Bulk Flow in Diffusion Coefficient Studies

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The viewpoint is taken that bulk flow terms in the general equation of molecular diffusion must be measured in apparatus which offers no constraint to the molecular flux in either direction. It is proposed to carry this out in a miniaturized experiment operating with one side of the diffusion gradient as an infinite sink. Dimethyl acetamide–water diffusivities computed from such an experiment were found to be 7.02×10^{-6} sq.cm./sec. over a wide range of compositions. These are compared with values showing considerably wider variation with composition, namely, 2.45 to 7.00 $\times$ 10^{-6} sq.cm./sec. by estimating methods and 11.45 to 14.05 $\times$ 10^{-6} sq.cm./sec. by large cell experiments. Arguments are presented in support of the values obtained by the proposed method operating on a nonideal binary *N, N*-dimethyl acetamide and water.

In the literature of the phenomenon of diffusion and its measurements, the diaphragm cell figures prominently as an experimental device for the determination of diffusivities. The earliest recommendation of its use is attributed to Northrup and Anson (*8*) in 1929. McBain and Liu (*7*) exploited this device in extensive studies. The very careful analysis of the two-compartment cell by Gordon (*5*), with a mathematical analysis of the optimum configuration, is a keystone in the development of the method. The works of Stokes (*12*) and then of Dullien and Shemilt (*3*), who used the critique of Gordon (*5*) as a basis to further develop this technique, are representative of the importance of this method as a means for experimental evaluation of diffusivity. In addition, Dullien and Shemilt (*4*) have presented equations of very useful and general character for application to the evaluation of diffusivity.

There is, however, a very distinct disparity between the actual method whereby diffusion in a diaphragm cell is experimentally practiced and the equations used to describe the process. Thus from the use of the descriptions of Dullien and Shemilt (*3*) and/or Stokes (*12*) as an example of a horizontal diaphragm cell, it is seen that during a run the lower chamber is sealed off and operated at constant volume, while the upper chamber is allowed to operate at ambient pressure. Should there be other than an equispecific volume countercurrent overall transport of materials resulting from diffusion, then the static pressure between the chambers will change and transport by a mechanism other than molecular diffusion will occur. With such a nonideal system in mind, it becomes evident that the determination experimentally of the transport does not necessarily establish that portion of the transport which occurs by molecular diffusion. Again in the use of the vertical diaphragm cell shown in Figure 1, unless equispecific volume counterdiffusion is the primary process, there is no way to describe by material balance or other means just how much transport is by a molecular diffusion mechanism and how much is by a hydraulic gradient caused by the molecular diffusion transport, except that the rule of transport be independently determined. In addition to this difficulty in the vertical diaphragm cell operation it has been reported by Plank (*10*) and Pike (*9*) that the rate of stirrer revolution was critical. Stokes (*12*) and Dullien and Shemilt (*3*) found for their horizontal diaphragm cells that stirrer rate influenced their results, although a wide plateau of uniform result was found. In the former cases there is the possibility that at the higher stirring rates the agitator bar was acting to pump through the diaphragm by impeller action.

Here, then, are two sources of bulk flow through the diaphragm which are impossible to determine in advance of the experiment. They cannot be determined by virtue of any instrumentation of the regular diaphragm cell experiment. In the first instance the experiment does not tend to minimize the possible influence of the nondiffusive bulk flow. Having examined experimental practice one must consider the equations used to relate the data. A material balance in one compartment of the cell will give a value for the net transport of the A and of the B species of a binary as a function of time. Physical properties of the binary system measured in advance will make it possible to express these data in such concentration, flux, or/and volume units as one desires. Attribution of this transport, as has been shown above, to molecular diffusion is only presumable, if reasonable. When one is satisfied that he is dealing only with all of the molecular diffusion process mass transport, the usual equation to relate the information can be found in many texts. That of Bird (*2*) is an effective form (in molecular units):

$$N_A = c\,\mathcal{D}_{AB}\,\nabla X_A + X_A\,(N_A + N_B) \qquad (1)$$

In seeking to find out more about the term $X_A(N_A + N_B)$ one learns that this combination arises very naturally in the development of the equation. The N_A and N_B cited here are actually the specific fluxes resulting from transport incidental to the molecular diffusion process. They do not refer to transport by hydraulic, thermal, kinetic, or other forces (see references *6* and *11*).

In summary, it has been shown that the present practice of diaphragm cell employment will not give data from which only the molecular diffusion process transport can be defined. It has been shown by analysis of the bulk transport terms of the general equation that only this diffusive transport must be obtainable from the data somehow to apply properly the equations to describe a valid value of diffusivity. As a result methods should now be developed in which these ambiguities are either minimized, resolved, or nonexistent. It is the purpose of this work to present a miniaturized method in which these ambiguities are nonexistent. To achieve this, compromises were made which introduce other equivocations but the usual and currently used techniques were employed to minimize their importance.

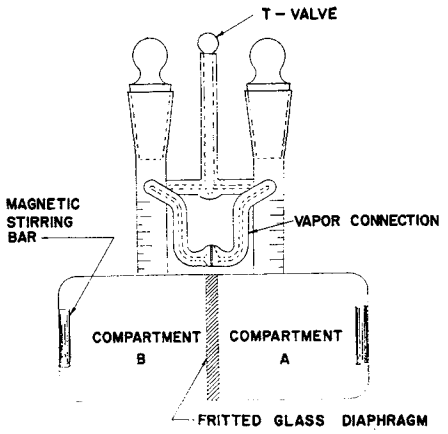

Fig. 1. Diaphragm cell apparatus.

A diaphragm of much higher resistance to flow under a hydraulic gradient than the fritted glass disks was selected. A film prepared from a copolymer of 94% acrylonitrile 6% vinyl acetate was used. This film had never been allowed to dry in a liquid water-containing state; it was cast, precipitated, frozen in liquid nitrogen and freeze-dried. This processing was necessary to avoid loss of microstructure. Cellophane which has never been dried or which has been freeze-dried in this same manner undoubtedly can be cast and precipitated to gain a morphology similar to this acrylic film.

It was expected that no osmotic effects would be encountered by semipermeability because of the gross size of the passages. Experiments were performed with artificially established hydraulic heads. These indicated that no transport of significance occurred during the time lapse between points —0.2% by volume over 30 min. under a 25 mm. gradient. Even less transport would be expected by virtue of the activities of the agitator systems as pump impellers when operating against such a diaphragm material. Also since the films were never allowed to dry out after wetting, they became well stabilized as regards swelling and selective sorption effects.

In order to operate without constraint both sides of the diaphragm must be in contact with a common or ambient atmosphere and at relatively identical liquid pressures. To achieve this an infinite sink was adopted as one side so that the volume on this side could be adjusted to maintain the required liquid head relations throughout the experimental run. The material balance data to evaluate the forward and reverse flux were taken from a relatively small cell: 2 to 3 ml. or approximately 1% of the volume of the infinite sink. See Figure 2 for the actual details of this cell. By maintaining the liquid sink level lower by the amount of the capillary rise throughout a 30-min. run, it was presumed that all changes in the small cell were only the result of an unconstrained molecular diffusion. In each extended series the infinite sink was made more dilute in solute by about 5 mole %. As a result of this choice the net diffusion was found (for the aqueous systems studied) to be into the small cell. The diffusion therefore tended to replenish the cell for amounts removed as samples, while removal of the samples tend to minimize changes in total molar concentration. Approximately eight points could be obtained from a given experiment over a 4-hr. period. Because the net flux was changing, it was not possible to treat this cell as a steady state case. But since the time intervals were short the volume of the cell was constant from point to point time intervals (within 2%). Similarly, the value of C, the total molar concentration, in the cell was considered to be a quasi constant with the resultant simplifications usually made being held to be applicable in these reported studies as well. The final integrated equation used to treat the diffusion data was

$$\mathcal{D}_{AB} = \frac{1}{dt}\left\{\left[1 + X_{A_t}(r-1)\ln\frac{\Delta C_{A_0}}{\Delta C_{A_t}}\right] + (r-1)(X_{A_0} - X_{A_t})\right\} \quad (2)$$

Of course $\mathcal{D}$ and α are interchangeable here and their use depends on whether one is obtaining diffusivity for an unknown binary system with the cell constant known or vice versa.

EXPERIMENTAL

Because this work deals with quantities of a rate process, it considers matters which are at the differential equation level and which must per force be integrated to be of maximum interest and of most general utility. For this reason, then, part of the program of evaluation should devote itself to assurance that those things are constant which were assumed constant for purposes of integration. Part of the program was then devoted to using conventional equipment in conventional mode of operation to gain a check. Finally, the program made use of the proposed method and apparatus to gain the required numbers for diffusivity of the system checked or otherwise known.

As can be seen from the delta quantities, time and concentration were the integrating base; therefore all the other parameters must either be argued to be constant or experimentally shown constant in the system explored.

The technique for operating the miniaturized diaphragm cell is as follows (16).

Mounting and testing the film and set up: The freeze-dried film was carefully clamped in the assembly of Figure 2 and the excess trimmed off with a razor. Sealing wax was found to be insoluble in the binary systems to be tested and was melted and flowed into the angle formed between the flange and glass cell to engulf the trimmed edge and thus seal off the joint at this point. Water, one of the binary components, was then added to the cell up to the initial markings fired into the capillary stand pipe, after the film supporter or keeper was placed in the steel flange opening. The weight of water so added was determined on a gravimetric balance, then increments of water were made and weighed, bringing the level along the stand pipe to various heights. Thereby the volumetric character of the apparatus was established. These increments were made with a hypodermic syringe as were all subsequent solution handling in and out of the cell. This calibration could therefore be used for all subsequent running without weighing the cell each time, requiring only that the supporter be inserted and reading be made on the standpipe.

After having determined the volumetric behavior of the cell, the water was removed. The solution to be studied was in-

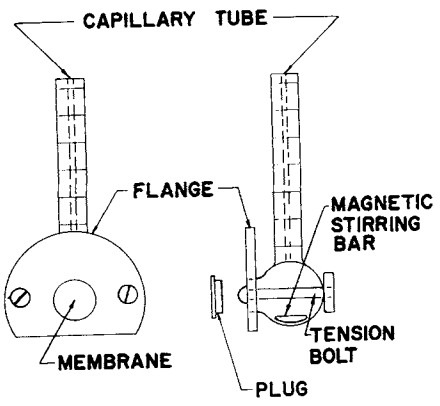

Fig. 2. Microcell apparatus.

Table 1. Tests of Assumptions

Time, min.		30	60	90	120	150	180	210	240	Mean
α, cm.$^{-2}$		23.9	17.9	22.4	23.4	24.2	23.9	27.9	23.4	23.4
r	Dimethyl acetamide	12.5	10.8	12.5	12.5	12.0	12.3	12.6	11.3	12.1
r	Acetone	4.07	4.92	5.05	5.91	5.15	6.11	6.83	5.26	5.51
r	Acetone	3.37	2.89	3.61	3.55	3.05	3.66	3.69	—	3.40
r	Acetone	2.22	1.51	2.64	2.10	2.38	2.61	—	—	2.28

jected and then sampled for analysis by refractometry. The capillary level was left high deliberately so that as many points as possible could be obtained before the sample removal could lower the volume below the calibrated range. By making the highest water concentration side the infinite bath side, diffusion was into the cell. Eight samplings could easily be obtained over a 4-hr. period at 0.5-hr. intervals. Therefore, by a knowledge of the density-concentration-refractive index relations for each system used, the number of moles of each component at time, time = 0 and $t = t$, up to 1,800 sec. corresponding to the changes occurring from point to point could be computed. Meanwhile, the infinite sink was set in volume so that the level was below the capillary level by the amount of the capillary rise for the solution in the cell. Any deviation was adjusted for by adding (withdrawing if required) bath solution to the infinite sink during the diffusion. The bath was sampled as a check and was well agitated with a turbomixer. The cell solution was agitated by spinning a magnet below the bath container bottom. The stirrer bar within the cell followed this motion provided there was not more than about a ¾-in. gap. Thus, lively action could be attained.

To test the variance expected of the method two measurements were made. First the variance to technique was taken using the same cell and film and the same initial concentration gradient and average concentration level. Of the sixty-four points taken in sets of eight, forty passed the qualifying test of consistent values of the transfer ratio (shortly to be further described) for each set of eight. The experimental variance of the log term of Equation (2) for these forty points was found to yield a confidence envelope of 95% about the regression line. In calculating what the variation in the log term should be, as caused by the allowable tolerance in reading the refractometer, since it would be reflected in an error in concentration, this confidence envelope should have been 93%. Second, the method was tested for variations in nominally defined films by the expedient of making up three different cells. For each of these cells the film used was taken from a different film sample, each nominally said to be identical to the other in all respects of preparation. The experimentally determined points from these three cells were found to fall within the 95% confidence envelope. The method was held therefore to be limited only by the accuracy of the analysis. With such a foundation, then, data were gathered to test the various assumptions made:

1. Volume of solution in the cell is relatively constant during any given 30-min. interval. The increase in volume in the cell in general was 2% or less; oftentimes this volume change would be less than 1%.

2. Total molarity of solution in the cell was constant. This is related directly to the volume change in the cell and will be of the same order of magnitude.

3. In considering the membrane geometry the area of the exposed face is, by the nature of the apparatus, constant. The thickness of the membrane is stable as long as it is not allowed to be dried out or to be heated to collapse the spongey character of the tortuous paths. Cell volume is also collected in this as a group α, then defined as a so-called cell constant. This may be evaluated then by an experiment series for which the diffusivity has already been determined by interferometric methods (*1*).

Table 1 gives information relating to the constancy of this group, α (*16*).

4. Transport ratio presents the quantitative function relating the flux of the A species to the B species molecules in a diffusion. Some of the possibilities are: both are zero; one is zero; they are equal and opposite; one is some negative fraction of the other, $N_A = -rN_B$; and so on to more and more complexity. The two systems explored here were reasonably nonideal. Therefore the assumption that one flux is negative in direction and some fraction r of the other was selected and tested. The results of typical runs are shown in Table 1 in terms of r moles of water per mole of solute specified.

Cell Constant Determination

In Equation (2) the grouping α appears, which in the course of its elaboration arises from the geometry of the cell and film and has a dimension of cm.$^{-2}$ and is defined as the cell constant. The mean value for this number taken from some twenty-four points was 22.5 cm.$^{-2}$. The binary system used was acetone-water, the data for which are presented elsewhere (*1*). With this information, the system dimethyl acetamide-water was studied to obtain values of diffusivity for this binary shown in Table 2.

For check, data were obtained by the conventional technique of a vertical diaphragm cell. These were analyzed with the equation

$$\ln \frac{\Delta C_o}{\Delta C t} = \beta \mathcal{D} M t;\ M = \frac{\ln \left[\dfrac{1 + (r-1)X_{AL}}{1 + (r-1)X_{AR}} \right]}{(r-1)(X_{AL} - X_{AR})} \qquad (3)$$

where β is a cell constant obtained by running a system of known $\mathcal{D}$ such as potassium chloride and r is the ratio of molecular volumes.

Finally, estimations from the method of Wilke and Chang (*15*) were made for the dimethyl acetamide-water system.

Table 2. Estimation of *N*, *N*-Dimethyl Acetamide-Water Liquid-Liquid Diffusivity

Wt. % Water	r	Film diaphragm $\mathcal{D}$, sq. cm./sec.	M	Two-compartment $\mathcal{D}$, sq. cm./sec.	Wilke-Chang $\mathcal{D}$, sq. cm./sec.
89	12.1	8.05×10^{-6}	0.908	14.05×10^{-6}	7.00×10^{-6}
80	10.6	6.48	0.836	12.90	5.23
72	12.0	6.65	0.763	12.61	4.00
65	—	—	0.728	10.10	
60	9.6	7.63	—	—	
54	8.3	7.86	0.622	11.45	3.05
49	8.8	6.40	—	—	2.45

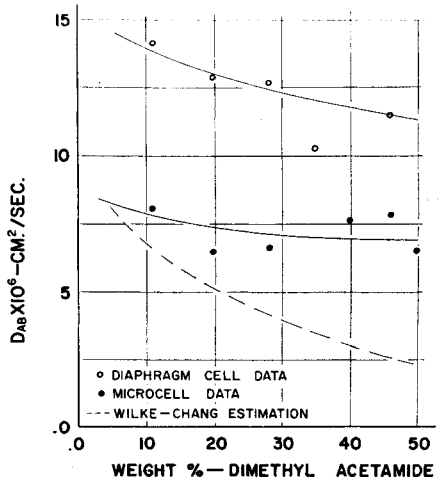

Fig. 3. *N,N*-dimethyl acetamide–water integral diffusion coefficients at 25°C.

Results of all these determinations are given in Table 2 and Figure 3 (*16*).

For the binary system selected for study, *N, N* dimethyl acetamide-water, the new method gave substantially smaller values. These were more or less constant in integral diffusivities over the range covered. With conventional techniques a value almost twice as large was obtained for this same range and the integral diffusivities showed approximately a 20% change over the range examined. The Wilke-Chang estimation gives values considerably closer to the film method yet it is a curved relation similar to that of the conventional method. Studies using collapsed film show no notable transport at all for these systems. Therefore, the tortuous cavernous passages are carrying the molecular flux and the possible transport through the polymer substance by solution and dissolution must be ignored. To try to make judgment as to which experimental diffusivities are representative of the system, one may look to the self-diffusion constant of water. Wang (*14*) reported values of the range 30 to 40 $\times$ 10^{-6} sq.cm./sec. With a somewhat bulkier molecule of super dielectric constant taken with water, one expects the occurrence of a very considerable association of the solute with water. This association should remain quite stable with concentration change. Therefore, values of the binary diffusivities substantially smaller than the self diffusivity of water are to be expected. To find them constant or nearly so with concentration should also be expected. A similar anomaly exists in the density relations of water —*N, N* dimethyl acetamide solutions down to 40% water. The relative change in density is of the order of 0.2%. Therefore, it is the film diaphragm results that merit the most confidence. So it is that independent of the fact that theoretical adherence of the method with the equation of analysis is superior in the new method, one is influenced to accept a much smaller value of the diffusivity compared to the self diffusivity of water and a reasonably constant diffusivity in the range of pure water to 50% water.

CONCLUSION

In summary, it has been pointed out that the manner in which diaphragm cells are often operated can give rise to an unmeasured amount of material transport originating from a pressure gradient, not a diffusion gradient. The pressure gradient originates, in turn, from unequal transport in the diffusion gradient. The equations are only able to yield acurate results when the real transport in a diffusion gradient can be defined. A method has been suggested with more tortuous diaphragms and an infinite sink on one side whereby an approximation to purely diffusional gradient transport constitutes the measured quantity. Argument has been advanced supporting the values obtained by the new method as constituting the most likely value of diffusivity for the system.

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NOTATION

A = area perpendicular to net diffusion direction
C = total concentration in molarity (may be subscripted to specify species)
$\mathcal{D}$ = diffusivity of a binary system sometimes subscripted AB
M = subgroup in an equation for the conventional cell operation
N = molar flux usually subscripted to designate species
r = transport ratio, or ratio of fluxes, or $\frac{[N_A]}{[N_B]} = r$
t = time
V = volume of cell or cell compartment subscripted to design
X = mole fraction subscripted to designate species and compartment
Z = linear distance positive in net flow direction

Greek Letters

α = geometry group $\frac{A}{3 \cdot V_c}$ or film diaphragm cell constant
β = proportionality constant or cell constant for sintered glass diaphragm cell

Subscripts

A = species A
B = species B
b = bath
c = cell
L = compartment as faced by observer which is to his left
R = compartment as faced by observer which is to his right

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