Northrup Model 7662 *p*H meter equipped with a special glass electrode for high *p*H range. The *p*H meter was calibrated with a standard buffer solution, 0.05 *M* sodium tetraborate decahydrate *p*H 9.18 ± 0.01 at 25°.[10]

The results are summarized in Tables II and III. The calculations were based on methods discussed by Glasstone.[11,12]

TABLE II

CF_3CH_2OH, 25.00 ml. of a 0.0323 *M* Solution

Run	0.100 *N* NaOH, ml.	*p*H	μ	$K \times 10^{-13}$ mole/liter
I	1.00	11.20	0.00385	4.6
	3.00	11.71	.0107	4.1
	5.00	11.94	.0167	3.9
	7.00	12.10	.0219	3.6
II	2.00	11.54	.0080	4.4
	4.00	11.84	.0138	4.0
	6.10	12.03	.0196	3.8
	8.10	12.17	.0245	3.3

The ionization constant of 2,2,2-trifluoroethanol was obtained by plotting the ionic strength, μ, *versus* K and extrapolating to $\mu = 0$. In the case of the diols, the ionization constants were calculated by means of an equation of the form $K_1K_2 + AK_1 - B$, where A and B are calculated from the experimental data.[11] B was plotted against A and the slope of the straight line obtained was K_1 while the intercept was K_1K_2.

TABLE III

$HOCH_2(CF_2)_2CH_2OH$, 25.00 ml. of a 0.123 *M* Solution

0.100 *N* NaOH, ml.	*p*H, measured	$A \times 10^{12}$[a]	$B \times 10^{24}$[a]
1.00	10.52	4.6	3.95
2.00	10.78	2.5	2.3
3.00	10.99	1.5	1.3
4.00	11.11	2.2	1.8
5.00	11.21	0.88	0.81
6.00	11.31	0.68	0.61

$HOCH_2(CF_2)_4CH_2OH$, 25.00 ml. of a 0.253 *M* Solution

0.100 *N* NaOH, ml.	*p*H, measured	$A \times 10^{11}$	$B \times 10^{25}$
1.00	11.12	11	8.8
2.00	11.45	4.5	4.2
3.00	11.62	3.1	2.7
4.00	11.74	2.2	2.1
5.00	11.84	1.6	1.7

[a] $A = \frac{1 - R}{2 - R} a_{H^+}$; $B = \frac{R}{2 - R} (a_{H^+})^2$; $R = \frac{a_{OR^-} - a_{OH^-}}{C_{HOR} + a_{OR^-}}$

LAFAYETTE, INDIANA

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[10] S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 327.

[11] S. Glasstone, *ibid.*, p. 350.

[12] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 980.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Self-diffusion Coefficients of the Ions in Aqueous Sodium Chloride and Sodium Sulfate at 25°

BY JULIAN M. NIELSEN,[1] ARTHUR W. ADAMSON AND JAMES W. COBBLE

Procedures are reported whereby the diaphragm cell technique may adequately be adapted to the measurement of ion self-diffusion coefficients in aqueous solution through the use of isotopic labelling of an ion. The problems of stirring and of calibration are discussed: two methods of mechanical stirring are shown to give values of the cell constant that are the same for mean diffusion and for self-diffusion experiments, and two calibration methods, by mean diffusion and by conductance, are shown to give accurate self-diffusion constants. Enhancement of the apparent self-diffusion coefficient at low concentrations is reported and discussed as a surface transport process. The presence of the effect limits the range of concentrations over which accurate solution diffusion coefficients can be determined. Values for the self-diffusion coefficients of Na^+ and Cl^- ions in aqueous sodium chloride and of Na^+ and $SO_4^=$ ions in aqueous sodium sulfate at 25 ± 0.01° are reported for concentrations up to 3 *N*. The results are compared with existing limiting laws and with mean diffusion coefficient data.

The study of ion self-diffusion in electrolyte solutions has received increasing attention during recent years. By means of the convenient diaphragm cell technique, values have been obtained for Na^+ ion in aqueous sodium chloride[2] and sodium iodide,[3] and for Ag^+ ion in aqueous silver nitrate,[4] at 25°, while by the more elaborate, but absolute, free diffusion method, early values are available for Na^+ and Cl^- ions in aqueous sodium chloride at 35°[5] and, recently, for Na^+ and I^- ions in aqueous sodium iodide at 25°.[6] The work presented here comprises results for Na^+ and Cl^- ions in sodium chloride solutions which, being more accurate, supplant those briefly reported previously,[2] results for Na^+ and $SO_4^=$ ions in sodium sulfate solutions, and a detailed experimental analysis of the sources of systematic error involved in the diaphragm method for the determination of self-diffusion coefficients.

Experimental

Apparatus and General Procedure.—The diaphragm cells used were of the type shown in Fig. 1 and described earlier by McBain and Dawson[7]; they consisted of a Pyrex glass cylinder divided into two 25-ml. compartments by means of a medium to fine Corning sintered glass disk. The volumes were determined by filling each compartment in turn with mercury and weighing. Each compartment had two small attached stopcocks, thus permitting filling or emptying without disturbing the liquid in the diaphragm. The general procedure was as follows. One compartment was filled with labeled solution by means of a pipet, after rinsing with four small portions, each of which was drawn through the sintered disk. The stopcocks were closed, and the other compartment filled with unlabeled solution, again after several rinsings. Two to four hours of preliminary

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[1] This paper is based in part on a portion of a dissertation submitted by Julian M. Nielsen, a Frederick Gardner Cottrell Fellow, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Southern California. Present address: Michelson Laboratory, Naval Ordnance Test Station, Inyokern, California. Send inquiries to the second author.

[2] A. W. Adamson, J. W. Cobble and J. M. Nielsen, *J. Chem. Phys.*, **17**, 740 (1949).

[3] A. W. Adamson, *ibid.*, **15**, 762 (1947).

[4] S. G. Whiteway, D. F. MacLennan and C. C. Coffin, *ibid.*, **18**, 229 (1950).

[5] L. P. Jehle, Ph.D. Dissertation, University of Calif., Berkeley, 1938.

[6] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

[7] J. W. McBain and C. R. Dawson, *ibid.*, **56**, 52 (1934).

diffusion were allowed, after which the initially unlabeled solution was drained out, the compartment rinsed with fresh solution (at thermostat temperature), and refilled. Diffusion was allowed to proceed until about 25% of the tracer had passed through the diaphragm (two to five days in time), the tips of the stopcocks carefully cleaned of thermostat liquid, and the compartments drained in a manner so as to leave the contents of the diaphragm undisturbed. The cells were thermostated in a water-bath at 25 ± 0.01°.

Mean diffusion experiments were carried out similarly, except that one compartment was filled with the solution in question, and the other with water; the latter was replaced after the preliminary diffusion period.

Nearly all points were determined in duplicate; for all such points the average value is given, with the per cent. deviation.

The solutions within the cells were stirred by one of several procedures. The first, to be referred to as "*alternate rotation*" stirring, consisted of rotating the cells about the long axis, which was made horizontal, in the case of self-diffusion experiments. A one to two mm. diameter glass rod was placed in each compartment, and to further increase their effectiveness, the direction of rotation was reversed every four turns (not abruptly, but with a short delay interval). With this arrangement, as is discussed later, the standard rotational speed was 60 r.p.m. The procedure was adapted to mean diffusion runs by mounting the cells, without the glass rods, with the long axis accurately vertical and rotating as described above. The solution was placed in the upper compartment.

The second procedure was a modification of the Stokes method,[8,9] referred to here as "*magnetic*" stirring. The cells were again rotated about the long axis, which, however, was now made vertical. A sealed glass tube containing iron wire was inserted into each compartment, the buoyancies of the two tubes being such that each rested *lightly* against the diaphragm. The tubes, immobilized by means of a stationary magnet mounted so that the cell was between the poles, swept the upper and under surfaces of the diaphragm with each turn of the cell. Again, as discussed later, a standard speed of 60 r.p.m. was employed. This procedure was employed without modification for mean diffusion runs; the solution was placed in the lower compartment.

Stokes reported that the constant contact of the stirrers caused only a slow wear of the diaphragm; we find, similarly, that over a period of some 45 days of use, cell constants remained constant within 1%.

Some experiments were carried out without any mechanical stirring. The cells were mounted vertically and, in mean diffusion runs, the solution was placed in the upper compartment. Some self-stirring occurs because of density and temperature gradients, and the procedure will be referred to as "*density*" stirring.

The determination of diaphragm resistances as a means of evaluating cell constants was achieved by means of a demountable cell. The diaphragm was sealed to standard taper glass joints so that, by the use of the appropriate end sections, conductance, diffusion and transference measurements could be made with the same diaphragm. For the conductance measurements, end sections were used having platinum electrodes cut to the same diameter as the diaphragm and mounted on short, stiff coils of platinum wire joined to tungsten seals. The electrodes were platinized and each was slightly dented in three places along the circumference so that on assembly the platinized area was kept about one tenth of a mm. from the diaphragm. This separation introduced *ca.* 1% error since, on varying it, it was noted that the resistance increased 5% per mm. of total separation of the two electrodes. All the data were corrected for this effect, as well as for the conductance of the water used. The cell was kept in an oil thermostat at 25 ± 0.002°.

The resistance measurements were made with a Leeds and Northrup Jones–Dike Bridge, audio-frequency oscillator, null detector and an oscilloscope. Due to the low resistance of the cell, a standard resistance was added in series.

The diaphragm showed some memory of preceding solutions and, therefore, fresh solution (at temperature) was drawn through the cell at intervals, until on so doing a rapid measurement of the resistance showed no change. The measurements were made with minimum current passage in order to avoid internal heating of the diaphragm and consequent drift in results. With these precautions, the resistances even for the dilute solutions were reproducible over a period of 12 hours. As also noted by Mysels and McBain,[10] there was some effect of treatment with strong acids. In one instance, cleaning with 6 *M aqua regia*, to remove deposited platinum black, changed the resistance by 3% (compare Tables IV and VI).

The end sections used for diffusion measurements converted the demountable cell into a cell of the type shown in Fig. 1. These same end sections were employed for the measurements with metal diaphragms. The metal diaphragm was gasketed with a thermosetting methyl methacrylate plastic, and clamped between glass flanges fitted with standard tapers to fit those of the end sections.

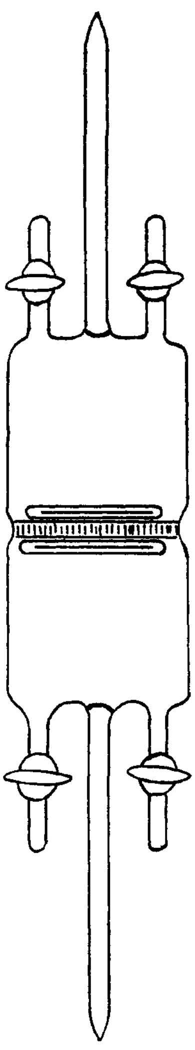

Fig. 1.—Diaphragm diffusion cell.

Preparation of Solutions.—All solutions were prepared from doubly-distilled water with a specific conductance of less than 2×10^{-6} mho cm.$^{-1}$. Analytical quality sodium and potassium chlorides and sodium iodide were used without further purification. Sodium sulfate of C. P. quality was recrystallized before use. The salts, dried for 24 hours at 110° and cooled in a desiccator, were weighed out to give solutions of the indicated concentrations, except that those less than 0.01 *M* were prepared by dilution. Dissolved gases were removed from the solutions, just prior to use, by boiling for one minute in the vacuum of a water pump. As a test, 20 minutes of such boiling was found not to change the concentration of a sodium chloride solution by more than a tenth per cent. Concentrations here given are considered accurate to one or two tenths of one per cent.

Preparation of the Tracers.—The radiosodium was either Na^{24} or Na^{22}, the former supplied by the Isotopes Division of the Atomic Energy Commission and the latter by the Massachusetts Institute of Technology and the Carnegie Institute of Terrestrial Magnetism. The Na^{24} was received as the carbonate, and was converted to the chloride or the sulfate before use, by titration with sulfuric acid; radiochemical impurities gave it an apparent half life of 15.6 hours, but comparison runs with Na^{22} tracer made within the interval of this half-life determination gave identical diffusion results. The Na^{22} was received as sodium chloride sufficiently free of impurities that no chemical processing was considered necessary.

Radiosulfur (S^{35}) was obtained from the Isotopes Division as a constituent of neutron irradiated potassium chloride, and was treated as follows. A solution of the potassium chloride was converted to one of hydrochloric acid by passage through a column of hydrogen form Dowex 50 ion exchanger, and then treated with bromine water to convert the sulfur to sulfate. The excess bromine was boiled off, and the chloride precipitated as silver chloride. The filtrate was again passed through the hydrogen exchanger, and then boiled to near dryness to expel most of the acid, neutralized with one drop of 10^{-6} sodium hydroxide solution, and evaporated to dryness. The slight residue was taken up in water to give the stock solution of radiosulfate. A second shipment received as cadmium sulfide with added barium salt was treated similarly. The diffusional identity of the tracer to macrosulfate was tested by carrying out a mean

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[8] R. H. Stokes, THIS JOURNAL, **72**, 763, 2243 (1950).

[9] We are indebted to Professor Stokes for a pre-publication communication of his procedure.

[10] K. J. Mysels and J. W. McBain, *J. Colloid Sci.*, **3**, 45 (1948).

diffusion experiment with labeled solution. About 25% of the salt was allowed to diffuse, and the specific activities of the sulfate in the upper and lower compartments were measured and found to be the same within 1%.

High specific activity radiochloride (Cl^{36}) was obtained from the Isotopes Division as sodium chloride, and was used as received.

In all cases, the stock tracer solutions were of such specific activity that only a few lambda were used in each run; this added neither enough salt nor water to measurably change the concentration of the solutions. Exceptions were runs with tracer added to pure water; for these the concentrations were estimated from the conductance.

Counting Procedures.—The solutions containing Na^{22}, Na^{24} and Cl^{36} were counted as such by means of a glass jacketed Geiger counter connected to a standard high voltage supply, amplifier and scaling circuit. The measurements were corrected for background, coincidence, and, in the case of Na^{24}, for decay in the short interval between comparison samples. Radiosulfate specific activities were determined by counting barium sulfate precipitates formed as thin films on weighed aluminum disks of 5.7 cm.² area. The procedure for preparing the disks was similar to that previously reported for radiocyanide analysis,[11] as was the method of determining the self-absorption correction curve. The data for the latter are given in Table I, as obtained with the use of a gas flow counter using an atmospheric pressure mixture of 1.3% butane in helium. Normal samples weighed about 1.5 mg./cm.².

TABLE I

SELF-ABSORPTION OF S^{35} IN $BaS^{35}O_4$

Mg./cm.²	% of true count	Mg./cm.²	% of true count	Mg./cm.²	% of true count
0.305	99.4	2.18	89.8	5.68	68.6
.498	98.7	2.58	87.3	6.97	61.1
.594	98.3	3.56	81.0	7.41	58.4
1.518	93.7	3.72	80.4	9.67	47.9
1.603	93.2	4.61	75.0	11.25	43.7

It is noteworthy that these results agree closely with those of Hendricks, *et al.*,[12] since they used a mica end window counter, argon–alcohol filled at 10 cm. pressure, and probably only about 2% as efficient as the flow counter employed here.

Results of Calibration and Stirring Tests

Diffusion constants are calculated from diaphragm cell measurements by application of Fick's law and an assumed physical situation, namely, that two reservoirs of volume V_1 and V_2 contain solutions of initial concentrations C°_1 and C°_2, respectively, which are uniform up to a boundary region of length l and area A, across which a linear concentration gradient is established. This leads to the equations

$$\mathfrak{D} = \frac{1}{Kt}\log\frac{C_1 + \frac{V_2}{V_1}C_2}{(C_1 - C_2)} \qquad (1)$$

$$K = \frac{1}{2.303\,(l/A)}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) \qquad (2)$$

The parameters l and A are approximately identified with the mean pore length and the pore volume of the diaphragm and, not being directly measurable, are incorporated into the cell constant, K. This constant is determined empirically for each cell; it is not a fixed property, moreover, since l/A depends upon the manner and degree of stirring of the solutions in the compartments. Since the diaphragm cell method is a relative one, it is only important that K as determined in the calibration be also the effective K in the experiments to determine diffusion coefficients. Self-diffusion experiments present a special problem since the solutions in the two compartments are physically identical, whereas in calibration one usually allows aqueous potassium chloride to diffuse into water, with attendant viscosity and density gradients. It was thus not obvious that a calibration procedure satisfactory for mean diffusion coefficient determinations would be so for self-diffusion experiments. The experiments described below were designed to establish satisfactory practice for the latter case.

Tests of Stirring Methods.—The first self-diffusion runs[3] were carried out without any mechanical stirring of the cells; since temperature was regulated only to a few tenths of a degree, thermal convection currents provided some measure of mixing. Later results, with thermostating to ±0.01°, yielded diffusion constants that were larger for a given solution, the smaller the cell constant, a clear indication of incomplete stirring of the solutions. The alternating rotation and magnetic mechanical stirring methods were then tried (see Experimental), and the efficacy of each judged by whether there was a range of rotational speeds over which constant products of diffusion coefficient x cell constant could be obtained.

The results are presented in Table II in terms of actual diffusion coefficients of Na^+ ion in 0.02 *M* sodium sulfate. This anticipates the discussion of cell calibration, but avoids repetition of data. It is seen that the values of $\mathfrak{D}$ are constant over the range 25 to 60 r.p.m. The standard rotational speed was taken to be 60 r.p.m. in dilute solutions.

TABLE II

EFFECT OF STIRRING RATE ON $\mathfrak{D}_{Na^+}$ (CM.²/DAY) IN 0.02 *N* SODIUM SULFATE AT 25°

	Stirring rate (r.p.m.) 25	35	50	60
Alternate rotation	1.13	1.13	1.14	1.14 ± 0.2%
Magnetic	1.03	1.13	1.13	1.12 ± 0.0%

Turning to Table III, it is seen that at higher salt concentrations the alternating rotation and magnetic stirring methods failed to agree; duplicate runs also did not check as closely as at lower concentrations. It was found that for solutions of sodium sulfate and sodium chloride greater than about 1.5 *M* a speed of 100 r.p.m. was necessary, and that even this may have been inadequate for 3 *M* sodium sulfate. The results with sodium iodide solutions were similar. This need for increased stirring is presumably due to the increased viscosity and to the varying buoyancy of the floats in magnetic stirring, and serves warning that assurance of adequate stirring should be obtained before determining diffusion coefficients for solutions of unknown character.

TABLE III

EFFECT OF STIRRING RATE AND CONCENTRATION ON $\mathfrak{D}_{Na^+}$ (CM./DAY) AT 25°

Concn. (eq./l.)	Wang and Kennedy[6]	Alt. rot., r.p.m. 60	Alt. rot., r.p.m. 60	Magnetic, r.p.m. 80	Magnetic, r.p.m. 100
		Sodium sulfate			
0.02		1.14 ± 0.2%	1.12 ± 0.0%		
1.2		0.84 ± 0.6	0.85 ± 0.8		
1.5		.80 ± 0.3	.81 ± 0.3		0.80 ± 0.5%
2		.73 ± 0.4	.73		.77 ± 0.4
3		.63 ± 0.8	.57 ± 1.0		.73 ± 1.2
		Sodium chloride			
1			1.04		
1.5		0.97 ± 0.4%	1.02 ± 0.5%		1.03 ± 0.6%
2			0.97 ± 0.6	1.01	1.01 ± 0.4
3.5		0.69 ± 0.7	0.76	0.99	1.00 ± 0.3
		Sodium iodide			
0.05	1.107		1.10 ± 0.3%		
0.6	1 098		1.10 ± 0.5		
2	1.071		1.02	1.06	1.08
3.5	1.070	0.91 ± 1.5%	0.78 ± 1.1	1.08	1.08

Calibration of the Cells.—The cell constant, K (equation (2)), is usually determined by calibration of the cell with a solution of salt having a known diffusion constant. The procedure employed here was the widely accepted one of allowing 0.100 *M* potassium chloride solution to diffuse into water until 25% has passed through the diaphragm. The effective diffusion constant for this case is a type of average of the differential coefficients over the concentration range

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[11] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[12] R. H. Hendricks, L. C. Bryner, M. D. Thomas and J. O. Ivie, *J. Phys. Chem.*, **47**, 469 (1943).

and has been discussed in detail most recently by Stokes,[8] whose value of 1.613 cm.^{2}/day was used here. The above technique will be referred to as the *diffusion* calibration method. An independent check was desirable, however, since cell constants valid for mean diffusion measurements might not be so for self-diffusion ones.

A second method is that of Mehl and Schmidt[13] whereby l/A is determined as the ratio of the resistance of the diaphragm when filled with solution to the known specific resistance of the solution. A comparison of this method with the diffusion calibration procedure was made by means of the demountable cell (see Experimental). Conductance cell constants were determined for diaphragms M_1 and M_2, using sodium sulfate and sodium chloride solutions, rerespectively, each at three concentrations between 0.004 and 0.1 M. The diaphragms were then fitted with end sections converting them to diffusion cells, and the cell constants determined by diffusion calibration both with magnetic stirring at 60 r.p.m. and with no mechanical stirring.

The results are presented in Table IV; the specific conductances used were taken from MacInnes.[14] The close agreement is gratifying and indicates that the magnetic stirring gave mixing up to but not into the diaphragm. Diffusion calibration with alternate rotation stirring was compared to that with magnetic stirring, using normal diffusion cells and the standard speed of 60 r.p.m. The following sets of cell constants were obtained, using three different cells:

Alt. rot.	0.07601 ± 1.0%	0.08443 ± 0.4%	0.1077 ± 0.5%
Magnetic	.07587 ± 0.5	.08427 ± 0.1	.1080

Thus the mechanical stirring methods agree within 1%.

TABLE IV

COMPARISON OF CONDUCTANCE AND DIFFUSION CALIBRATION OF CELLS

	Conductance calibration		Diffusion calibration, K	
Cell	l/A (cm.$^{-1}$)	K	Magnetic	Density
M_1	0.308 ± 0.8%	0.0480 ± 0.8%	0.0482 ± 0.0%	0.0448 ± 0.0%
M_2	.464 ± 0.5	.0327 ± 0.5	.0326 ± 0.5	.0309 ± 0.3

A completely independent check upon the validity of the calibration methods became possible with the appearance of results for Na^+ and I^- ions in sodium iodide solutions, obtained by Wang and Kennedy[6] by a free diffusion technique. Values for $\mathfrak{D}_{Na^+}$ agreed closely with those of these authors, as shown in Table III. It was thus confirmed that diffusion calibration with either stirring method gave cell constants valid for the determination of self-diffusion coefficients.

Returning to Table IV, it is seen that diffusion calibration with density stirring gave values of K smaller, and hence l/A values larger by about 10% than the ones proper for self-diffusion work. This effect could be duplicated in the conductance cell constants by displacing the electrodes about two millimeters from the diaphragm.

Surface Effects

The first results with dilute solutions yielded diffusion coefficients several per cent. higher than the Nernst limiting values[3]; representative values are given in Table V. Stokes[8] observed a similar effect. These observations parallel those of Mysels and McBain,[10,15] that the apparent equivalent conductivities for dilute aqueous potassium chloride were anomalously high in sintered glass diaphragms, and earlier work with more simple glass surfaces[16] indicating appreciable surface conductivity at the Pyrex–solution interface, presumably due to a mobile electric double layer, with anions primarily adsorbed.

The conductance calibration was extended to higher dilutions in order to measure the effect with our solutions, with the results shown in Table VI. Deviations began at 0.001 N sodium chloride and at 0.01 N sodium sulfate, and the percentage effect increased on dilution. The magnitude, as measured by ΔK, the difference between the measured conductivity and that predicted from the constant l/A values for the more concentrated solutions, decreased somewhat with dilution.

The simple correction procedure of employing the variable conductance cell constants in calculating the diffusion coefficients at each concentration causes the values for Na^+ and $SO_4^=$ ions in sodium sulfate to fall in line, but overcorrects those for Na^+, and undercorrects those for Cl^- ions in sodium chloride, assuming that "correct" results should extrapolate smoothly to the Nernst limiting values. It is apparent that one cannot assume the surface transference numbers to be the same as in solution, and some attempts were made to determine them by fitting the demountable cell with end sections converting it to a transference cell of the type described by Brady and Salley.[17] Difficulties were experienced, however, in obtaining values for sufficiently dilute solutions because of current leakages.

TABLE V

COMPARISON OF THE EFFECT OF ADSORPTION ON THE APPARENT DIFFUSION COEFFICIENTS

			$\mathfrak{D}$ (cm.^{2}/day)	
Ion	Concn., N	Nernst lim. value	Glass diaphragm	Stainless steel diaphragm
Na^+ in NaCl	*ca.* 10^{-5}	1.154	1.47 ± 0.8%	1.15 ± 0.4%
	0.000344		1.25 ± 0.8	
	.002			1.13 ± 0.3
	.02		1.13 ± 0.3	1.10 ± 0.4
Cl^- in NaCl	*ca.* 10^{-5}	1.754	2.70 ± 1.0	2.41 ± 0.9
Na^+ in Na_2SO_4	*ca.* 10^{-6}	1.154	(1.47)	(1.15)
	0.000324		1.28 ± 0.4	
	.002			1.27
	.01		1.12_5 ± 0.8	1.17 ± 0.6
$SO_4^=$ in Na_2SO_4	*ca.* 10^{-5}	0.919	0.98 ± 0.4	0.94 ± 0.6
	0.0025			0.88

Some experiments were carried out with sintered stainless steel diaphragms, with results also given in Table V. Calibration was by magnetic stirring. Little or no increase in diffusion coefficient was found for Na^+ ion in sodium chloride, but the positive effects found in the other cases indicate that some adsorption occurred.

Wang and Kennedy[6] observed values of $\mathfrak{D}_{Na^+}$ in 10^{-4} to 10^{-5} M sodium iodide that were 7% higher than the Nernst value, and the surface to volume ratio of their plastic capillary diffusion apparatus may well have been sufficient to lead to appreciable surface transport.

TABLE VI

CONDUCTANCE CELL CONSTANTS AT 25°

Sodium sulfate			Sodium chloride		
Concn., N × 10^3	l/A	ΔK × 10^6	Concn., M × 10^3	l/A	ΔK × 10^6
0.10	0.2780	0.58	0.1	0.3271	1.13
.15	.2861	.66	.4	.3972	1.81
.30	.2938	.94	.9	.4355	1.56
.50	.2970	1.5	1.6	.4506	
.91	.2994	2.1	2.5	.4615	
1	.3048	1.7	4	.4614	
2	.3089	2.1	7	.4685	
3	.3097		10	.4633	
4	.3124				
5	.3148				
9	.3174				
15	.3173				
30	.3165				
50	.3167				
100	.3170				

Results and Discussion

The self-diffusion coefficients for Na^+ and Cl^- ions in sodium chloride solutions and for Na^+ and

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(13) J. W. Mehl and C. L. A. Schmidt, *Univ. Calif. Pubs. Physiol.*, **8**, 165 (1937).

(14) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 339.

(15) We are indebted to Professor Mysels for calling our attention to this work.

(16) J. W. McBain and C. R. Peaker, *J. Phys. Chem.*, **34**, 1033 (1930).

(17) A. P. Brady and D. J. Salley, THIS JOURNAL, **70**, 914 (1948).

TABLE VII

SELF-DIFFUSION COEFFICIENTS, 𝔇 (CM.^{2}/DAY), OF THE IONS IN AQUEOUS SODIUM CHLORIDE AND SODIUM SULFATE AT 25°

Concn. (eq./l.)	Sodium chloride 𝔇 Na$^+$	Sodium chloride 𝔇 Cl$^-$	Sodium sulfate 𝔇 Na$^-$	Sodium sulfate 𝔇 SO$_4^=$
0.000	(1.154)	(1.754)	(1.154)	(0.919)
.005	1.13_5 ± 0.9%	1.70_5 ± 0.4%	....	....
.01	....	....	1.12_5 ± 0.8%	0.83 ± 1.0%
.02	1.13 ± 0.3	1.66 ± 0.1	1.12 ± 0.0	....
.03	....	....	....	0.75 ± 0.4
.04	1.12 ± 0.2	....	....	....
.05	....	....	1.09_5 ± 0.6	0.72 ± 0.7
.1	....	1.63 ± 0.1	....	0.65
.16	1.09 ± 0.0	....	....	....
.2	....	1.62 ± 0.3	1.05 ± 0.0	0.61 ± 0.3
.3	1.08_7 ± 0.3	....	....	....
.4	....	....	1.00 ± 0.5	0.57 ± 0.4
.5	....	1.58 ± 0.7	....	....
.55	....	....	....	0.57
.6	1.05 ± 1.0	....	....	....
.7	....	1.50 ± 0.4	0.93_5 ± 0.3	0.55_5 ± 0.6
.8	1.05 ± 0.3	....	....	....
1	1.04	1.46 ± 0.2	....	....
1.2	....	....	0.84_5 ± 0.8	0.53 ± 0.0
1.4	1.03_5 ± 0.6	1.43 ± 0.4	....	....
1.5	1.03 ± 0.6	....	0.80 ± 0.5	0.50
2	1.01_5 ± 0.4	1.41	0.77 ± 0.4	0.52_5 ± 0.4
3	....	....	0.73 ± 1.2	0.54 ± 0.6
3.5	1.00 ± 0.3	1.41 ± 0.5	....	....

SO$_4^=$ ions in sodium sulfate solutions are presented in Table VII and plotted in Figs. 2 and 3. Because of the surface transport effect, all the points given in Table V have not been considered sufficiently significant to plot; instead the curves through the data have been extended smoothly to the Nernst limiting values.

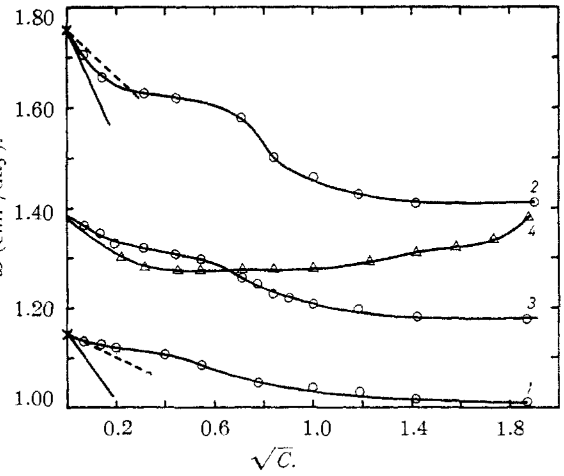

Fig. 2.—Diffusion of aqueous NaCl at 25°: curve 1 $\mathfrak{D}_{Na^+}$; curve 2, $\mathfrak{D}_{Cl^-}$; curve 3, "$\mathfrak{D}_{NaCl}$" calculated from 1 and 2; curve 4, measured $\mathfrak{D}_{NaCl}$.

The behavior in dilute solution provides a partial test of proposed limiting laws. The results are in approximate accord with the relaxation effect equation of Gosting and Harned,[18] for Na$^+$ ion in sodium chloride, and for the ions of sodium sulfate, but deviate in the case of Cl$^-$ ion in sodium chloride, as shown by the dashed straight lines. On the other hand, the equation suggested by Adamson, *et al.*,[2,3] and by Whiteway, *et al.*,[4] considering self-diffusion as giving ion differential diffusion coefficients, does not agree well with the first three cases listed above, but is in approximate agreement with the fourth; these limiting slopes are given by the solid straight lines (they are computed with the use of limiting conductance mobilities). It is hoped to present a discussion of the limiting law for self-diffusion in a later paper.

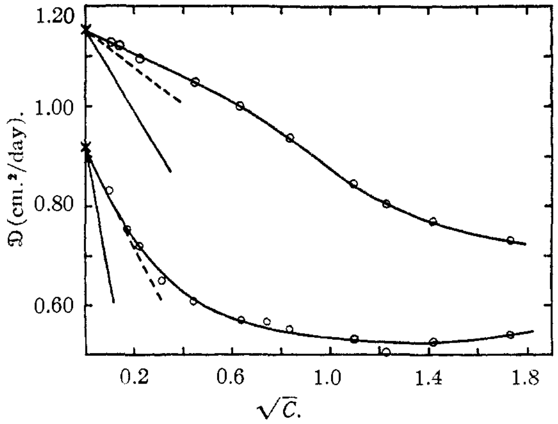

Fig. 3.—Self-diffusion coefficients for aqueous Na$_2$SO$_4$ at 25°: upper curve, $\mathfrak{D}_{Na^+}$; X, Nernst limiting value.

The variation of the diffusion coefficients in the more concentrated solutions is also of some interest. The inflection points, most marked in the curves for $\mathfrak{D}_{Cl^-}$, and for $\mathfrak{D}_{Na^+}$ in sodium sulfate, were reproducible, and no source of systematic error has been detected. Wang and Kennedy[6] report values for $\mathfrak{D}_{I^-}$ in aqueous sodium iodide at 25° that likewise show an inflection point. This behavior cannot

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[18] L. J. Gosting and H. S. Harned, THIS JOURNAL, 73, 159 (1951).

be accounted for by any simple viscosity correction, and waits interpretation. The phenomenon is the more interesting in that it is not observed with mean diffusion coefficients, nor with conductance mobilities.

It is of interest to compare qualitatively the self-diffusion data with mean diffusion coefficients for the salt, and for this purpose a "mean" diffusion coefficient for sodium chloride has been calculated from the ion self-diffusion coefficients by means of the limiting Nernst equation, $\mathfrak{D}_{\pm} = \dfrac{2}{\dfrac{1}{\mathfrak{D}^{+}} + \dfrac{1}{\mathfrak{D}^{-}}}$. The results are given as curve 3, Fig. 2, and the measured mean diffusion coefficients[9] by curve 4. The gross discrepancy at high concentrations is in large part due to the fact that mean diffusion coefficient measurements, being made in a constant volume system, yield an average of the values for the salt and for the *solvent*, an effect not present in self-diffusion. By use of the equation

$$\mathfrak{D}_{\text{obs.}} = F_{H_2O}\mathfrak{D}_{\text{Salt}} + F_{\text{Salt}}\mathfrak{D}_{H_2O}$$

for a binary system, where F_{H_2O} and F_{Salt} are the volume fractions, and of the value 2.28 cm.^{2}/day for $\mathfrak{D}_{H_2O}$,[19] the point for 3.5 N sodium chloride on curve 4 may be brought to agreement with that on curve 3, providing the not unreasonable value of 50 cc. is taken for the molar volume of sodium chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclopentane[1,2]

BY DON W. VANAS, NANCY M. LODGE AND W. D. WALTERS

The homogeneous thermal decomposition of cyclopentane has been investigated in the neighborhood of 555°. Addition of nitrogen, hydrogen or a small quantity of nitric oxide does not alter appreciably the rate of pressure rise during the initial stages of the decomposition. In the presence of a mixture of products, or in the presence of added ethylene, propylene or cyclopentadiene, an increase in the rate of pressure rise is observed. Small amounts of diallyl or allene accelerate the rate. Analyses for cyclopentadiene and hydrogen indicate that the dehydrogenation of cyclopentane is accelerated by the addition of ethylene or propylene.

Introduction

Earlier studies[3] have shown that the homogeneous thermal decomposition of cyclopentane in the neighborhood of 600° proceeds mainly by two reactions: (a) a dehydrogenation reaction to yield cyclopentadiene and hydrogen probably by way of cyclopentene as an intermediate and (b) a ring-cleavage reaction to form propylene and ethylene. However, the products formed at 900° under a pressure of 10 mm., were found to contain the substances mentioned above and also an appreciable quantity of C_3H_4, either allene or methylacetylene.[3d]

Küchler studied the kinetics of the cyclopentane decomposition in a static system by means of pressure measurements and by analyses for hydrogen, ethylene and propylene.[3e] In the over-all pressure–time curve for cyclopentane, as in the cases of cyclohexane[4,5] and methylcyclopentane,[5] an induction period was observed. Although the dehydrogenation was assumed to proceed in two steps, the first of these, loss of one molecule of hydrogen to form cyclopentene, was regarded as the rate-determining step in the dehydrogenation. On the basis of the analytical data the ring cleavage reaction seemed to have an induction period, but the dehydrogenation appeared to be a first-order reaction. Küchler reported that the rate of the ring cleavage could be accelerated by the addition of propylene. He postulated that the ring cleavage is autocatalytic and that another product ethylene would be twice as effective as propylene in accelerating the reaction. The present study was undertaken to investigate further the possible effects of the products upon the decomposition of cyclopentane. Moreover, the rate of formation of cyclopentadiene during the decomposition appeared to warrant additional attention.

Experimental

Materials.—The cyclopentane used in the majority of the experiments was National Bureau of Standards Sample No. 219-5s which had a stated purity of 99.95 ± 0.02 mole per cent. Another source of cyclopentane was the hydrogenation of cyclopentadiene. The cyclopentane after fractionation showed no test for unsaturation with bromine. The sample used was taken from a fraction which had a corrected boiling point of 49.3° and $n^{21}D$ 1.4064 compared with the values of the Bureau of Standards,[6] 49.262° and 1.4059 (interpolated).

Ethylene, propylene and cyclopropane were obtained in cylinders from the Ohio Chemical and Manufacturing Company and had a stated purity of 99.5% in each case. All of these gases were subjected to thorough degassing before use. In two experiments propylene prepared from *n*-propyl alcohol and purified by chemical treatment and distillation was used as a check. Hydrogen and nitrogen obtained from

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[1] Abstracted from the Ph.D. thesis of Don W. Vanas, du Pont Fellow in Chemistry, 1945–1946, and the M.S. thesis of Nancy M. Lodge. A portion of this work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I.

[2] For data supplementary to this article, order Document 3350 from the American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[3] (a) F. E. Frey, *Ind. Eng. Chem.*, **26**, 198 (1934); (b) B. A. Kazansky and A. F. Plate, *Ber.*, **67**, 1023 (1934); (c) P. P. Borisov, E. M. Shaknazarova and E. I. Margolis, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 1385 (1934); (d) F. O. Rice and M. T. Murphy, THIS JOURNAL, **64**, 896 (1942); (e) L. Küchler, *Z. physik. Chem.*, **B53**, 307 (1943).

[4] R. N. Pease and J. M. Morton, THIS JOURNAL, **55**, 3190 (1933).

[5] L. Küchler, *Trans. Faraday Soc.*, **35**, 874 (1939).

[6] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).