentally by calibration of the diffusion cell. For a sufficiently long time of the diffusion $(t_f > t_0)$, it is possible to write Eq. (49) after neglecting the whole sum and the terms with λ^2 in the form

$$D = (1/\bar{\beta}t_f)\ln\left[(\Delta c')_{00}/(\Delta c')_f\right] + \ln(1 + \lambda/6)/\bar{\beta}t_f, \tag{53}$$

where

$$(\Delta c')_{00} = (c_2')_{00} - c_2''. \tag{54}$$

This equation enables to use the simplified diafragm method for a diffusion cell with one compartment. It is analogous to that derived by Holmes[8] and Mills with coworkers[7] for the calculation of D in the simplified diafragm method with a two-compartment diffusion cell.

Eq. (53) can be in the first approximation rewritten in the form

$$D = (1/\bar{\beta}t_f)\ln\left[(\Delta c')_{00}/(\Delta c')_f\right] + \lambda/6\bar{\beta}t_f. \tag{55}$$

The last term represents a correction for the case where the diffusion measurement commences from the beginning of the experiment at $t = 0$. (Compare with Eq. (51).)

Eq. (55) shows that the logarithmic formula of the diafragm method can be used in the simplified diafragm method when, *e.g.*, the following procedure is observed:

a) The diffusion measurement is carried out for such a long time that the correction term in Eq. (55) is negligible. For example, at the optimum time of diffusion (calculated analogously as in ref.[6] for a one-compartment diffusion cell) neglecting of the correction term in (55) results in an error lying, as a rule, within the limits of error of the determination of diffusion coefficients by the diafragm method.

b) The time of the diffusion measurement and calibration is chosen inversely proportional to the ratio of the corresponding diffusion coefficients, as can be derived from what follows.

We denote the time for which the calibration is carried out as $t_{f,1}$ and according to Eq. (55) we have

$$\tilde{\beta} = (1/D_1 t_{f,1}) \ln \left[(\Delta c')_{00}/(\Delta c')_{f,1} \right] + \lambda/6 D_1 t_{f,1} . \tag{56}$$

The diffusion coefficient of the system used for calibration is denoted as D_1. We define

$$\bar{\bar{\beta}} = (1/D_1 t_{f,1}) \ln \left[(\Delta c')_{00}/(\Delta c')_{f,1} \right] \tag{57}$$

and we denote as D^* the diffusion coefficient calculated from the logarithmic formula:

$$D^* = (1/\bar{\bar{\beta}} t_f) \ln \left[(\Delta c')_{00}/(\Delta c')_f \right] . \tag{58}$$

Then we have with respect to Eqs $(55)-(58)$:

$$D\tilde{\beta} t_f = D^* \bar{\bar{\beta}} t_f + \lambda/6 , \quad D_1 \tilde{\beta} t_{f,1} = D_1 \bar{\bar{\beta}} t_{f,1} + \lambda/6 , \tag{59}, (60)$$

whence

$$D^* = D[1 + (\lambda/6\bar{\bar{\beta}}) (1/D_1 t_{f,1} - 1/D t_f)] . \tag{61}$$

From this equation it can be concluded that if

$$D_1 t_{f,1} = D t_f , \tag{62}$$

the diffusion coefficient D^* calculated according to Eq. (58) will be equal to the diffusion coefficient D. The expression in brackets in Eq. (61) enables to estimate the error due to neglecting the mentioned condition.

CONCLUSIONS

It follows from the last section that the simplified diafragm method can be applied also to the one-compartment diffusion cell, especially if the time of measurement and calibration is inversely proportional to the corresponding diffusion coefficients. Such a procedure enables to use the results from the preceding section even if the time of attainment of the pseudostationary state, t_0, is not considered and the values corresponding to the very beginning of the measurement at $t = 0$ are introduced into the derived equations. The derived expressions (40) and (41) enable to estimate with a sufficient accuracy the concentration at which the value of $\tilde{D}$ after Eq. (20) is equal to the diffusion coefficient D. The error due to the determination of the diffusion coefficient by the simplified diafragm method can be easily estimated from the mentioned equations. An experimental verification of this method will be the subject of a subsequent work.

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Translated by K. Micka.