"THE DIFFUSION DIAPHRAGM CELL: A STATE-OF-THE-ART-REVIEW"

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ABSTRACT

The diffusion diaphragm cell is considered one of the simplest and most reliable devices for measuring liquid-phase diffusivities. The design of such diaphragm cells has passed through many stages of refinement over the years. This review follows the stages of development of the cells since the first "real" diaphragm cell was introduced by Northrup and Anson in 1929 until the present and discusses the advantages and disadvantages of each design. The development of the calibration technique for calibrating the cell and the development of the cell equation are also presented and discussed.

1. INTRODUCTION

Diffusion is a mechanism that results in a net transfer of material across a reference plane. However, difficulties are often encountered in measuring pure diffusive flows in liquids since mass transfer can also take place across the same reference plane by bulk flow.

Bulk flow can result from (i) the existence of a temperature gradient, (ii) a volume change on mixing, and (iii) mechanical effects such as vibration or pulsation. Minimizing the bulk flow due to temperature gradients can be achieved by proper temperature control. The effect of the volume change of mixing on diffusion coefficients can be determined and diffusion coefficient corrected accordingly. Minimization of mechanical effects requires confining the liquid under investigation to capillary tubes of various types. Such capillaries offer

considerable resistance to bulk flow yet allow the diffusion process to occur without hindrance. This gave rise to the use of diaphragm cells employing sintered materials for the measurement of diffusive flows. Such sintered materials are essentially matrices of capillary tubes confining the liquid in which diffusion is occuring [1].

In his extensive review on the diaphragm cell method of measuring diffusivities, Gordon [2] concluded that "it is still unsurpassed in its simplicity and in the precision of the data it yields." This statement is as true today as it was about forty years ago.

The diffusion diaphragm cell design has gone through many refinements over the years until it has become today the simplest and probably the most reliable device for measuring diffusivities.

In the last fourteen years, there has been no comprehesive review of the diffusion diaphragm cell. During this period, there were new cell designs, calibration techniques, and a new equation for calculating diffusivities from diaphragm cell data. All these developments have made an up-to-date review timely.

2. DEVELOPMENT OF THE DIFFUSION CELL DESIGN

The earliest reference for a diffusion experiment in liquids dates back to 1843 when the physiologist Von Bruke placed turpentine and olive oil on opposite sides of a leather membrane. However, the presence of the membrane obscured the analysis of the diffusion process [3].

Thomas Graham (1850), was probably the first researcher to build a diffusion apparatus that can be considered a crude forerunner of the diffusion cell in use today. That apparatus consisted of two bottles (Figure 1) initially containing solutions of different concentrations. After several days, the two bottles were separated and their contents analyzed. Thomas Graham's results were simple and definitive [3].
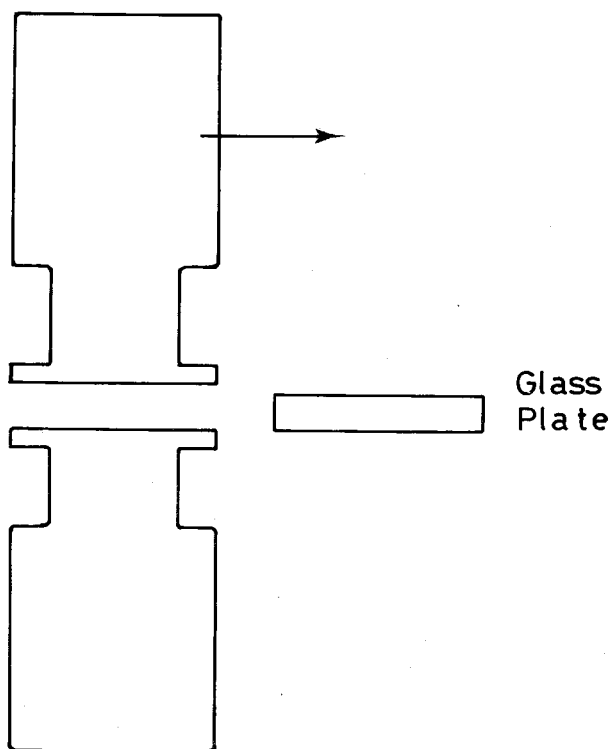
Figure 1: The Thomas Graham Cell

The first "real" diaphragm cell incorporating a sintered disc was made by Northrop and Anson in 1929 [4]. Their cell is shown in Figure 2. The main advantage of using a sintered disc is reducing mechanical convection to a negligible level. This is achieved by confining the liquid to capillary tubes of various types. The capillary tubes offer considerable resistance to convective flow, whereas permitting diffusion to occur without hindrance. Therefore, a sintered disc is an ideal candidate since it is essentially a matrix of capillary spaces. Northrop and Anson [4] also presented a mathematical treatment for the diffusion process in such cells.
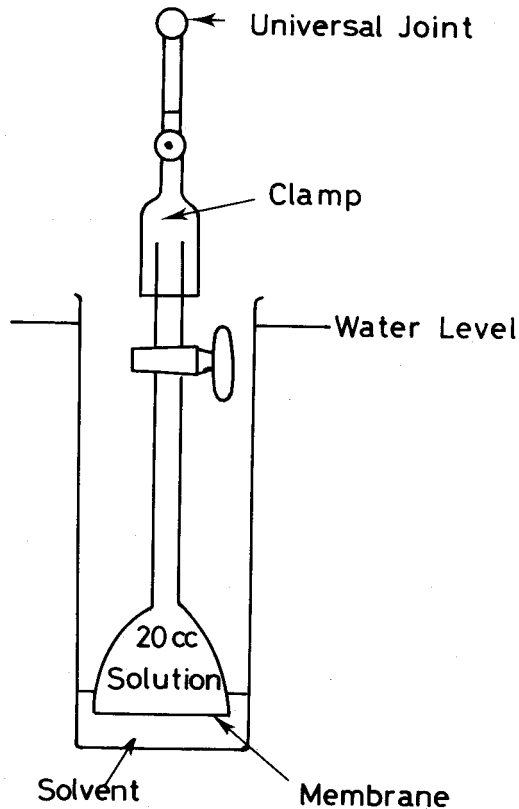
Figure 2: The Northrop and Anson Cell

Mills and Woolf [1] argued that there are two logical consequences for confining the diffusion process to a sintered disc :

(i) As it is impossible to analyze the solution at any point within the sinter, the diffusion coefficient must be determined from measurements of material passing through its boundaries. If, in addition, the volumes of liquid in contact with the sinter are large and separately uniform in composition, then these conditions approximate those required for steady-state diffusion.

(ii) As the internal geometry of the sinter is constant but generally unknown, a cell constant must be obtained by calibration using systems of known diffusion coefficients.

The work of McBain and Liu [5], McBain and Dawson [6], Hartley and Runnicles [7], and Gordon [2] aimed at refining the technique of calibrating and using the diaphragm cell. At the time this work was undertaken, a two-compartment diaphragm cell with a sintered glass disc in-between was also developed.

In 1946 Aten and Dreve [8] described a simple method for measuring diffusion coefficients, especially those of high molecular weight substances. Their method allows the solute to diffuse into a porous glass disc filled with the solvent. They argued that their cell (Figure 3) and method are superior to those of Northrop and Anson [4] because
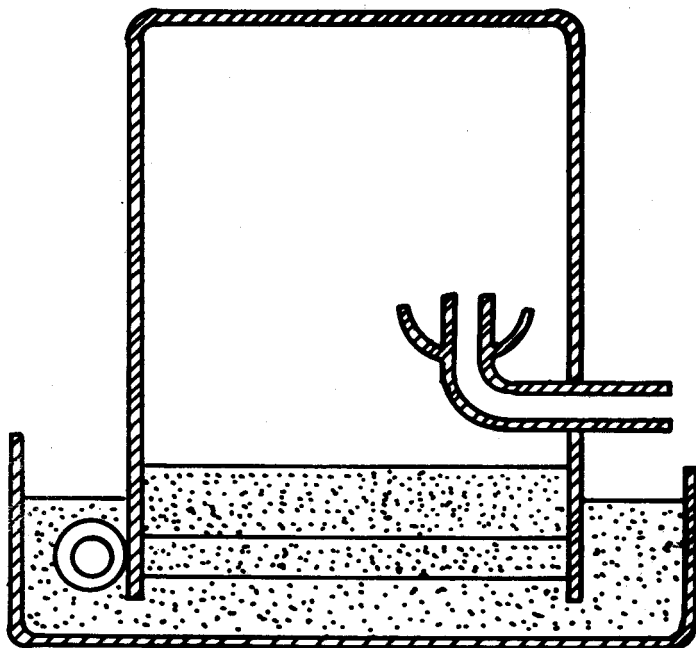

Figure 3: The Aten and Dreve Cell

(i) The Northrop and Anson cell requires very close temperature control.

(ii) The Northrop and Anson cell cannot be used for liquids which liberate small quantities of gases.

Because of those very reasons, the accuracy of diffusion coefficients measured using the Aten and Dreve cell becomes questionable. In fact, Wedlake and Dullien [9] showed that a 0.2°C change in cell temperature resulted in a 0.017% error in the diffusion coefficient, if the diffusion time is the optimum time determined by Robinson's rule [10]. Moreover, Wedlake and Dullien argued that had the diffusion time been shorter, or the temperature disturbance greater, the error might have been significant. In addition, if the temperature fluctuations occur repeatedly or even periodcally, each disturbance will contribute an error of similar magnitude and the final error will be the sum of the errors caused by all the disturbances. To substantiate their argument, Wedlake and Dullien showed that the error in the difffusion coefficient caused by a temperature fluctuation of ±0.0025°C in the time interval corresponding to a half-period of a periodic temperature fluctuation in the cell (about 6 minutes) would be about 1%.

Gage [11] developed a diffusion cell (Figure 4) designed to give fast results (diffusion periods of 2 to 3 hours). This cell is probably only suitable for measurement of diffusion coefficients of molecules of the size and nature of glucose. This is because the length of time required by the Northrop-Anson cell, as Gage argued, could be the source of serious errors when the solutions under investigation supported microbiological growth resulting in partial blockage lof the membrane. However, Gage admitted that in other respects his cell would result in much less precise diffusion coefficients than those obtained by a Northrop-Anson type cell. The only advantages of the Gage cell over the Northrop-Anson cell are simplicity of construction and operation and rapidity of measurements.

Gage [11] attributed the lower precision of his cell to two factors :

(i) Lack of rigidity of the membrane (filter paper as opposed to sintered glass disc in the Northrop-Anson cell).

(ii) Errors inherent in the analytical method used at low concentrations.
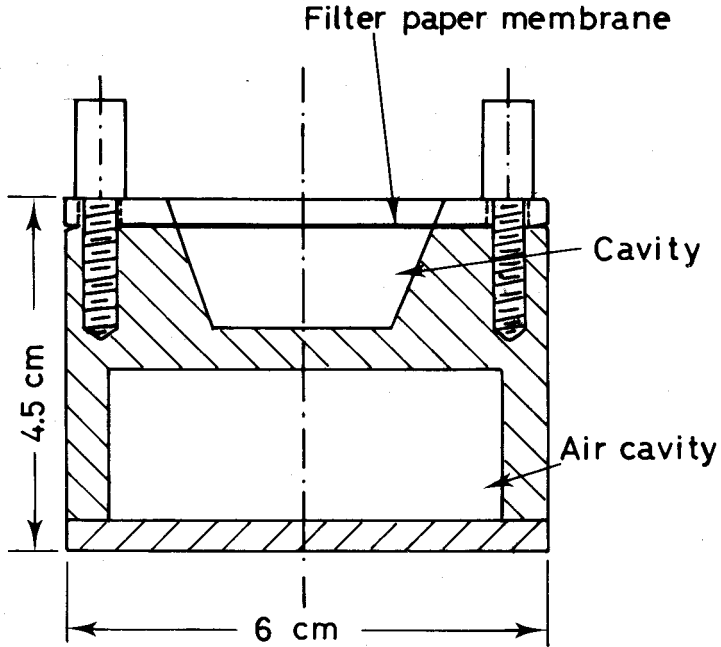
Filter paper membrane

Figure 4: The Gage Cell

At the time, Gàge probably did not realize that a more important factor is his relatively very short diffusion time. It was later shown by Robinson in 1964 [12] that if the diffusion time is about one-half of the optimum time, $t_{optimum}$, required for diffusion and calculated by

$$t_{optimum} = \frac{1.2}{\beta \overline{D}} \tag{1}$$

where

β = cell constant

$\overline{D}$ = integral diffusion coefficient

the expected deviation of the diffusion coefficient from that calculated at the optimum time is about 25%. The optimum time was defined by Robinson [12] as the time required to minimize the fractional standard deviation in the diffusion coefficient.

Stokes in 1950 [13] published a paper that contained the results of an investigation on an improved diaphragm cell developed by him (Figure 5). This cell consisted of two almost identical compartments divided by a sintered glass diaphragm. Magnetic stirrers were used to keep the solutions uniform on both sides of the diaphragm and prevent concentration polarization.
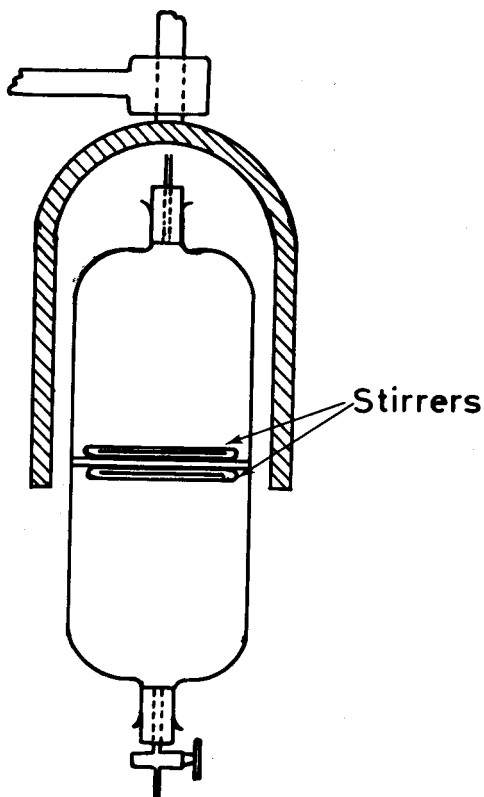

Figure 5: The Stokes Cell

In a subsequent publication, Stokes [14] investigated the calibration of the diaphragm cell developed by him and laid down calibration procedures. His calibration procedure has become the standard since.

Smith and Storrow [15] described a diaphragm celll that employed two electrodes in each compartment of the cell to measure the change of the conductivity of the solution under investigation. The cell is depicted in Figure 6. Smith and Storrow indicated that such a sensitive conductivity method of analysis allows the use of very low concentration differentials. They used their cell to measure the diffusion coefficients of the ethanol-water system over the complete composition range. The results reported by them [15] for the ethanol-water system disagreed by as much as 100 per cent with the results reported a year later by Hammond and Stokes [16]. A few year later, Dullien [17] confirmed the results obtained by Hammond and Stokes.
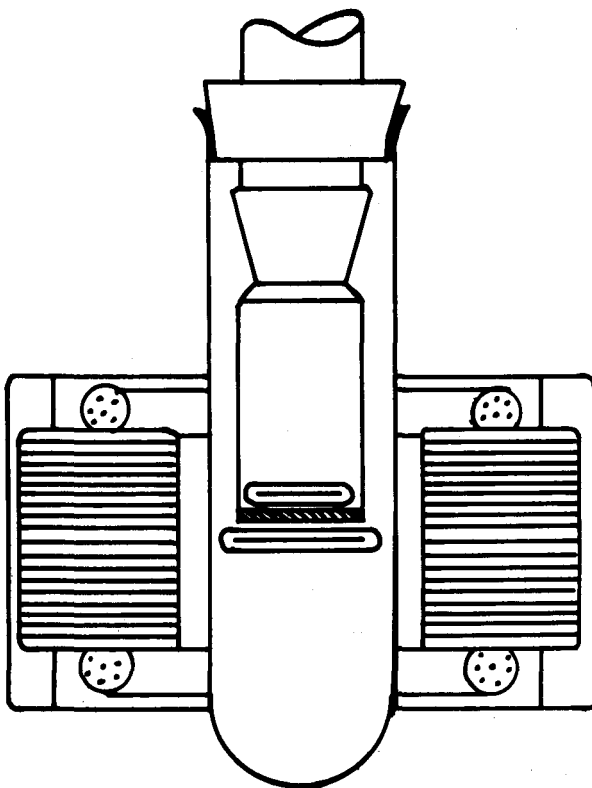

Figure 6: The Smith and Storrow Cell

Lewis [18] described the design of an "improved" diaphragm cell. The new features of the cell designed by Lewis included shaft-mounted stainless steel stirrers in the cell. The stirrers were rotated by a ring of eight soft-iron cored solenoids which circle the cell at the plane of the sinter as shown in Figure 7. Mills and Woolf [1] reported developing cells similar to the one described by Lewis. However, they discarded that design because of heat effects associated with the electromagnets requiring the development of an efficient heat exchange system.
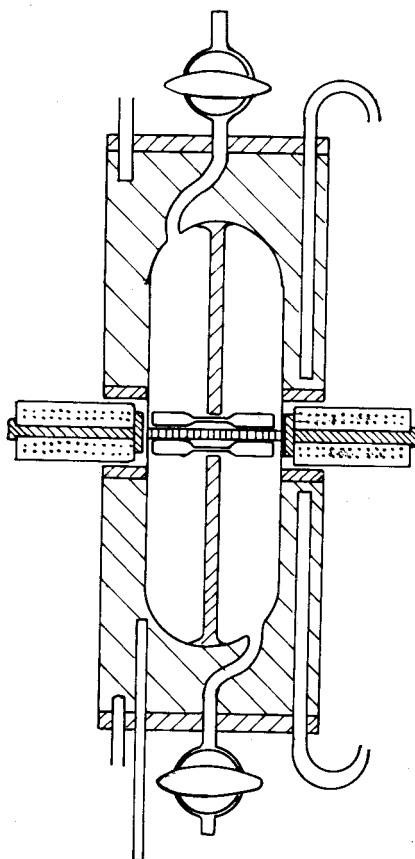

Figure 7: The Lewis Cell

Dullien [7] and Dullien and Shemilt [19] described a design of a diaphragm cell in which they eliminated the use of rubber stoppers and lubricated or unusually well-fitting ground glass parts. This cell is filled and emptied through two narrow (0.5 mm i.d.) capillaries. It is shown in Figure 8.

Figure 8: The Dullien Cell

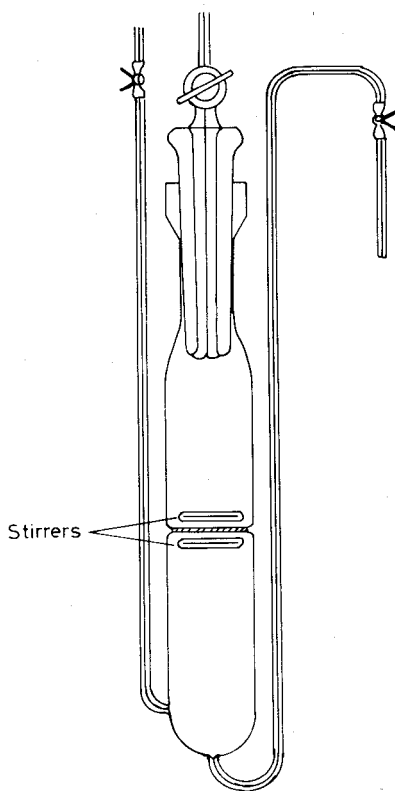Based on personal experience, it is the opinion of the authors that the cell described by Dullien [17] and Dullien and Shemilt [19] is very awkward to use. Extreme caution must be exercised in handling this type of cell. The capillaries are extremely liable to breakage and, if the cell is repaired, recalibration must be carried out before use. Therefore, the use of a Stokes - type cell [13] is preferable.

In 1963 Holmes et al. [20] described a stirred horizontal glass diaphragm cell. This cell was "unconventional" since the diaphragm was vertical as opposed to horizontal in "conventional" cells. Whereas the vertical diaphragm helps eliminate bulk flow due to density difference, it raises questions about the existence of stagnant layers near the diaphragm, since the stirrers are positioned away from it as shown in Figure 9.
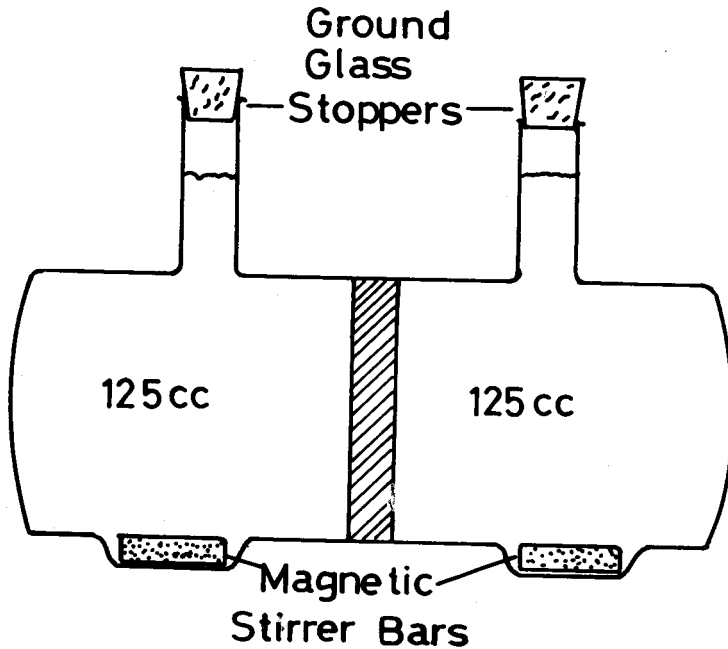

Figure 9: The Holmes Cell

The effect of stagnant layers was studied in some detail by Holmes et al. [20]. They found that relatively higher speeds of stirring are required in vertical diaphragm cells (≈ 300 rpm) to obtain reproducible results in the case of "normal" diffusivity and viscocity liquids than those required in the case of "conventional" cells (≈ 50-60 rpm). However, if highly porous diaphragms or fluid systems of high viscosity and low diffusivity are employed, external mass transfer resistance may be an appreciable fraction of the resistance of the diaphragm and the use of a correction factor given by Holmes et al. [20] is warranted.

In a recent study by Frey and King [21] cells identicall to that described by Holmes et al. [20] were employed. Values for the cell constants, as reported by Frey and King, were generally reproducible to within ± 3%. However, since the accuracy of determining diffusion coefficients is largely influenced by the precision of determining cell contants, "conventional-type" cells would be preferable since it was reported in the literature, e.g. Robinson [12], Wedlake [22], Dullien [17], and Asfour [23] that such cell constants were reproducible to better than ±0.25%. In fact, Asfour [23] reported that conventional cell constants were reproducible, in general, to within ±0.07%.

Albright and Mills [24] in a study of diffusion in the ternary system labeled urea-urea-water reported the use of a diaphragm cell patterned after that described earlier by Stokes [13]. However, they described a more sophisticated design for the bottom plug of the cell. It is the opinion of the authors that the modifications introduced to the Stokes cell by Albright and Mills have made it more cumbersome to handle and more expensive to make. The bottom plug designed by Albright and Mills [24] is shown in Figure 10.
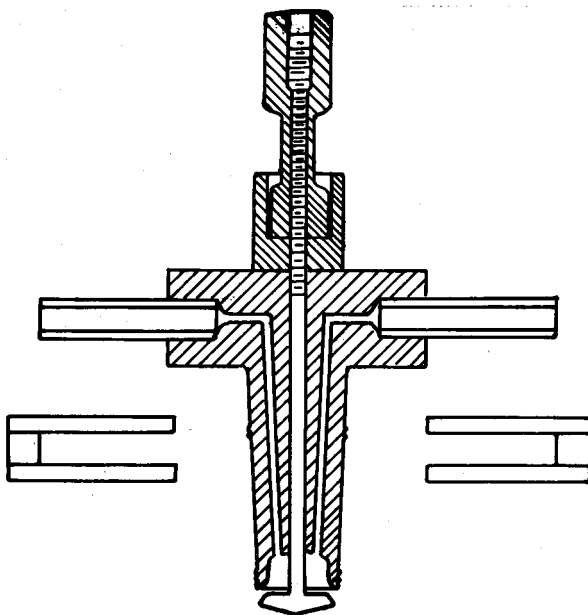

Figure 10: The Albright and Mills Cell

Sanni and Hutchison [25] criticized earlier diaphragm cells and cited two main disadvantages: (i) The difficulty of handling volatile organic liquids at any temperature other than room temperature. (ii) The great loss of information resulting from measuring concentration in the compartments only at the beginning and end of the experiment.

As far as the first disadvantage is concerned, it is the opinion of the authors that the Sanni-Hutchison design is not any better than, say, the Stokes-type cell when volatile organic liquids are used at temperatures appreciably higher than room temperatures. The second disadvantage, however, is not a serious one. It has been established, as indicated earlier, by Robinson [12] and Robinson et al. [10] that there is an optimum duration for a diffusion run. Any data collected before the optimum time are not of critical significance and could be erroneous.

The cell designed by Sanni and Hutchison [25] is provided with a conductivity measuring cell in the top compartment for the calibration run which can be replaced by a capacitance measuring head for the runs using organics. The Sanni-Hutchinson cell lis depicted in Figure 11. Cell preparation, calibration, and filling
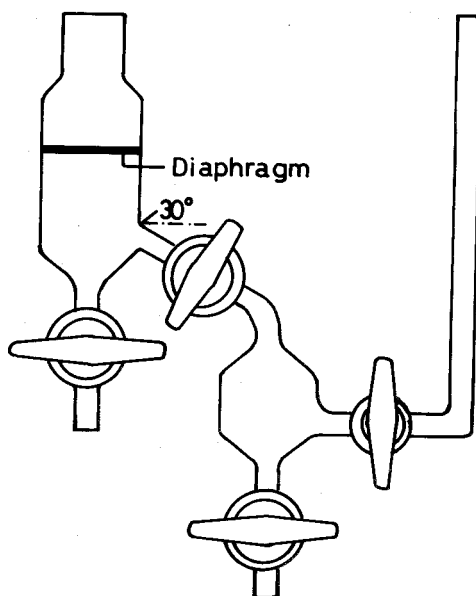

Figure 11: The Sanni and Hutchison Cell

are clumbersome and require strict sequential procedures. Moreover, the cell is relatively expensive to build.

Mills and Boland [26] described a "novel" (diaphragm cell) design. This cell contained a very small magnetic pump which was used to remove solutions from the end of the compartments and pump them into inlets immediately above and below the sinter. The solutions are sprayed horizontally over the diaphragm surfaces. This "pumping-around" of the solution within each compartment achieves the required stirring and minimizes concentration polarization. Mills and Boland [26] claimed that heat input due to pumping was negligible and that the pumped cell operated for over 3000 hours without trouble. They recommended using their cell with viscous as well as electolyte solutions. The Mills-Bolland cell is shown in Figure 12.
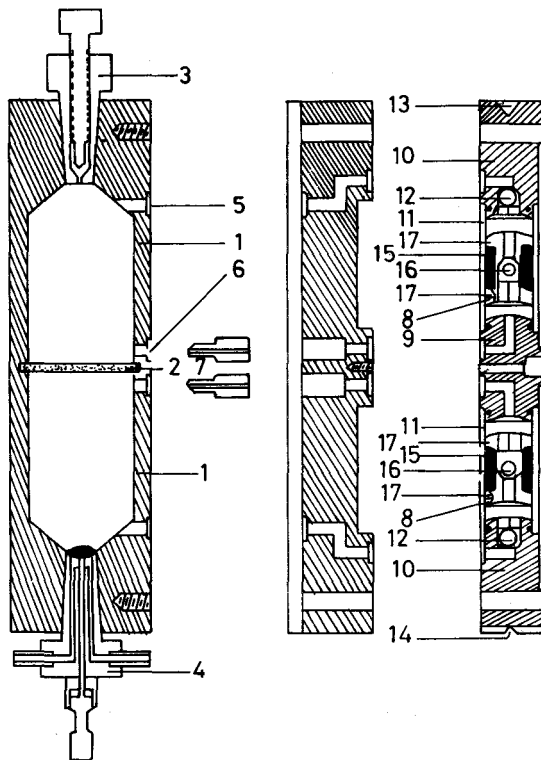

Figure 12: The Mills and Boland Cell

However, according to the authors, the Mills-Boland cell represents a very expensive solution to a relatively simple problem, viz. stirring. Iron stirrers encased in glass and placed in each compartment lightly touching the diaphragm from each side and rotated from the outside of the cell by rotating magnets, as described by e.g., Asfour [23], would "do the trick" inexpensively. The only advantage of the pump cell is that it could enable continuous monitoring of concentrations in the cell compartments.

Rao and Bennett [27] described a diffusion cell utilitilizing a porous diaphragm that differs from the conventional diaphragm cell in that it facilitates accurate control of pressure drop across the diaphragm and, at the same time, allows continuous sampling of the liquid flowing out of the cell. The main advantage of this cell, as argued by Rao and Bennett, over the conventional diaphragm cell is that it requires less time (usually less than 10 hrs) than the latter (2 or 3 days).

Rao and Bennett [27] reported that the maximum absolute error for the systems they investigated, i.e. ethanol-benzene, aniline-benzene, and aniline-carbon tetrachloride, did not exceed 5%. Maximum absolute errors for systems using conventional diaphragm cells not exceeding 1% are very common in the literature, i.e. Robinson [12], Wedlake [22], Dullien [17], Asfour [23]. Therefore, rapidity of measurements at the expense of precision is the main feature of the Rao and Bennett cell. This cell is depicted in Figure 13.
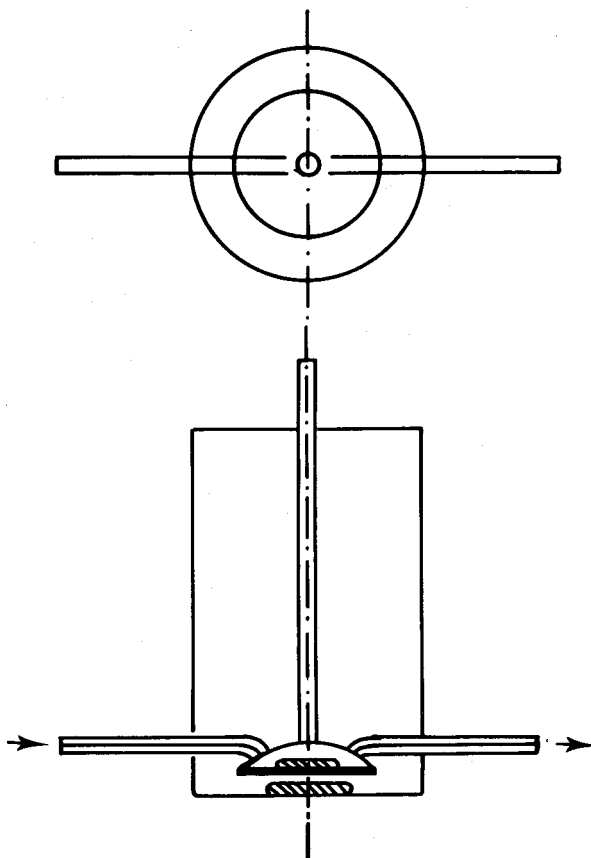
Figure 13: The Rao and Bennett Cell

Asfour [23] and Asfour and Dullien [28], realizing the unsurpassable advantages of the Stokes cell, introduced modifications to this cell to make it even simpler to use. This improved cell is shown in Figure 14.

Both the top and the bottom plugs of the cell described by Asfour [23] and Asfour and Dullien [28] are made of teflon; there is a capillary bore in the top plug which permits volume changes of the liquid in the upper compartment, while the stainless steel screw cap prevents evaporation losses. There is no bore in the bottom plug. The brass bottom cap,threaded on the inside, screws onto the brass ring glued on the extension of the lower compartment providing a

SS Screw Cap

Top Plug

Diaphragm

Bottom Plug

Brass Bottom Cap

Figure 14: The Asfour Cell

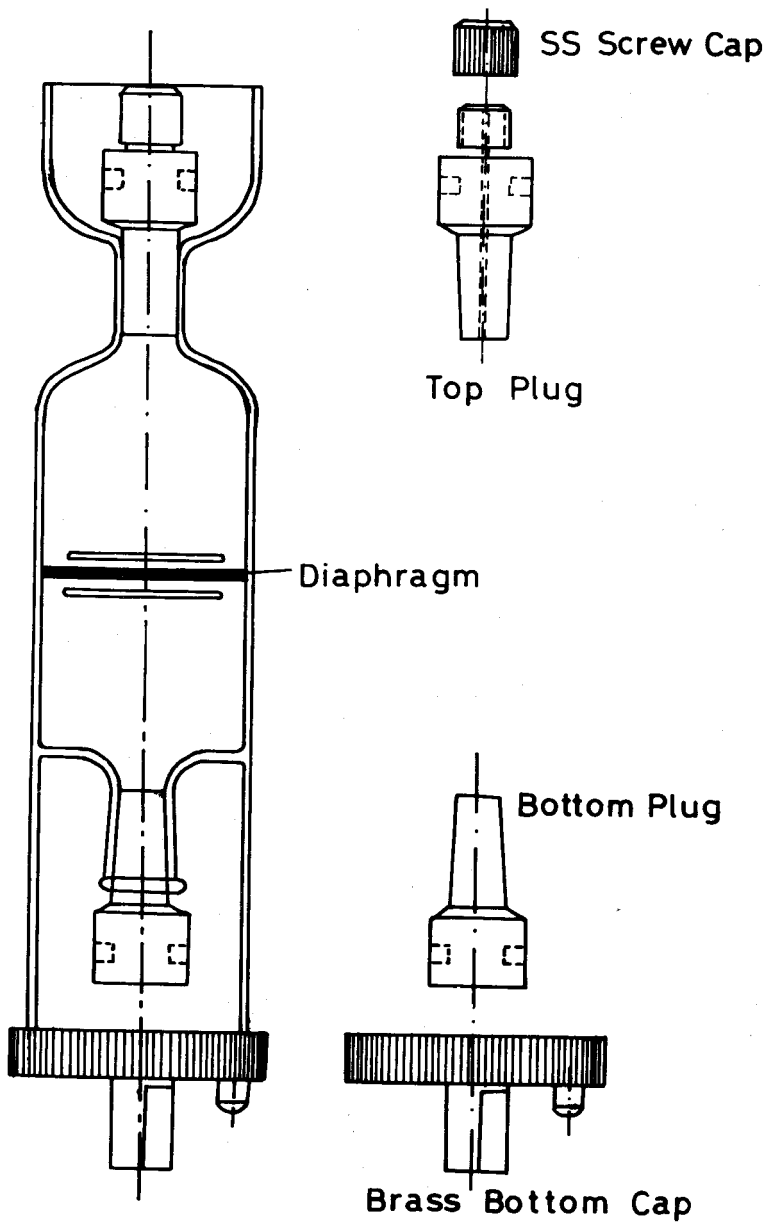water-tight seal. The bottom cap fits into a mount at the bottom of the constant temperature bath containing oil, allowing the cell to be placed in the bath reproducibly and in a fixed position. As shown in Figure 14, each compartment contains a magnetic stirrer which in operation lightly touches the diaphragm.

This is by far the simplest and least expensive diaphrgam diffusion cell that is in use at present. Despite its simplicity, this cell yields results comparable, or even superior, to those obtained by more sophisticated cells.

3. DEVELOPMENT OF THE ANALYSIS TECHNIQUE FOR CELL CALIBRATION RUNS

Since the diaphragm cell method can only measure relative diffusivities, it is necessary to calibrate the cell with systems of known diffusion coefficients. It has been the general practice to calibrate the diffusion diaphragm cell following the diffusion of 0.5 N potassium chloride into water.

The accuracy of determining diffusion coefficients is largely influenced by the precision of the calibration experiments use to obtain the cell constant which in turn are largely influenced by the method of analysis used.

In 1935 McBain and Dawson [6] described a gravimetric technique for analyzing potassium chloride solutions resulting from calibration runs. This technique was accepted and used by almost all investators in diffusion research. It is the opinion of the authors that the method of McBain and Dawson is lengthy, cumbersome, and prone to serious errors since is requires heating potassium chloride solutions to 60°C to evaporate the water, then heating up to 310°C for 20 hours to completely dry the KCℓ crystals. It is always possible that spurting of KCℓ crystals may occur during the heating process and this would result in erroneous values for the cell constants.

Mills et al. [29] used a Jones-type conductance bridge to analyze compartment solutions after diffusion. This method is easier, more comvenient, and would result in more reproducible cell constants than that of McBain and Dawson.

Asfour [23] described a method of analysis of potassium chloride comparment solutions that proved to be as easy, convenient, and reproductible as that of Mills et al. [29]. An Anton Paar K.G. DMA 02C digital precision density meter was used to analyze the potassium chloride solutions by measuring their densities. The same density meter could also be used to analyze solutions from runs using organics by measuring their densities. Asfour [23] was capable of reproducing the cell contants of his cells with a maximum absolute error of 0.07%.

Values of integral diffusion coefficients of potassium chloride solutions were reported by Stokes [14]. Revised values of the same diffusion coefficients were reported by Woolf and Tilley [30]. They fitted their values to an equation of the form

$$\overline{D} \times 10^5 = \sum_{i=0}^{8} A_i x^i \,,$$
(2)

(where $x = C^{1/2}$)

The values of the coefficients A_i were reported by Woolf and Tilley [30].

4. DEVELOPMENT OF THE DIAPHRAGM CELL EQUATION

Assuming that (i) the diffusion coefficient is independent of composition and (ii) steady state conditions exist in the diaphragm, several authors, e.g. Wedlake [22] and Asfour [23], showed that combining Fick's first law with a mass balance leads to the diaphragm cell equation

$$D_F = \frac{1}{\beta t} \ln \left[\frac{C_B^o - C_T^o}{C_B - C_T} \right]$$
(3)

where C_B^o and C_T^o are the initial concentrations in the bottom and top compartments and C_B and C_T the final concentrations in the bottom and top compartments, respectively. The time of the diffusion run is given by t and β is the cell constant given by

$$\beta = \frac{A}{\ell} \left[\frac{1}{V_B} + \frac{1}{V_T} \right]$$
(4)

where A is the effective area of the diaphragm and ℓ is the effective length of the diffusion path in the diaphrgam. V_T and V_B are the volumes of the top and bottom compartments, respectively.

The diffusion coefficient, D_F in Equation (3), is derived with respect to a stationary co-ordinate system. D_F is not exactly equal to D_{AB}, the integral diffusivity, except for systems in which the partial molal volumes of the constituents do not vary with composition. It has been shown, however, by Dullien and Shemilt [31] that D_F is equal to D_{AB} to within 1%, under the usual conditions of diaphragm cell experiments, even for systems with the greatest known volume changes on mixing. Therefore, Equation (3) can be rewritten as follows:

$$\overline{D_{AB}} = \frac{1}{\beta t} \ln \left[\frac{c_B^0 - c_T^0}{c_B \quad c_T} \right] \tag{5}$$

where $\overline{D_{AB}}$ is the integral diffusivity.

One of the assumptions used in deriving Equation (3) is the linearity of the concentration gradient across the diaphragm. There are two conditions required for such a linear concentration gradient to exist, viz. (i) concentrations in cell compartments must be constant so that true steady-state conditions exist and (ii) diffusion must be independent of concentration.

True steady-state conditions do not exist in the diaphragm in a strict sence. However, although the concentrations in the top and bottom compartments of the cell change with time, those changes are so small that the concentration gradients can be considered approximately constant. Therefore, the diffusion process occurs under pseudo- or quasi-steady-state conditions. Dullien [17] proved by calculation that this assumption is an excellent one.

Barnes [32] retained the assumption that the diffusion coefficient is independent of concentration and solved Fick's second law diffusion for two cases, viz., (i) solvent filling the diaphragm and the top compartment at the beginning of the diffusion run and (ii) solvent filling the top compartment at the beginning of the diffusion run and a linear concentration gradient in the solution in the diaphragm.

Mills et al. [29] extend the treatment of Barnes to include a third case, i.e. (iii) the diaphragm and bottom compartment initially filled with solution, the top compartment with solvent.

Solution of Fick's second law according to the boundary conditions stated in (i) and (iii) above resulted in the expression

$$\ln \left[\frac{C_B^0}{C_B - C_T} \right] (1 - \frac{\lambda}{6}) = \frac{DtA}{\ell} (1 - \frac{\lambda}{6}) \left[\frac{1}{V_B} + \frac{1}{V_T} \right]$$

$$= \beta \, D \, t \tag{6}$$

where $\lambda = 2 V_D / (V_T + V_B)$, $V_D =$ volume of diaphragm, and

$$\beta = \frac{A}{\ell} \left[1 - \frac{\lambda}{6} \right] \left[\frac{1}{V_B} + \frac{1}{V_T} \right]$$

The solution of Fick's second law for the boundary conditions given in (ii) above results in the equation

$$\ln \left[\frac{C_B^0}{C_B - C_T} \right] = \frac{DtA}{\ell} (1 - \frac{\lambda}{6}) \left[\frac{1}{V_B} + \frac{1}{V_T} \right] \tag{7}$$

$$= \beta' \, D \, t$$

Holmes [33] argued that the effects of the term $(1 - \lambda/6)$ on both sides of Equation (6) tend to cancel and, therefore, the following equation should be used:

$$\ln \left[\frac{C_B^0}{C_B - C_T} \right] = \frac{DtA}{\ell} \left[\frac{1}{V_B} + \frac{1}{V_T} \right] \tag{8}$$

$$= \beta \, D \, t$$

Holmes also argued that the use of Equation (8) instead of Equation (6) would only introduce errors in D of a few tenths of one per cent.

In the treatment of Barnes as well as in that of Mills et al. [29] V_T and V_B are assumed to be identical.

Equation (5) gives values of the integral diffusion coefficient whereas Equations (6) - (8) yield differential diffusivities.

Asfour [23] and Asfour and Dullien [28] argued that the concentrations in Equation (5) can be replaced with the corresponding densities, ρ, and that should introduce, in most cases, a completely negligible error. Therefore, Equation (5) can be rewritten as

$$\overline{D_{AB}} = \frac{1}{\beta t} \ln \frac{\rho_B^0 - \rho_T^0}{\rho_B - \rho_T} \tag{9}$$

where the superscript o refers to initial conditions and subscripts B and T refer to bottom and top compartments, respectively. There were two assumptions made in developing Equation (9), viz. (i) ρ is a monotonically increasing or decreasing function of C in the concentration range covered by the diffusion run and (ii) the relationship between C and ρ is sufficiently well·approximated by a polynomial of the form

$$C = \sum_{i=0}^{n} A_i \, \rho^i \tag{10}$$

Asfour and Dullien [28] indicated that the main advantage of Equation (9) is that it saves a great deal of painstaking effort in obtaining very precise concentration values. Despite such efforts, a great deal of doubt as to the accuracy of the concetration values would still exists. Asfour and Dullien also argued that when the new method, given by Equation (9), of calculating diffusivities is used, only high precision density readings are needed to assure high precision diffusivity values. The need for concentration measurement is altogether eliminated.

In conclusion, the diaphragm diffusion cell is the most reliable and simple instrument for measuring diffusion coefficients in liquid systems. In particular, the cell design reported by Asfour and Dullien [28] represents a further simplification over previous designs. Based on results achieved [23], it also represents the most accurate instrument avialable to date. In addition, use of Equation (9), as proposed by Asfour [23] and Asfour and Dullien [28], for calculating integral diffusivities further simplifies the necessary measurements because liquid system densities can be determined faster and more accurately than the concentrations involved in previous equations of this type.

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NOMENCLATURE

A	:	Effective area of diaphragm or constant coefficient
C	:	Concentration
D	:	Diffusion coefficient
$\overline{D}$	:	Integral diffusivity
ℓ	:	Effective length of diffusion path
t	:	Diffusion time
V	:	Volume
x	:	Mole fraction

Greek Letters

β	:	Cell constant
ρ	:	Density
λ	:	Constant equal to $2\,V_D / (V_T + V_B)$

Superscripts

°	:	Initial
'	:	Modified

Subscripts

B	:	Bottom
D	:	Diaphragm
F	:	Fickian
T	:	Top