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A Remeasurement of the Self-diffusion Coefficients of Sodium Ion in Aqueous Sodium Chloride Solutions

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A new diffusion apparatus for measuring the self-diffusion coefficients of Na^+ ion in aqueous sodium chloride solutions by means of open-ended capillaries has been designed and developed. By proper selection of flow rate over the capillaries, a series of coefficients for the above ion have been evaluated. These values, over the concentration range 0.02 to 4 M now agree with those obtained from diaphragm cells. Measurements of the coefficients using the diaphragm cell method have been extended and subjected to additional tests in the high concentration region.

In a recent paper Mills and Adamson[1] have given a critical survey of the methods used in determining self-diffusion coefficients of ions in solution and have presented the results of their investigations into the disagreement existing between values obtained by the diaphragm and open-ended capillary methods. Their work involved primarily a remeasurement of $\mathfrak{D}_{Na^+}$ in sodium chloride solutions with the diaphragm cell and a preliminary study of the source of error leading to the higher results obtained with open-ended capillaries. Evidence was provided that convectional losses might be responsible for these high values and in this complementary paper a systematic study of this aspect of the problem is presented. Confirmation and extension of the diaphragm cell results have also been undertaken.

Experimental

Open-ended Capillary Apparatus.—In order to minimize the effect of turbulent convection of solution at the mouths of the capillaries, an apparatus has been designed to provide a streamlined flow over their faces. The principle of design is similar to that used in wind-tunnels for aerodynamic research, in which a large stilling volume of fluid is provided to even out turbulent eddies and currents. The two propellers beneath the grating in a small compartment A circulate solution downwards and then through another grating into the large stilling compartment B of 6–7 liters volume. The liquid in the top section of B flows into A through a slot C in the partition between the two compartments. The capillaries are lowered into this slot in a vertically moving holding device which controls the amount of solution spilling over, by its depth below the surface. A pulley system connected to the propeller shafts allows a range of speeds to be obtained and by these two devices the flow rate can be controlled at will. Tests with potassium permanganate crystals and illuminated bubbles demonstrate that the fluid flow through this slot is essentially streamlined in character. Operating conditions are such as to ensure that the flow adjacent to the capillary surfaces is laminar. The faces have been ground as flat and smooth as possible and rounded off at the edges. A threaded bolt in the top of the apparatus allows the capillary holding device to be lowered slowly into and raised from the bath solution. In this way it was hoped that boundary formation and breaking would be less apt to produce convection, the effect of which has previously been discussed by Mills and Kennedy[2] and Mills and Adamson.[1] A midway position has the effect of submerging the capillaries almost to their rims to allow temperature equilibrium to be reached before complete immersion. The body of the apparatus as well as the partitions and gratings have been made of Perspex sheet and all metal parts of stainless steel.

The velocity of solution flow across the gap C was measured by observing the movement of oil droplets. These droplets consisted of a mixture of benzene and carbon tetrachloride so adjusted as to have the density of the solution under examination. When injected into the solution in the vicinity of the gap, a fine spray of droplets is formed which then move across it in parallel straight paths normal to its leading edge. For ease of observation the bubbles were illuminated with a strong light. By use of a stopwatch, a large number of measurements were made of times of transit of individual bubbles over a known distance within the gap and at approximate height of the capillary faces. Velocities measured were in the range 0 to 8 mm./sec.

The analysis of the radioactive solutions in the capillaries follows essentially the same method as described in the above two papers.

Diaphragm Cells.—The cells were stirred magnetically and were essentially similar to those developed by Stokes[3] with some small modifications. Following a suggestion by Stokes[4] the use of grease (usually regarded as a source of error) has been almost entirely eliminated. This has been achieved by sealing the compartments with ground glass stoppers which were fitted very precisely and shown to be water-tight under vacuum. The glass sinters used were of "F" grade. A geared stirring mechanism was developed which could provide stirring speeds in the range 50–110 r.p.m. and constant to ± 1 r.p.m. when connected to a stabilized voltage source. Difficulty has been experienced at higher stirring speeds using the ordinary "horseshoe" type magnet with its rather diffuse field, due to the riding up of the magnets away from the diaphragm surface. In this work the trouble has been eliminated by using very small and powerful magnets[5] which are carried round the circumference of the sinter by a metal framework.

The general filling and sampling procedure was essentially the same as that described by Mills and Adamson.[1] Calibrations, using potassium chloride solutions, have again been made over a concentration range. The chloride contents of the samples have been determined by the potentiometric method described by Stokes.[3,4] Cell constants have been redetermined after long periods of use and show about a 1% increase per 1000 hours, which is similar to that found by Stokes.[6] A graph showing the variation of cell constant with hours of use was constructed and the appropriate cell constant for each run obtained by interpolation. Measurements of radioactive material were made by accurately pipetting 10-ml. aliquots of the solutions into test-tubes and counting in the liquid phase in a well-type scintillation counter.

Experiments using the two diffusion methods were performed side by side in a constant temperature bath which was controlled to ±0.01°. The bath temperature was standardized to 25° by calibration of a Beckmann thermometer against a standard (N.S.L. (Aust.) Certificate) thermometer. All solutions used in these diffusion experiments were carefully defibered by filtration through glass sinters and also degassed with a water pump immediately before use.

The tracer isotope used in both series of experiments was radiosodium Na^{22} and was obtained in aqueous solution as sodium chloride from the Radiochemical Centre, Amersham, England.

Results and Discussion

Calibration of Diaphragm Cells.—Mills and Adamson[1] have shown that "cell constants" deter-

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(1) R. Mills and A. W. Adamson, THIS JOURNAL, **77**, 3454 (1955).

(2) R. Mills and J. W. Kennedy, *ibid.*, **75**, 5696 (1953).

(3) R. H. Stokes, *ibid.*, **72**, 763 (1950).

(4) R. H. Stokes, private communication.

(5) These magnets were made of a synthetic magnetic material with the trade name "Ferroxcube" and kindly supplied by Phillips Electrical Industries Pty. Ltd., Sydney.

(6) R. H. Stokes, THIS JOURNAL, **72**, 2243 (1950).

mined over a range of concentrations are indeed constant, except for an increase of about 1% in dilute solutions. In this parallel series of experiments, cell constants have been measured over similar ranges of concentration using as a calibrating standard Gosting's[7] differential values for potassium chloride diffusion. Constancy over a concentration range is again evident as shown in Table I, but with the same *ca.* 1% increase in dilute solutions, and of course the increase due to aging already mentioned. In this table, c_1 and c_2 are the initial concentrations of the solutions in the compartments, $\overline{\mathfrak{D}}$ the integral diffusion coefficient calculated from Gosting's curve and K the cell constant. It seems likely that this apparent increase in cell constant in dilute solution can be attributed to anomalous surface transport of ions on the glass sinter. The effect is quite marked for more dilute electrolyte solutions (<0.05 *M*) as has been described by Stokes[3] and also by Nielsen, Adamson and Cobble.[8] Its magnitude should be dependent on the fineness of the sinter and the nature of the ions, and in many cases may not be significant at concentrations as high as 0.1 *M*. It would seem valid, therefore, to use at all concentrations, the cell constants determined in the ranges above 0.1 *M* KCl where the effect is negligible. Use of these constants would raise the value of $\mathfrak{D}_{Na^+}$ in 0.1 *M* NaCl, as given by Mills and Adamson[1] from 1.292 to 1.305 × 10^{-5} cm.²/sec. This correction has been applied in Fig. 1.

TABLE I

CELL CONSTANTS FROM DIFFERENTIAL DIFFUSION OF KCl

c_1 moles/l.	c_2	$\overline{\mathfrak{D}} \times 10^5$ (cm.²/sec.) Gosting	K
0.1	0	1.866	0.0346
0.1	0	1.866	.0345
0.5	0	1.842	.0339
0.5	0	1.841	.0339
2.0	0	1.899	.0341
3.5	2.0	2.097	.0341
0.7	0.2	1.849	.0346[a]
0.7	0.2	1.847	.0350[a]

[a] After 3000 hours use.

There remained some doubt concerning the value of the cell constant determined by Mills and Adamson[1] in dilute sodium chloride solutions using Clack's[9] data. This constant was 5% higher than the constants determined with the same data for high NaCl concentration and also with Gosting's KCl data. We have since noted that Harned and Nuttall[10] found a similar discrepancy when comparing their data for differential diffusion for dilute KCl solutions with Clack's values, and they concluded that his figures were probably 4% low. If his NaCl values in this dilute concentration region were also low by the same percentage, it would also cause an erroneous 4% increase in Mills and Adamson's cell constant. If a correction is made on this assumption, the cell constant in dilute solution is no longer anomalous but agrees within experimental error with all other values of the cell constant in regions of concentration >0.1 *M*. The constancy of these cell constants over many regions of concentration for KCl diffusion gives an indirect confirmation of the consistency of Gosting's figures.

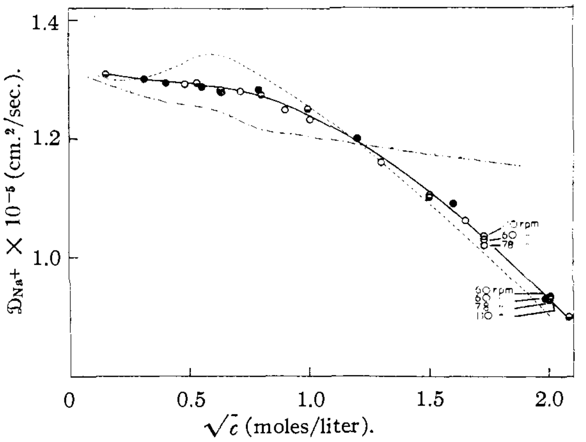

Fig. 1.—Self-diffusion coefficients of Na⁺ in aqueous sodium chloride at 25°: ●, Mills and Adamson (diaphragm cell); ○, this work (diaphragm cell); ⊖, this work (open-ended capillary); ------, curve of Wang and Miller; – – – – –, curve of Nielsen, Adamson and Cobble.

Stirring Speed Effect.—Nielsen, Adamson and Cobble[8] found that when using stirring speeds >60 r.p.m. in concentrated solutions, they obtained higher values of $\mathfrak{D}$, and that these became constant at speeds of about 80 r.p.m. They assumed therefore that these higher stirring speeds were necessary to keep the compartment solutions uniform in this viscosity range. However Adamson and Mills,[1] who used 60 r.p.m. throughout their experiments, found when calibrating their cells in the high concentration region with both NaCl and KCl solutions that they obtained cell constants similar to those in dilute solutions. This seemed to indicate that 60 r.p.m. was a sufficiently rapid speed at all concentrations. To verify this evidence, for two concentrations (3.0 and 4.0 *M*) stirring speeds have been varied and a direct comparison of the $\mathfrak{D}_{Na^+}$ values obtained. By this study it has been shown conclusively that increasing the stirring speed from 60 to 110 r.p.m. does not increase the value of $\mathfrak{D}_{Na^+}$ within experimental error in this concentration range. The results are given in Table II and shown also in Fig. 1. It will be observed that the values at all speeds are virtually the same

TABLE II

SELF-DIFFUSION OF Na^{22} AT 25°

c, moles/l.	Stirring speed, r.p.m.	$\mathfrak{D}_{Na^+} \times 10^5$, cm.²/sec.	c, moles/l.	Stirring speed, r.p.m.	$\mathfrak{D}_{Na^+} \times 10^5$, cm.²/sec.
0.23	60	1.294	3.00	60	1.033
0.50	60	1.279	3.00	78	1.019
0.81	60	1.247	3.00	110	1.036
1.00	60	1.234	4.00	60	0.936
1.69	60	1.161	4.00	78	0.923
2.25	60	1.110	4.00	110	0.932
2.72	60	1.061			

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(7) L. J. Gosting, THIS JOURNAL, **72**, 4418 (1950).

(8) J. M. Nielsen, A. W. Adamson and J. W. Cobble, *ibid.*, **74**, 446 (1952).

(9) B. W. Clack, *Proc. Phys. Soc.*, **36**, 313 (1924).

(10) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **71**, 1460 (1949).

and agree with Mills and Adamson's values, and the capillary values measured in this work. The reason for Nielsen, Adamson and Cobble's higher values (of the order of 20% at 4 *M* NaCl) is inexplicable but a lead to the source of error may be found in the fact that they rotated their cell keeping magnet stirrers stationary, whereas in these investigations the reverse and more usual procedure has been followed.

Extension of Measurements.—The measurement of $\mathfrak{D}_{Na^+}$ in NaCl solutions begun by Mills and Adamson[1] has been considerably extended over the whole concentration range. Values so obtained have been found to fall consistently on the curve connecting $\mathfrak{D}$ and $\sqrt{c}$. The values are given in Table II and the complete curve plotted in Fig. 1. The precision of these results averages ±0.5%, the error quoted in this and subsequent tables being the root mean square deviation.

Open-ended Capillary Measurements.—The preliminary studies of Mills and Adamson[1] have shown that capillary measurements of the differential diffusion coefficients of NaCl and KCl are higher (on an average by about 4%) than the values given by optical and diaphragm methods. The most likely cause of error producing high results would seem to be mechanical convection at the mouth of capillaries due to unduly fast or turbulent stirring of the outer solution. Although some workers[1] have used no stirring at all, it would seem that a definite fluid movement of the outer solution ought to be maintained to prevent a local concentration of the diffusing species being built up at the mouth of the capillary. The equations used to calculate $\mathfrak{D}$ are of course based on the premise that the bath solution which extends outwards from the plane of the face of the capillaries is of constant composition. On the other hand too vigorous or turbulent stirring may scoop out diffusate mechanically from the bore of the capillary. Previous workers[1] who have considered the problem have usually tried to eliminate the effect by using capillaries of different length and then adjusting the stirring speed until the measured $\mathfrak{D}$'s agree within experimental error. This method is not entirely satisfactory, however, because of the ±2% uncertainty in measuring the coefficients which is probably of the same order of magnitude as the effect.

In this investigation a different approach to the problem is presented. An apparatus was designed to provide over the capillaries a streamlined flow which could be controlled to any required fluid velocity. In addition laminar flow over the capillary faces was obtained by suitably fixing such parameters as the diameter of the capillary faces and the velocity of the fluid over them. By these two modifications a flow was provided which would sweep away diffusing material while producing only a minimum of turbulence.

Experiments with varying flow rates at a particular concentration show a definite trend in the value of $\mathfrak{D}_{Na^+}$. These values which have an average precision of ±0.8% are tabulated in Table III.

It will be observed that the values of the coefficients increase with flow rate and straddle the new diaphragm cell curve. The one question remaining is to specify which liquid velocity gives valid diffusion coefficients. Some experiments were made using Gosting's differential values of KCl as a basis for determining the correct flow rate but these were not entirely satisfactory. The titration errors involved in the potentiometric analyses of the capillary contents (*ca.* 10 λ of 0.2 *M* *KCl solution) are each of the order of 1% and so do* not allow an unequivocal statement of correct flow rate to be made. For instance a value of 1.850 ± 0.040 was obtained at a flow rate of 2.8 mm./sec. for 0.5 *M* KCl diffusing into 0.2 *M* compared with the value of 1.846 calculated from Gosting's curve. The limits of error are of course too great to give any certainty to a calibration figure of this type.

TABLE III

VARIATION OF $\mathfrak{D}_{Na^+}$ WITH FLOW RATE

c, moles/l.	Flow rate (mm./sec.) 0	0.5–1	1–3	6–8	Diaphragm value, this work
0.286	1.234	1.283	1.293	1.309	1.290
0.400			1.282	1.293	1.285
0.638	1.247	1.265	1.273		1.270
4.373		0.870	0.905	0.931	0.895[a]

[a] From extrapolation of curve.

It would be desirable to be able to calibrate the capillaries for flow rate by an independent method (optical or conductometric). Present limitations on this type of calibration are firstly the difficulty of finding a solution to the capillary diffusion equation where $\mathfrak{D}$ is a function of concentration and secondly the precision of the available analytical techniques in the only suitable case where $\mathfrak{D}$ is reasonably constant. However, when these limitations are overcome, an attempt will be made to confirm the correct flow rate by such an independent calibration.

Meanwhile, the following method has been adopted. Since the capillary values given in Table III straddle the diaphragm cell curve, the flow rates at which the former values fall along the curve have been measured over the whole concentration range (0.02–4.373 *M*). It was found that this agreement is obtained with the narrow velocity range, 1–3 mm./sec. The inference that can be drawn is that this figure is very close to the correct one.

The capillary and diaphragm values obtained in this work are now plotted on the one curve in Fig. 1 and tabulated in Table IV which shows correspondence along the entire length using the above velocity range.

TABLE IV

SELF-DIFFUSION COEFFICIENTS OF Na^{22} AT 25°

Flow rate of 1–3 mm./sec.

c, moles/l.	$\mathfrak{D} \times 10^5$, cm.²/sec.	*c* moles/l.	$\mathfrak{D} \times 10^5$, cm.²/sec.
0.023	1.310 ± 0.005	0.981	1.251 ± 0.008
.286	1.293 ± .004	2.270	1.104 ± .010
.400	1.282 ± .008	4.373	0.905 ± .007
.638	1.273 ± .010		

It will be noted from the values of $\mathfrak{D}_{Na^+}$ tabulated in Table IV that the precision of the capillary method has been improved from *ca.* ± 2 to ±0.8%

and is in fact now mainly limited by the statistical counting error. This improvement is probably attributable to the provision of streamlined flow and to the use of solution counting procedures.

An explanation for Wang and Miller's[11] agreement with these values in very dilute regions and the divergence of their curve at about 0.2 *M* is not easy to obtain. Experience with the capillary method has shown that it is quite sensitive to operating conditions; for instance, as well as the effect of flow rate, there may be incomplete defibering and degassing of solutions which can lead to anomalous high results.

No discussion of the final $\mathfrak{D}_{\mathrm{Na}^+}$ values and their concentration dependence will be made at this time. However, the almost linear dependence of $\mathfrak{D}_{\mathrm{Na}^+}$ with *c*, up to concentrations of 4 *M* is noteworthy, as well as the extrapolation of the points on the same plot to the Nernst limiting value. The linear relation between $\mathfrak{D}\eta/\eta_0$ and $\sqrt{c}$ found by Mills and Kennedy[2] for unhydrated ions is not observed.

Acknowledgments.—I wish to acknowledge the help given me by Capt. F. D. Bethwaite in designing the capillary apparatus and by Mr. M. Vernon who performed many of the analyses.

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[11] J. H. Wang and Sara Miller, THIS JOURNAL, **74**, 1611 (1952).

[CONTRIBUTION NO. 51 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

3-Methyl-2-thiabutane: Calorimetric Studies from 12 to 500°K.; the Chemical Thermodynamic Properties from 0 to 1000°K.[1]

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The chemical thermodynamic properties of 3-methyl-2-thiabutane were investigated between 0 and 1000°K. Low temperature calorimetric studies were made from 12 to 344°K., and values were obtained of the heat capacity in the solid and liquid states [C_{satd}], the heat of fusion (2236 cal. mole^{-1} at the triple point, 171.65°K.), and the entropy of the liquid at saturation pressure at 298.16°K., 62.88 cal. deg.$^{-1}$ mole^{-1}. From flow calorimetric studies, there were obtained values of the heat of vaporization (ΔH_{v}), heat capacity in the ideal gaseous state [C_{p}°], and the second virial coefficient [$B = V(PV/RT - 1)$]. Some of the results are represented by the following empirical equations: (A) C_{satd} (liq.) $= 50.83 - 0.16245T + 5.951 \times 10^{-4} T^2 - 5.318 \times 10^{-7} T^3$, cal. deg.$^{-1}$ mole^{-1} (177–344°K.); (B) $\Delta H_{\mathrm{v}} = 10{,}761 - 4.661\,T - 0.01369\,T^2$, cal. mole^{-1} (318–358°K.); (C) $C_{\mathrm{p}}^{\circ} = 3.78 + 9.489 \times 10^{-2}\,T - 3.944 \times 10^{-5}\,T^2$, cal. deg.$^{-1}$ mole^{-1} (347–500°K.); and (D) $B = 211 - 147.0 \exp(800/T)$, cc. mole^{-1} (318–500°K.). The entropy in the ideal gaseous state at 298.16°K., 85.87 cal. deg.$^{-1}$ mole^{-1}, and the standard heat of formation from graphite, hydrogen and gaseous diatomic sulfur, −36.83 kcal. mole^{-1} at 298.16°K., were computed from these data and heat of combustion data to be reported elsewhere. Values of the functions $(F^{\circ} - H_0^{\circ})/T$, $(H^{\circ} - H_0^{\circ})/T$, $H^{\circ} - H_0^{\circ}$, S° and C_{p}° were computed from spectroscopic and molecular structure information. The parameters required to describe restricted internal rotation and to evaluate anharmonicity corrections were chosen to give agreement between calculated and experimental values of the entropy and vapor heat capacity. Values of the heat, free energy and equilibrium constant of formation of 3-methyl-2-thiabutane were computed from the calculated thermodynamic functions and the experimental value of heat of formation at 298.16°K.

Investigations of the thermodynamic properties of selected organic sulfur compounds are being conducted in this Laboratory. Intensive studies are made of those compounds that will yield data required in approximate calculations[2] of the properties of entire families of sulfur compounds. Attention is now being given to the seven isomeric $C_4H_{10}S$ thiols and sulfides—the most useful group of compounds for obtaining information regarding the effects of structural isomerism on thermodynamic properties. Data for this group of isomers may also find application in the construction of theories on the origin of petroleum; for it will be possible to compare calculated equilibrium concentrations of the $C_4H_{10}S$ compounds with those found in crude oil.[3]

Published reports on the thermodynamic properties of the $C_4H_{10}S$ isomers give results obtained in studies of 3-thiapentane[4] and 2-methyl-2-propanethiol.[5] A forthcoming article[6] will present the results of concurrent determinations of the heats of combustion, formation and isomerization, at 298.16° K., of all seven isomers. This paper reports thermodynamic data for 3-methyl-2-thiabutane (methyl isopropyl sulfide), another member of the group of $C_4H_{10}S$ isomers. Thermal data have previously been published for two lower alkane sulfides, 2-thiapropane[7] and 2-thiabutane.[8] The present investigation included experimental studies of 3-methyl-2-thiabutane that provided (1)

[1] This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties" which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] *E.g.* (a) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); (b) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

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[4] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **74**, 4656 (1952).

[5] J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **75**, 1818 (1953).

[6] W. N. Hubbard, W. D. Good, F. R. Frow and Guy Waddington, to be published.

[7] (a) D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942); (b) G. M. Barrow and K. S. Pitzer, *Ind. Eng. Chem.*, **41**, 2737 (1949); (c) J. L. Binder, *J. Chem. Phys.*, **18**, 77 (1950).

[8] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).