C— bond angle is 121°. Using this value for φ, the angle between the bond moment vectors is calculated to be 105.4°. Substituting the above values in the cosine relation, assuming $\mu_{\text{C-H}} = 0.4D$, one obtains $\mu_{\text{Car.-N}} = 1.17D$.[8] Since the observed moment of chlorobenzene is $1.56D$,[9] then $\mu_{\text{Car.-Cl}} = 1.16D$, which exactly equals $\mu_{\text{Car.-N}}$. Similarly, using the observed moment of diisopropylcarbodiimide, $2.08D$, one obtains $\mu_{\text{C-N}} = 1.28\,D$.

The above analysis clearly indicates that the unsymmetrical structure proposed for carbodiimide, indicated in Fig. 1, is reasonably correct, and given a suitable technique, it should be possible to separate the optical antipodes.

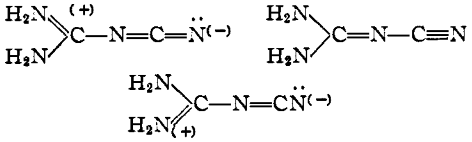
Acknowledgment.—The author wishes to express his indebtedness to the American Cyanamid Company for permission to publish these results and to Drs. D. J. Salley and R. F. Stamm for much helpful discussion.

Summary

1. The dipole moments of cyanamide (4.52D), dicyandiamide (8.16D), diisopropylcyanamide (4.76D), diisopropylcarbodiimide (2.08D) and *p,p'*-dichlorophenylcarbodiimide (0.0D) have been determined at 35° in dioxane solution.

2. The essential identity of the moments of cyanamide and diisopropylcyanamide compared with the moment of diisopropylcarbodiimide precludes any extensive tautomerism between cyanamide and carbodiimide.

3. The observed high moment of dicyandiamide is best explained by assuming resonance among the structures



4. The finite moment of diisopropylcarbodiimide and the observed zero moment of *p,p'*-dichlorophenylcarbodiimide support the asymmetrical structure assumed for carbodiimide.

5. The carbon–nitrogen bond moment in carbodiimide derivatives has been found to be approximately 1.2D compared to 0.6D in such compounds as trimethylamine.

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[8] It can be calculated from the data of Sutton, *Nature*, **128**, 639 (1931), that the carbon-nitrogen linkage in aromatic azides has approximately this value.

[9] Meyer and Buchner, *Physik. Z.*, 390 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CAMBRIDGE]

An Improved Diaphragm-cell for Diffusion Studies, and Some Tests of the Method

By R. H. STOKES[1]

Recent very precise measurements by Harned and Nuttall[2,3] of the diffusion coefficients of potassium chloride in solutions up to half normal concentration provide a valuable standard by which to test the accuracy of the porous-diaphragm technique due to Northrop and Anson.[4] The development of this method up to 1945 has been reviewed by Gordon[5]; since then there have been modifications designed to give more rapid results,[6] and some applications of tracer techniques,[7] but little new work on electrolytes is reported.

It is clear from Gordon's discussion that the chief points needing further investigation are: the effect of stirring; the extent to which bulk flow occurs, as distinct from diffusion; the choice of a suitable standard for calibration; and the possible disturbing effects of the large surface provided by the diaphragm pores. The present paper deals with these matters, as a preliminary to work on the diffusion coefficients of a number of electrolytes at high concentrations.

I. Design and Operation of a Stirred Diaphragm-cell.—Most users of diaphragm-cells have followed Northrop and Anson[4] in mounting the cell with the diaphragm in a horizontal plane, with the denser solution uppermost, so that the density changes resulting from diffusion lead to the circulation of the liquid in each compartment. One may reasonably doubt whether such circulation is adequate to maintain a really uniform composition, especially if the solutions are very dilute or if the salt studied has only a small density change per unit concentration. There is furthermore the possibility that an appreciable thickness of the liquid near the surface of the diaphragm is held in a stagnant condition. Gordon[5] points out that though such layers have been proved to behave reproducibly, it is by no means certain that they are of equal importance at all concentrations or for different electrolytes. Another disadvantage of this set-up is that the system is inherently unstable with respect to gravity, so that when large concentration differences are used there may well be a certain amount of bulk flow through the diaphragm in addition to diffusion.

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[1] Imperial Chemical Industries Research Fellow, University of Cambridge.

[2] H. S. Harned and R. Nuttall, THIS JOURNAL, **69**, 736 (1947).

[3] H. S. Harned and R. Nuttall, *ibid.*, **71**, 1460 (1949).

[4] J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

[5] A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

[6] A. Aten and J. v. Dreve, *Trans. Faraday Soc.*, **44**, 202 (1948); J. C. Gage, *ibid.*, **44**, 253 (1948).

[7] A. W. Adamson, *J. Chem. Physics*, **15**, 762 (1947); E. B. Robinson and J. B. Drew, *ibid.*, **15**, 417 (1947).

The type of stirring used by Hartley and Runnicles,[8] in which glass spheres are made to roll on the diaphragm by rotating the cell about an inclined axis, ensures adequate mixing within each compartment, but does not entirely eliminate the possibility of stagnant layers on part of the diaphragm. Though one might expect that the slanting position of the diaphragm might encourage bulk flow, their work makes it clear that, using no. 4 diaphragms, no such trouble in fact occurred with concentrations differing by up to 0.1 *N* in potassium chloride solutions. Other methods of stirring have been described; in general they do not sound as adequate as that of Hartley and Runnicles.

The system of stirring adopted in the present work makes it possible to keep the diaphragm horizontal, and to have the denser solution on the lower side, thus using gravity as a stabilizing rather than a disturbing force. At the same time both sides of the diaphragm are continuously wiped by stirrers operated magnetically from outside the cell; these also maintain a uniform composition in each compartment. The arrangement is shown in Fig. 1. The cells are of Pyrex, each end having a volume of about 50 ml. The diaphragms are of no. 4 porosity, 40 mm. in diameter and 2–3 mm. thick. Each compartment contains a stirrer of glass tubing, 3 mm. in diameter and of length slightly less than the diameter of the diaphragm. Inside each stirrer is sealed a length of iron wire; the thicknesses of the wire and the tube walls are so adjusted that the stirrer in the upper compartment sinks while that in the lower floats. In this position they are rotated by a pulley-driven permanent magnet mounted around the cell. (A suitable magnet may be obtained from an old ignition magneto: it needs neither great field strength nor close fitting to the cell.) Thus both sides of the diaphragm are wiped twice per revolution of the magnet, and tests with liquid containing suspended particles show that the stirring extends throughout the compartments.

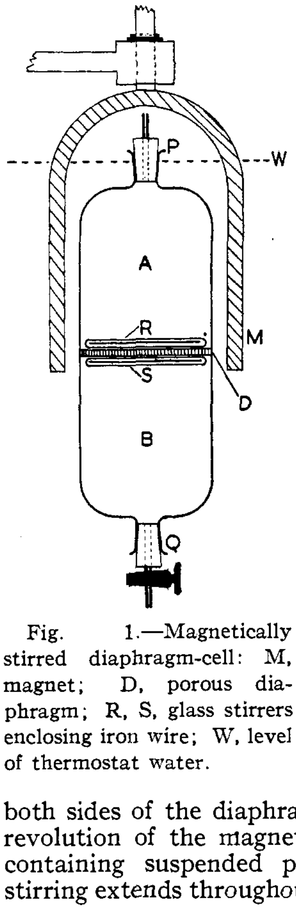

Fig. 1.—Magnetically stirred diaphragm-cell: M, magnet; D, porous diaphragm; R, S, glass stirrers enclosing iron wire; W, level of thermostat water.

Since earlier workers[5,8] have found that stopcock grease causes the diaphragms to behave erratically, the two necks of the cell are closed by rubber stoppers. As the neck diameter is only about 8 mm., it is possible by pushing the stopper in to a definite mark on the neck to reproduce the volume within 0.01–0.02 ml. However, in order to avoid disturbing the liquid in the diaphragm when withdrawing or inserting the stoppers, they are fitted with capillary outlets. That of the lower stopper is normally closed by a small stopcock, which is opened prior to removing the stopper. The upper capillary opens to the air above the thermostat, thus permitting the slight changes of volume which sometimes occur during diffusion. The small stopcock has to be greased lightly, but the grease does not readily work its way along the two or three cm. of fine tubing to the cell.

To set up the cell, stocks of solution and distilled water are freed from gas on the water-pump, and the cell is filled with solution and pumped out from the upper end to remove bubbles from the diaphragm. Some gas is usually left in compartment B after this operation: it is removed by refilling A, closing it with a temporary stopper, then inverting the cell, refilling B, pushing the stopper home to the mark and closing the stopcock. After thermostating for ten minutes the solution in A is sucked off and replaced by distilled water after several rinses. In withdrawing liquid from A, care is taken not to allow the suction tube to rest on the diaphragm, as this might disturb the liquid in it. The cell is then set under the magnet in a thermostat controlled to 0.01° for a preliminary diffusion of a few hours duration. The cell is then removed from the magnet but kept in the thermostat, while the solution in A is again replaced, after repeated rinsing, with gas-free water at the thermostat temperature. The run is taken as beginning when the final replacement occurs, and within half a minute the cell can be placed under the magnet and the stirring begun again. After a run of one to four days, the cell is removed and the rims of the necks are wiped with filter paper. End A is drained into a sample bottle, and the run is taken to end at this point. Then the cell is held with end B uppermost, the stopcock is opened and the stopper Q withdrawn. Solution immediately begins to drip through the diaphragm, which stops any further diffusion from the diaphragm into B during the removal of a sample from this compartment. The whole operation to this point can be completed within a minute of removal from the thermostat, so that no significant error is introduced by the slightly indefinite nature of the exact moment of beginning or ending a run of over a thousand minutes.

II. Effect of Stirring Rate.—A rate of 50 revolutions a minute was adopted for the main work. This choice is justified by the data plotted in Fig. 2, which show the effect of varying the stirring rate from 5 to 80 r. p. m. when

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(8) G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.* (*London*), **A168**, 401 (1938).

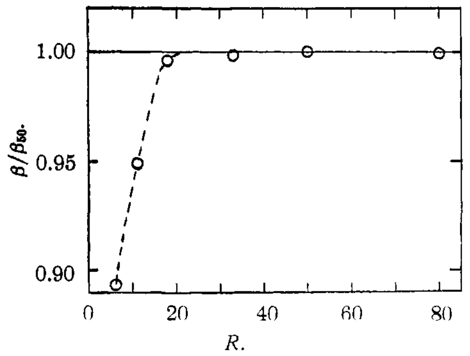

Fig. 2.—Effect of stirring-rate on the cell-constant: R is stirring rate, revs. per minute; β/β_{50} is cell constant relative to the value at the standard rate of 50 r. p. m.

diffusing 0.1 N potassium chloride into water. There is clearly a threshold rate of about 25 r. p. m., below which stirring is inadequate, but above which the rate is without further effect. It is also clear that even the fastest rate, 80 r. p. m., does not have the effect of forcing liquid through a no. 4 diaphragm. For comparison with the effect of density stirring, cells were set up as shown in Fig. 3, with the solution in the upper compartment and with a fine capillary leading from the lower compartment to above the surface of the thermostat. These cells were stirred by gravity only, but in order to preserve the volumes unchanged the stirrers were left in; owing to the inversion of the cells they were not in contact with the diaphragm. Using the cell to which Fig. 2 refers, this method gave an apparent diffusion coefficient for 0.1 N potassium chloride 6.4% lower than that obtained by adequate magnetic stirring. But—an important point—when 0.1 N hydrochloric acid was used, the density-stirred result was 8.4% lower than the magnetic stirring gave, and with 0.01 N hydrochloric acid, 11.4% lower. These results prove that density stirring cannot be relied upon when different electrolytes are being compared. They also go a long way toward clearing up the apparent anomaly in the diffusion of hydrochloric acid,[5] since they show that a density-stirred cell calibrated with 0.1 N potassium chloride will yield results from two to five per cent. low when used for hydrochloric acid in the range 0.01 to 0.1 N.

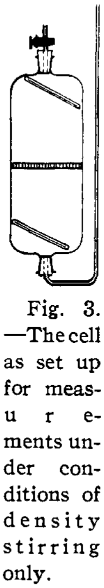

Fig. 3.—The cell as set up for measurements under conditions of density stirring only.

III. Bulk Flow Through the Diaphragm.—With the arrangement of Figure 3, it is possible to set up a cell with the denser liquid above the diaphragm, and, by interchanging the stirrers, to use magnetic stirring in addition to the density stirring which also takes place in this position. When diffusing 0.1 N potassium chloride into water, this arrangement gave a result within 0.2% of that obtained with the denser liquid below the diaphragm. (In these tests, as in those described below, the stirrers were driven at the standard speed of 50 r. p. m.) It seems therefore that a density difference of 0.005 g./cc. between the compartments does not produce any significant amount of bulk flow through no. 4 diaphragms. With 2 N sodium chloride diffusing into water, the density difference is some fifteen times as great, and in this case it was found that the inverted position (sodium chloride above diaphragm) gave an apparent diffusion coefficient 1.4 per cent. greater than the normal position (sodium chloride below), indicating that bulk flow had become an appreciable fraction of the total transport. However, Dr. G. S. Hartley pointed out in conversation that slanting positions of the cell should show a greater effect, and suggested that when the denser solution was below, the amount of bulk flow should increase as an approximately quadratic function of the angle by which the diaphragm departed from the horizontal. This prediction was strikingly confirmed by measurements of the apparent diffusion rate of 2 N sodium chloride into water in runs of about twenty-hours duration, as shown in Fig. 4. Clearly the use of diaphragm-cells in a sloping position should be confined to cases where the density difference between the two sides is very small. We may, however, draw from Fig. 4 the reassuring conclusion that errors of a degree or two in levelling the diaphragm will not produce bulk flow exceeding about 0.1 to 0.2% of the total transport. There is no difficulty in levelling with this accuracy by visual observation through the thermostat window. If very large density gradients are present, as for instance with 4 N potassium bromide and water, correspondingly greater care should be taken in levelling.

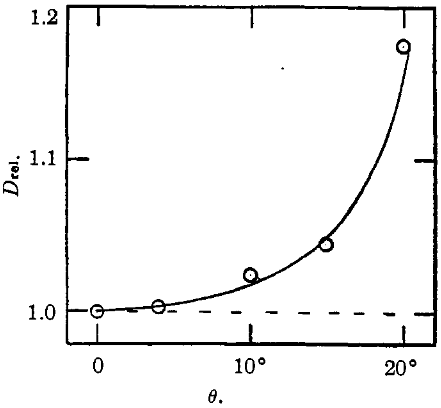

Fig. 4.—Effect of departures of diaphragm from horizontal plane: tests made by diffusing 2 N sodium chloride into water: θ is angle of diaphragm to horizontal; $\bar{D}_{rel.}$ is apparent integral diffusion coefficient, relative to the value obtained with the diaphragm horizontal.

IV. Choice of the Standard for Calibration of Diaphragm-cells.—It has been the general practise to determine the "cell constant" by measuring the rate of diffusion of 0.1 N potassium chloride into water. For experiments of such short duration that the compositions on each side do not change appreciably, the integral diffusion coefficient measured by the diaphragm-cell is readily shown to be related to the true or differential diffusion coefficient D by the relation

$$\bar{D}^0 = (1/c) \int_0^c D\mathrm{d}c$$

Though such vanishingly short runs are of course not experimentally convenient, it is a simple matter to derive from the more complex average diffusion coefficient $\bar{D}$, measured in longer runs, the straightforward concentration-average $\bar{D}^0$. A method of making this small correction (which does not in ordinary cases exceed one per cent.) will be given in detail in a later paper.

For potassium chloride at 25°, tabular integration of the differential diffusion coefficients found by Harned and Nuttall[2] leads to the $\bar{D}^0$ values of Table I. The value of 1.873×10^{-5} cm.^{2} sec.$^{-1}$ is some two per cent. greater than the standard which seemed most reasonable for the 0.1 N calibration solution in the absence of really convincing absolute data, *i. e.*, than Gordon's choice of 1.838. The higher value is however supported by two careful measurements at 20°, by two entirely independent methods. In view of the close agreement of the 25° results with the Onsager–Fuoss theory, it seems perfectly safe to correct the 20° results in question (those of Lamm[9] and of Cohen and Bruins[10]) to 25° by applying the temperature factor demanded by that theory. In practice for solutions below 0.1 N this amounts merely to the simple Nernst[11] factor

$$[T\lambda_+\lambda_-/(\lambda_+ + \lambda_-)]_{25°}/[T\lambda_+\lambda_-/(\lambda_+ + \lambda_-)]_{20°} = 1.126$$

where the λ's are limiting equivalent conductances and the T's absolute temperatures. For Lamm's result this leads to a value of 1.877×10^{-5} sq. cm. sec.$^{-1}$. Unfortunately, though Lamm's result was obtained for 0.1 N potassium chloride diffusing into pure water from an initially sharp boundary, the method by which his optical data are treated to give the diffusion coefficient makes it very hard to decide just what kind of average coefficient it is. Clearly if it is similar to the simple concentration average, the agreement with the Harned and Nuttall figures is close indeed. According to Hartley and Runnicles,[8] the layer analysis method of Cohen and Bruins[10] should give for 0.1 N potassium chloride an average diffusion coefficient corresponding to a diaphragm-cell result for 0.06 N diffusing into water. Accepting this view, the Cohen and Bruins figure, which becomes 1.885×10^{-5} sq. cm. sec.$^{-1}$ on correction to 25°, should be compared with 1.888 computed from the data of Harned and Nuttall.

The value 1.873×10^{-5}, for a very short experiment, corresponds to 1.867×10^{-5} for the case where 0.1 N potassium chloride diffuses into water until the concentrations become 0.075 and 0.025 N (the conditions suggested by Gordon and adopted here for calibrations at 25°), and all results in the present and later papers will be on this basis. The work to be reported covers measurements at 25° on the chlorides and bromides of potassium, sodium, lithium and hydrogen at concentrations up to several normal, but the present paper will discuss mainly those for potassium chloride up to half normal, the range where comparison with the results of Harned and Nuttall is possible. The second row of entries in Table I gives the integral diffusion coefficients of potassium chloride as obtained from the magnetically-stirred cells, corrected to refer to very short duration.

Table I

Integral Diffusion Coefficients for Potassium Chloride Solutions at 25°

c = normality, $\bar{D}^0$ = integral diffusion coefficient for diffusion from concentration c into pure water for a vanishingly short time. (H. and N.) denotes values computed from the differential values of Harned and Nuttall; (S) denotes values obtained in the present work. Values in cm.^{2} sec.$^{-1}$ $\times 10^{-5}$

c	0.01	0.02	0.05	0.1	0.2	0.3	0.5
$\bar{D}^0$ (H & N.)	1.938	1.920	1.893	1.873	1.856	1.849	1.847
$\bar{D}^0$ (S)	1.980	1.937	1.899	(1.873)	1.858	1.848	1.841

V. Evidence for Surface Transport Effects in Dilute Solutions.—From Table I it appears that the diaphragm-cell results agree well with those from the free diffusion experiments in the region above about 0.05 N, but become increasingly high as the concentration is reduced below this limit. In view of the close agreement of Harned and Nuttall's results with the requirements of the Onsager–Fuoss theory[8] there can be no doubt about the correctness of their experimental data; consequently we must conclude that the diaphragm-cell results are wrong in this dilute region. Since doubts about stirring and bulk flow have been removed by the work described above, the natural conclusion is that the large surface of the diaphragm pores, which is of the order of a square meter in the present case, is responsible. This possibility was clearly envisaged by McBain and Liu[12] but their tests of diaphragms of different materials and porosities were made by comparing the diffusion coefficients of 0.1 N potassium chloride, 0.4 N hydrochloric acid, and 0.05 M sucrose, so that they were not in fact in the concentration region where surface effects become significant. Hartley and Runnicles[8] also found some suggestion of such an effect in the range below 0.01 N.

The present work was therefore extended to more dilute solutions to obtain further informa-

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[9] O. Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, IV **10** [6] (1937).

[10] E. Cohen and H. R. Bruins, *Z. physik. Chem.*, **103**, 337 (1923).

[11] W. Nernst, *ibid.*, **2**, 613 (1888).

[12] J. W. McBain and T. H. Liu, This Journal, **53**, 59 (1931).

tion about the phenomenon. However, the potentiometric titration technique used for the analyses was found unsatisfactory for very dilute chloride solutions, the solubility of silver chloride making the end-points rather indefinite. The measurements on solutions below 0.01 N were therefore made with potassium bromide. Diffusion was allowed to proceed until about a quarter of the solute had passed through the diaphragm; the resulting diffusion coefficients are given in Table II. These results are clearly quite incompatible with theory, since the Nernst limit is considerably exceeded. The agreement between different cells is also much poorer than occurs at higher concentrations. (The agreement between the two cells at 0.01 N potassium bromide is probably fortuitous, since four measurements on the chloride gave 1.958, 1.971, 1.986 and 1.994 at this concentration.)

TABLE II

SURFACE EFFECT IN DILUTE POTASSIUM BROMIDE SOLUTIONS

$\bar{D}_{\text{obs.}}$ denotes the observed integral diffusion coefficient for diffusion from an initial concentration c into water. $\bar{D}_{\text{theor.}}$ denotes the corresponding value from the Onsager–Fuoss theory

c	0.000	0.0025	0.004	0.005	0.01
$\bar{D}_{\text{obs.}}$	...	2.083	2.052	2.018	1.996
	...	2.106	2.076	2.041	1.996
$\bar{D}_{\text{theor.}}$	2.018	1.986	1.977	1.971	1.960

Above 0.05 N, as will be shown in a later paper, agreement between different cells was normally ±0.2%.

Valuable confirmation of an anomalously rapid transport mechanism through diaphragms is afforded by recent work of Mysels and McBain,[13] who have made conductivity measurements in a cell with a Pyrex diaphragm interposed between the electrodes. They find that while 0.1 N potassium chloride solutions behave quite reproducibly, 0.0005 N solutions give erratic values which change with time and depend on the previous treatment of the diaphragm. Furthermore they find that the ratio of the conductance of the 0.0005 N solution to that of the 0.1 N is five to ten per cent. higher than that found in the absence of the diaphragm. Surface conductivity is ascribed to the double layer, and should therefore depend on the pH; it is interesting to note that diffusion measurements on hydrobromic acid, carried out along with those described above, showed a much smaller enhancement of the diffusion coefficient as compared with theory. Dr. A. E. Alexander of the Department of Colloid Science of this University has pointed out to me that this is consistent with the fact that acid solutions in the range 0.01 to 0.001 N are closer to the isoelectric point of Pyrex, so that surface effects should be reduced as compared with neutral solutions.[14]

The conclusion therefore seems inevitable that the diaphragm-cell technique must be restricted to solutions of concentration greater than 0.05 N if an accuracy of the order of 0.2% is aimed at, at least with electrolytes. There is however no reason to doubt the accuracy of the method for solutions of higher concentration, and indeed Table I provides positive evidence of this.

I am indebted to Dr. J. N. Agar of this Department for many helpful discussions, and to Messrs. Imperial Chemical Industries Ltd. for a grant of funds and equipment.

Summary

An improved type of porous-diaphragm diffusion-cell, embodying a magnetically operated stirring system, is described. The necessity for stirring is demonstrated by comparing the rates of diffusion of potassium chloride and hydrochloric acid under conditions of "density-stirring" and mechanical stirring in the same cell. The conditions under which transport by bulk flow through the diaphragm becomes a serious source of error are determined experimentally. The recent absolute diffusion measurements of Harned and Nuttall are used to compute integral diffusion coefficients for potassium chloride solutions, which are compared with those given by the present technique. It is concluded that the diaphragm-cell results agree with the absolute data above 0.05 N, but become increasingly high at greater dilutions. This is ascribed to a surface transport effect, further evidence for which is provided by measurements on more dilute solutions and by recent work of Mysels and McBain.

CAMBRIDGE, ENGLAND RECEIVED JULY 7, 1949

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(13) K. J. Mysels and J. W. McBain, *J. Coll. Sci.*, **3**, 45 (1948).

(14) Footnote added in proof: Since this paper was submitted, independent evidence for anomalous transport through sintered diaphragms has been obtained by the use of radioactive tracer techniques—see A. W. Adamson, J. W. Cobble, and J. M. Nielsen, *J. Chem. Phys.*, **17**, 740 (1949).