Simplified Procedures for Diaphragm—Cell Diffusion Studies

R. MILLS, L. A. WOOLF, and R. O. WATTS
Australian National University, Canberra, A.C.T., Australia

Diaphragm cells are widely used both in the physicochemical and chemical engineering fields for the study of liquid diffusion. It is surprising therefore that no thorough study has been made of the effect of varying the initial concentration distribution in the diaphragm. The normal procedure for diaphragm-cell measurements uses a prediffusion period to establish a concentration gradient in the diaphragm. It would be much more convenient experimentally to have the diaphragm initially filled with either solvent or solution. The advantages, when large numbers of cells are being used, in savings of material and ease of manipulation are obvious. Also in experimentally difficult systems, such as molten salts, a rinsing and refilling step can be eliminated.

Holmes (*1*) from an analysis of Barnes' (*2*) equations has stated that the use of an initial solvent-filled diaphragm ought not to introduce errors greater than ± 0.2% and has used this technique in subsequent work. We considered, that before such techniques came into general use, experimental confirmation of both the solvent-filled and solution-filled cases should be sought. At the same time, we have extended Barnes' equations to obtain an expression for the solution-filled case.

EXPERIMENTAL

Apparatus and Materials

The diaphragm cells used in the experiments were basically of the magnetically-stirred type developed by Stokes (*3*) with Teflon bottom plugs of the type described by Albright and Mills (*4*).

For calibration the normal system of $0.5M$ potassium chloride solution diffusing into pure water was used. Analyses of compartment solutions after diffusion were made with a Jones-type conductance bridge. With this procedure, cell constants can consistently be reproduced to $\pm 0.1\%$ or better. Tracer diffusion runs were made with $^{22}\text{Na}^+$ diffusing in $0.4M$ sodium chloride solutions. Solutions were counted by weighing into specially constructed perspex counting bottles which were then placed reproducibly in a large cylinder of plastic scintillator. This assembly was inserted in a thermostatted counting apparatus fitted with twin, low noise photomultiplier tubes. A counting procedure in which top and bottom compartments were counted alternately, similar in principle to that described by Albright (*5*) was used to correct for drift in the electronic components. Diffusion coefficients calculated from the two independent counting apparatus agreed to $\pm 0.1\%$ or better.

'Analar' potassium chloride and sodium chloride were used without further purification and the solutions made up in water which had been distilled and deionized. Sodium-22 was used for the tracer diffusion experiments.

Procedures

To facilitate description we represent the three cases diagrammatically in Figure 1.

Solvent-Filled: Case 1.

The cell was completely filled with solvent, placed in the thermostat and allowed to come to temperature equilibrium. To obtain the concentration profile given in Figure 1(a) the solvent in the bottom compartment was then removed and replaced with equilibrated solution. The diffusion run was timed from this instant.

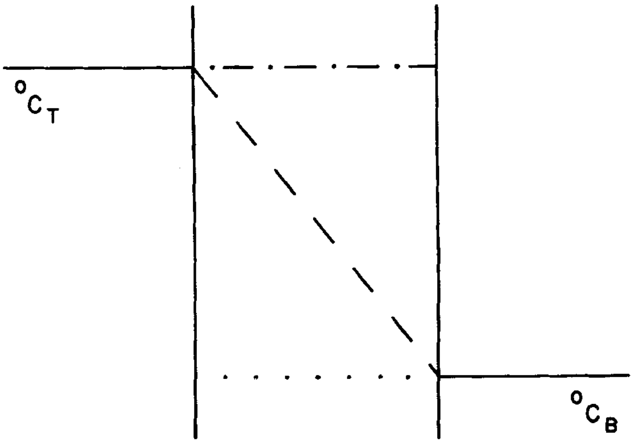

Fig. 1. Concentration profiles for initiating diaphragm-cell diffusion measurements: (a) —·—·, solvent-filled diaphragm, (b) ——, linear-gradient in the diaphragm, (c). · · ·, solution-filled diaphragm.

Gradient-Filled: Case 2.

The standard type of procedure was used. Solution and solvent were placed in the bottom and top compartments, respectively, and allowed to prediffuse. With the cell immersed in the thermostat, the top solution was then removed and the compartment rinsed with equilibrated solvent about five times. The diffusion run was timed from the final filling.

Solution-Filled: Case 3.

Two procedures were adopted to obtain a concentration profile similar to that of Figure 1(c). In each of them the cell was completely filled with solution and allowed to equilibrate in the thermostat. In Case 3*a* the top compartment was emptied and rinsed five times with equilibrated solvent. The diffusion was timed from the sixth and final filling; $^\circ C_T = 0$ and $^\circ C_B$ was directly measured. For Case 3*b* a procedure similar in principle to that of Case 1 was used. The top solution was removed and replaced immediately with solvent without rinsing.

Mass balance equations were used to calculate $^\circ C_B$ (Cases 1 and 2) and $^\circ C_T$ (Case 3*b*); these were derived on the assumption that there is a linear gradient in the diaphragm at the end of the diffusion experiment.

In all cases runs proceeded for the optimum diffusion time as given by Robinson, Edmister, and Dullien (*6*). This optimum time minimizes the cumulative analytical errors and ensures also that Dt is a constant for both calibration and test runs.

THEORY

In the gradient-filled case it is usually assumed that the gradient is linear in concentration across the diaphragm and that an approximate steady state condition applies.

In the other two cases there is not a linear gradient at the commencement of diffusion when the steady state assumption cannot be applied. Barnes (*2*) has given equations for C_B and C_T for both the linear-gradient and solvent-filled cases. We have derived corresponding equations for the solution-filled case by using mathematical methods similar to those of Barnes (*2*). Therefore we give only the final equations of the derivation

$$C_B = ({}^oC_B/2)\left\{1+\frac{\lambda}{2}-\frac{\lambda^2}{4}+\left(1-\frac{\lambda}{6}+\frac{\lambda^2}{45}\right)\right.$$
$$\exp\left[-2DAt\left(1-\frac{\lambda}{6}+\frac{\lambda^2}{45}\right)/lV_B\right]$$
$$-\frac{4\lambda}{\pi^4}\sum_{i=1}^{\infty}\frac{(-1)^{i+1}}{i^4}\left(1-\frac{10\lambda}{i^2\,\pi^2}\right)$$
$$\left.\exp\left[-Dt\,(i^2\,\pi^2+4\lambda)/l^2\right]\right\} \qquad (1)$$

$$C_T = ({}^oC_B/2)\left\{1+\frac{\lambda}{2}-\frac{\lambda^2}{4}-\left(1-\frac{\lambda}{6}+\frac{\lambda^2}{45}\right)\right.$$
$$\exp\left[-2DAt\left(1-\frac{\lambda}{6}+\frac{\lambda^2}{45}\right)/lV_T\right]$$
$$-\frac{4\lambda}{\pi^4}\sum_{i=1}^{\infty}\frac{1}{i^4}\left(1-\frac{10\lambda}{i^2\,\pi^2}\right)$$
$$\left.\exp\left[-Dt\,(i^2\,\pi^2+4\lambda)/l^2\right]\right\} \qquad (2)$$

Strictly speaking λ is defined only for the situation where top and bottom cell compartments are identical in volume; if these volumes are slightly different negligible errors will be introduced by defining

$$\lambda = 2\,V_D/(V_B+V_T) \qquad (3)$$

A convenient expression for the diffusion coefficient may be obtained by finding $C_B - C_T$ and rearranging; it is necessary to recognize that terms in λ^2 are negligible, that is, $\lambda << 1$, and that the rearranged summation terms are negligibly small. The resulting equation (after change of base of the logarithms) is

$$D = \frac{1}{\beta t}\log\left[\left(\frac{{}^oC_B-{}^oC_T}{C_B-C_T}\right)\left(1-\frac{\lambda}{6}\right)\right] \qquad (4)$$

(solution-filled)

For comparison Barnes' corresponding equations for the solvent-filled and gradient-filled cases are

$$D = \frac{1}{\beta t}\log\left[\left(\frac{{}^oC_B-{}^oC_T}{C_B-C_T}\right)\left(1-\frac{\lambda}{6}\right)\right] \qquad (5)$$

(solvent-filled)

$$D = \frac{1}{\beta t}\log\left(\frac{{}^oC_B-{}^oC_T}{C_B-C_T}\right) \qquad (6)$$

(gradient-filled)

where

$$2.303\ \beta = \frac{A}{l}\left(\frac{1}{V_T}+\frac{1}{V_B}\right)\left(1-\frac{\lambda}{6}\right) \qquad (7)$$

RESULTS AND DISCUSSION

Referring to Equations (4) to (7), it is clear that (4) and (5) are identical and differ from (6) by the $(1-\lambda/6)$ factor in the logarithmic term. The equality is somewhat surprising to the experimentalist. Therefore, in the experimental testing program we have sought to show firstly that, by using the three procedures in calibration runs (where D is practically constant), the cell constants would differ by the above logarithmic factor if the normal gradient-filled equation were used for their calculation. Secondly, if the mathematical derivations are correct, then it follows that if the same procedure is used in calibration and actual runs then the measured diffusion coefficients from all three methods should be the same. This is of obvious practical importance since λ does not then need to be evaluated. We have therefore studied the tracer-diffusion of Na^+ ion in aqueous 0.4M sodium chloride solutions using the three procedures.

In Table 1 are shown the data obtained in these studies. Cell I had a platinum sinter (8 to 10 μ) and cell II a glass one; their cell constants were widely different and covered the range of normal diaphragm-cell usage.

TABLE 1. DEPENDENCE OF DIFFUSION DATA ON INITIAL CONCENTRATION CONDITIONS

Cell	λ	Procedure	β^*		% Dev. from β	$D \times 10^5$ sq.cm./sec.
I	0.0232	1	0.4914 0.4906	0.4910	+0.36	1.278
		2	0.4894 0.4891	0.4892	0	1.277
		3*a*	0.4865 0.4882	0.4873	−0.4	—
		3*b*	0.4903		+0.23	1.274
II	0.0162	1	0.1040_2 0.1038_5	0.1039_3	+0.32	1.277
		2	0.1037_2 0.1034_8 0.1036_1	0.1036_0	0	1.274
		3*a*	0.1034_1 0.1036_0	0.1035_0	−0.10	1.273
		3*b*	0.1038_5		+0.24	—

Looking first at the cell constant data, the β^* are all calculated by using Equation (6). They differ in Cases 1 and 3 from the value β that would be calculated from Equations (4) and (5) by the factor $(1/Dt)\log(1-\lambda/6)$. The expected deviation that would result from this omission is *ca* + 0.29% in each case. It is evident therefore that for both cells and for procedures 1, 2, and 3*b* the agreement between theory and experiment is well within the precision limits of the measurements (ca. 0.1%) and the equations are fully confirmed. For Case 3*a* it will be recalled that a repetitive rinsing procedure was used to ensure that the top compartment contained only pure solvent. Evidently this rinsing technique causes some erosion of the solution in the diaphragm which would have the effect of giving a lower cell constant.

In Column 6 are shown the diffusion coefficients for Na^+ in 0.4M aqueous NaCl, as determined by using the three procedures and Equation (6) in all cases. The average D for these measurements is $1.275 \pm 0.0015 \times 10^{-5}$ sq.cm./sec. It is clear that very consistent results can be obtained and this is true even for Case 3*a*, which gave anomalous results in the calibration intercomparison.

CONCLUSION

This study has shown that the solvent-filled or solution-filled techniques can be used with complete confidence provided the same procedure is used in both calibration and actual runs.

NOTATION

A = effective area of diaphragm
C = solute concentration in molarity
D = differential diffusion coefficient
$\mathbf{D}$ = integral diffusion coefficient
l = effective length of diaphragm
M = molar concentration scale
t = time
V = volume (ml.)

Greek Letters

β = cell constant defined by Equation (7) and applicable to Equations (4) and (5)
β^* = cell constant determined experimentally by using Equation (6)
λ = ratio of diaphragm volume to cell compartment volume

Subscripts

B = bottom compartment
D = diaphragm
T = top compartment

Superscript

o = zero time

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On the Correlation of Critical Properties of Mixtures

L. M. SCHICK and J. M. PRAUSNITZ

University of California, Berkeley, California

New experimental measurements of critical temperatures and critical pressures have been reported by Kay and Hissong (*2*) for twenty-two binary hydrocarbon mixtures. We have reduced these data within the framework of the correlation recently presented by Chueh (*1*).

Chueh fits experimental critical temperatures and critical volumes to quadratic functions of the surface fraction θ:

$$T_c = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\ \tau_{12}\theta_1\theta_2$$

$$v_c = \theta_1 v_{c1} + \theta_2 v_{c2} + 2\ \nu_{12}\theta_1\theta_2$$

where τ_{12} and ν_{12} are binary parameters characterizing the 1-2 interaction. As shown by Chueh, reduced values of τ_{12} and ν_{12} follow definite trends within a chemical family. Critical pressures are found from critical temperatures and critical volumes by using a modified Redlich-Kwong equation (*1*).

TABLE 1. AVERAGE DEVIATIONS IN CRITICAL TEMPERATURES AND PRESSURES FOR 22 BINARY SYSTEMS

System	$\frac{2\tau_{12}}{T_{c1} + T_{c2}}$	Average deviation, % T_c	P_c
n-octane–*n*-heptane	0.0018	0.01	0.4
n-hexane–*n*-heptane	0.0027	0.01	1.5
n-hexane–*n*-octane	0.0086	0.02	1.1
o-xylene–benzene	0.0069	0.04	1.5
o-xylene–toluene	0.0008	0.02	0.3
o-xylene–ethylbenzene	—0.0002	0.02	0.5
toluene–benzene	0.0031	0.02	1.7
toluene–ethylbenzene	0.0018	0.02	3.9
ethylbenzene–benzene	0.0065	0.03	2.1
cyclopentane–methylcyclohexane	0.0742	0.61	4.6
cyclopentane–methylcyclopentane	0.0012	0.02	1.3
cyclopentane–cyclohexane	0.0066	0.03	0.1
cyclohexane–methylcyclohexane	0.0032	0.05	6.9
methylcyclopentane–methylcyclohexane	0.0035	0.01	5.5
methylcyclopentane–cyclohexane	0.0030	0.04	0.7
methylcyclopentane–*n*-hexane	0.0005	0.02	0.5
benzene–cyclopentane	—0.0062	0.01	0.7
benzene–methylcyclopentane	—0.0113	0.02	0.1
benzene–*n*-hexane	—0.0127	0.03	0.9
benzene–*n*-heptane	—0.0153	0.02	0.4
benzene–*n*-octane	—0.0124	0.05	2.0
benzene–*n*-nonane	—0.0056	0.09	4.0

Table 1 lists τ_{12} for the systems studied by Kay and Hissong. The temperature parameters τ_{12} shown for the first 16 systems in Table 1 are in good agreement with those calculated from Chueh's Figure 2 for paraffin-paraffin systems. Also shown are the average percent deviations between calculated and measured critical temperatures and critical pressures.

Since critical volumes were not measured for these systems, for each system we calculated critical pressures for various values of the unknown parameter ν_{12}. In all cases the optimum ν_{12} parameter was small, close to or equal to zero. We found that best results for the critical pressure were obtained as indicated:

1. For paraffin-paraffin systems use the ν_{12} curve presented by Chueh for such systems.
2. For aromatic-aromatic systems use $\nu_{12} = 0$.
3. For hydrocarbon systems containing at least one cycloparaffin use $\nu_{12} = 0$.
4. For systems containing one aromatic and one paraffin, use 83% of the ν_{12} values given by Chueh's curve for paraffin-aromatic systems.

Average deviations in critical pressure reported in Table 1 were obtained by following the procedure given above.

Extension of this method of correlation to systems containing more than two components is straightforward as discussed previously (*1*).

Values for k_{12} in the modified Redlich-Kwong equation were taken as zero except for the last six systems for which $k_{12} = 0.01$.

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