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The Variation of the Transference Numbers for Calcium Chloride in Aqueous Solution with Temperature. III

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Transference numbers for calcium chloride in aqueous solution have been determined for concentrations up to 0.15*N* at 15°, 25°, and 35°C. At all three temperatures autogenic cation boundaries using cadmium chloride as indicator gave transference numbers which showed no progression as the boundary moved and were independent of current. The same was true of anion boundaries (employing calcium iodate and paratoluene sulphonate as indicators) at 25°C provided the concentrations of the indicator ions were held within rather narrow limits. Where both t_+ and t_- were determined for a solution, their sum was unity within the precision of the measurements. These results differ, however, from Longworth's data by somewhat more than the apparent precision of the measurements. The variation of the transference numbers with temperature is normal in that they tend to approach one-half with increasing temperature. As in the case of sodium chloride, the variation of the transference number with concentration is independent of the temperature.

PREVIOUS papers from this laboratory^{1,2} have reported the temperature coefficients for the transference numbers of potassium and sodium chlorides; the work described here was originally undertaken several years ago to provide similar information for calcium chloride—a typical 2:1 electrolyte.

The experimental technique was the same as that previously used; the majority of the data were obtained with autogenic boundaries (cell II) using cadmium chloride as a cation indicator, but a considerable number of runs at 25° were made with sheared boundaries (cell III) employing calcium iodate and calcium paratoluene sulphonate as anion indicators; both these indicators of course give rise to ascending boundaries. In the case of the autogenic cation boundaries, no progression was ever observed in the measured transference number as the boundary moved up the tube. In all cases the current was varied by a factor of 2 from run to run for a given round concentration, and the measured t_+ was invariably independent of the current within the precision of the measurements. In this respect the behavior of calcium chloride resembles that

of potassium chloride and of sodium chloride rather than that of potassium bromide.³

For anion boundaries, the use of calcium iodate as indicator is restricted, owing to its low solubility, to calcium chloride solutions 0.02*N* or less. At 0.01*N* and 0.02*N*, however, iodate boundaries show no progression and are independent of the current if the indicator concentrations are 0.00595*N* and 0.0120*N*, respectively; it might be noted that these are approximately the concentrations predicted by the Kohlrausch rule.⁴ The same is true for indicator concentrations differing from these values by not more than 1 percent; beyond these ranges however, the measured t_- was lower, and while showing no progression, depended on the current.

With paratoluene sulphonate as indicator, transference numbers showing no progression and independent of current were obtained with indicator concentrations of 0.0103 and 0.0280*N* for 0.02*N* and 0.05*N* calcium chloride, respectively. Here again, the indicator concentrations were critical to about 1 percent; beyond this range, the measured t_- were high and varied with the current used, although showing no progression. Since the values obtained at 0.02*N* and 0.05*N* for t_- were in good agreement with

* Canadian Industries Limited Fellow in Chemistry, 1943–1944.

¹ R. W. Allgood, D. J. LeRoy, and A. R. Gordon, *J. Chem. Phys.* **8**, 418 (1940).

² R. W. Allgood and A. R. Gordon, *J. Chem. Phys.* **10**, 124 (1942).

³ A. G. Keenan and A. R. Gordon, *J. Chem. Phys.* **11**, 172 (1943).

⁴ D. A. MacInnes and L. G. Longworth, *Chem. Rev.* **11**, 171 (1932).

TABLE I.

Cell	Conc.	t_{\pm} obs.	Sol.+Vol. Corr.	t_{\pm}	Cell	Conc.	t_{\pm} obs.	Sol.+Vol. Corr.	t_{\pm}	Cell	Conc.	t_{\pm} obs.	Sol.+Vol. Corr.	t_{\pm}
15° Centigrade					25° Centigrade					25° Centigrade				
II	0.019990	0.4190	+0.0002	0.4192	III, i	0.019972	0.5763	+0.0004	0.5767	II	0.09985	0.4072	-0.0001	0.4071
II	0.019990	0.4189	+0.0002	0.4191	III, i	0.019972	0.5765	+0.0004	0.5769	II	0.14428	0.4020	-0.0003	0.4017
II	0.019995	0.4188	+0.0002	0.4190	III, p	0.019995	0.5766	+0.0004	0.5770	II	0.14997	0.4013	-0.0003	0.4010
II	0.029980	0.4153	+0.0001	0.4154	III, p	0.019995	0.5762	+0.0004	0.5766	II	0.15014	0.4015	-0.0003	0.4012
II	0.029970	0.4155	+0.0001	0.4156	II	0.019997	0.4231	+0.0003	0.4234	35° Centigrade				
II	0.05002	0.4104	0.0000	0.4104	II	0.020061	0.4232	+0.0003	0.4235	II	0.019999	0.4272	+0.0005	0.4277
II	0.05006	0.4101	0.0000	0.4101	II	0.029919	0.4202	+0.0001	0.4203	II	0.020007	0.4274	+0.0005	0.4279
II	0.05006	0.4101	0.0000	0.4101	II	0.029919	0.4200	+0.0001	0.4201	II	0.029967	0.4246	+0.0003	0.4249
II	0.05006	0.4104	0.0000	0.4104	II	0.030065	0.4202	+0.0001	0.4203	II	0.029968	0.4242	+0.0003	0.4245
II	0.05029	0.4104	0.0000	0.4104	II	0.049991	0.4150	0.0000	0.4150	II	0.029968	0.4242	+0.0003	0.4245
II	0.09987	0.4025	-0.0001	0.4024	II	0.049991	0.4151	0.0000	0.4151	II	0.030030	0.4244	+0.0003	0.4247
II	0.09987	0.4022	-0.0001	0.4021	II	0.050051	0.4150	0.0000	0.4150	II	0.049973	0.4198	0.0000	0.4198
II	0.10004	0.4024	-0.0001	0.4023	III, p	0.050051	0.5847	+0.0003	0.5850	II	0.049974	0.4200	0.0000	0.4200
II	0.14993	0.3967	-0.0002	0.3965	III, p	0.050051	0.5846	+0.0003	0.5849	II	0.049749	0.4201	0.0000	0.4201
II	0.14993	0.3967	-0.0002	0.3965	II	0.06977	0.4117	-0.0001	0.4116	II	0.050027	0.4198	0.0000	0.4198
II	0.15001	0.3968	-0.0002	0.3966	II	0.07001	0.4116	-0.0001	0.4115	II	0.09982	0.4119	-0.0002	0.4117
25° Centigrade					II	0.09618	0.4078	-0.0001	0.4077	II	0.09982	0.4118	-0.0002	0.4116
III, i	0.009997	0.5714	+0.0008	0.5722	II	0.09714	0.4078	-0.0001	0.4077	II	0.09993	0.4120	-0.0002	0.4118
III, i	0.009975	0.5712	+0.0008	0.5720	II	0.09721	0.4074	-0.0001	0.4073	II	0.14983	0.4059	-0.0004	0.4055
										II	0.14977	0.4061	-0.0004	0.4057

the corresponding values of t_{\pm} determined in the autogenic cell, and since the autogenic measurements in all cases satisfied two of the criteria for a transference number (absence of progression and independence of current), it seemed justifiable to employ the autogenic cell for the 15° and 35° runs.

As Shedlovsky and Brown⁵ have pointed out, the most serious difficulty in working with calcium chloride solutions is the preparation of a neutral solution of accurately known strength; we have followed essentially the procedure they recommend. B.D.H. "Analar" grade calcium chloride was crystallized twice from conductivity water; the crystals were collected on a Buchner funnel, and the residual moisture was allowed to distill off for several days into a dry ice trap under vacuum; the resulting material was practically anhydrous but slightly basic. A sample of the salt in a tared platinum boat was introduced into a silica tube electrically heated to 800°C, through which a stream of carefully dried nitrogen was passing. After the salt had melted, dry hydrogen chloride was passed over the melt for 10 minutes, and then nitrogen for a further 10 minutes; the boat was then pulled to the cold exit end of the tube, allowed to cool there in the nitrogen stream for 5 minutes, and then transferred to a stoppered weighing bottle, which after 30 minutes in a desiccator, was transferred to the balance case, and weighed after 10 minutes. Stock solutions were prepared gravimetrically

from the fused salt and conductivity water; when tested by means of a Coleman or Beckman glass electrode, the pH of the resulting solution never differed by more than one or two tenths of a pH unit from that of the conductivity water, viz. 5.8 to 6.2.

The necessity for having neutral solutions was demonstrated by some measurements in which the stock solutions, owing to an imperfect fusion, had a pH when first made up of approximately 9. Measurements at 0.01*N* and 0.02*N* with calcium iodate as anion indicator gave transference numbers which showed no progression and were independent of current but were approximately 0.25 percent too high, i.e., values of t_{\pm} obtained from them would have been low by roughly 0.3 percent.

As a further check on the method of preparation, some of the stock solutions were analyzed gravimetrically for chloride. A weighed sample (approx. 80 cc) of the 0.5*N* stock was diluted to 200 cc with conductivity water.⁶ The precipitation was carried out with a standardized 0.2*N* silver nitrate solution, the chloride solution being first inoculated with 3 cc of 0.05*N* silver nitrate; a slight excess of the fifth normal solution was then added slowly and with constant stirring in the cold until the final silver ion concentration was 0.05 grams per liter. The precipitate was allowed to stand for 15 hours in the dark, and the clear supernatant liquid was decanted through a

⁵ T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. 56, 1066 (1934).

⁶ Richards and Wells (J. Am. Chem. Soc. 27, 459 (1905)) have shown that occlusion in the precipitated silver chloride is negligible at concentrations 0.2*N* or less.

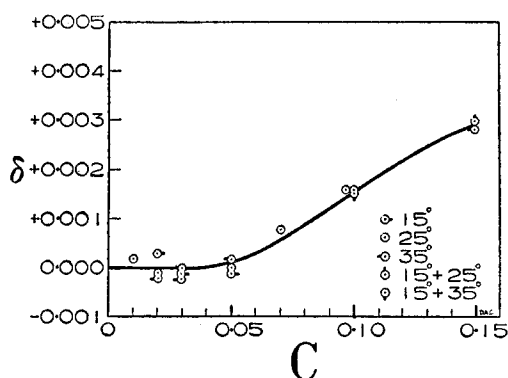


FIG. 1

tared Gooch crucible. The precipitate was vigorously washed with four 30-cc portions of 1 percent nitric acid, and was then transferred to the crucible, using about 200 cc of the acid for the transfer; it was finally washed in the crucible with three 10-cc samples of conductivity water, dried for 1 hour at 100°C and for 3 hours at 150°C, cooled for 45 minutes, and weighed. Duplicate analyses by this method under the conditions outlined above were carried out on 0.2N KCl and NaCl solutions prepared gravimetrically from samples of the recrystallized salts fused in platinum in an atmosphere of dry nitrogen,^{1,2} in both cases the results were 0.015 ± 0.002 percent too low. This small discrepancy was presumably due, in part at least, to the fact that no correction was applied for the trace of silver chloride dissolved in the washings. However, since the error is independent of the cation, it seemed permissible to apply a similar correction to the results of the calcium chloride analyses. When this is done, the resulting concentration of the calcium chloride solution agrees within 0.004 percent with that computed from the known weights of the salt and the water used in making it up. It therefore seems safe to assume that our concentrations are known to 0.01 percent or better. It should also be noted that at least two solutions, each prepared by gravimetric dilution of a different stock solution, were employed for a series of measurements at a given round concentration. In computing volume concentrations, all weights have been reduced to vacuum, and the density data in International Critical Tables⁷ were employed.

⁷ International Critical Tables, Vol. 3, p. 72. See also reference 5.

The calcium iodate was prepared by addition of calcium chloride solution to potassium iodate, the precipitated salt being recrystallized and dried in vacuum over Anhydrone. The calcium paratoluene-sulphonate was prepared by neutralizing an aqueous solution of the acid almost to pH7 with calcium hydroxide; the salt was crystallized from the filtered mother liquor by boiling off water at 30°C under reduced pressure, recrystallized from water at 30°, and dried in vacuum over phosphorus pentoxide.

The results are given in Table I. In the first column, II indicates the autogenic cell with cadmium chloride as indicator, III *i* and III *p* the sheared cell with calcium iodate, and paratoluene sulphonate as indicator. The second column gives the concentration in equivalents per liter, the third the uncorrected value of t_+ or t_- , and the fourth the sum of the solvent and volume corrections.^{4,8} The volume correction, $-C\Delta V/1000$, is given for cell II by

$$\Delta V = \frac{1}{2}\bar{V}_{\text{CaCl}_2} - \frac{1}{2}V_{\text{Ca}} - \frac{1}{2}t_+\bar{V}_{\text{CaCl}_2},$$

where V_{Ca} is the atomic volume of cadmium, t_+ is the transference number of calcium ion in chloride solution, and the other two symbols are the partial molal volumes of the salts in question. Since the cadmium anode forms the closed side of cell III, the volume correction in the sheared runs is the same as for cell II but with the opposite sign. The last column of the table gives the corrected value of t_{\pm} .

For purposes of comparison and interpolation, the deviation plot shown in Fig. 1 was used. Here the deviation δ is defined by

$$t_+ = t_+^{\circ} - 0.103\sqrt{C} + \delta, \quad (1)$$

where t_+° is the transference number of calcium

TABLE II.

<i>C</i>	t_+ , 15°	t_+ , 25°	t_+ , 35°
0.0	0.4334	0.4380	0.4427
0.005	0.4261	0.4307	0.4354
0.01	0.4231	0.4277	0.4424
0.02	0.4188	0.4234	0.4281
0.03	0.4156	0.4202	0.4249
0.05	0.4105	0.4151	0.4198
0.07	0.4067	0.4113	0.4160
0.10	0.4024	0.4070	0.4117
0.15	0.3964	0.4010	0.4057

⁸ L. G. Longworth, J. Am. Chem. Soc. 57, 1185 (1935).

ion at infinite dilution; the values of t_+° , viz. 0.4334, 0.4380, and 0.4427 for 15°, 25°, and 35°, respectively, were obtained from the Λ_0 of the accompanying paper⁹ and the revised values¹⁰ of λ_-° for chloride ion. It is apparent that within the precision of the measurements the change in transference number with concentration is independent of temperature—for this range at any rate; it will be remembered that the same was true for sodium chloride in aqueous solution between 15° and 45°C. It will also be noted that calcium chloride behaves normally in respect to the variation of the transference number with temperature for a given concentration, i.e., the transference numbers approach one-half as the temperature is increased. As Longworth⁸ has pointed out, however, the coefficient of the square root term in Eq. (1) is far from that predicted as a limiting law by the Debye-Onsager theory, e.g., -0.185 for 25°. Nevertheless, we believe that this method of plotting should give a reasonably accurate extrapolation to $0.005N$, a concentration low enough to interpret e.m.f. measurements on cells with transference. The smoothed values of t_+ , given in Table II, correspond to the continuous curve of the figure.

The only previous measurements by the moving boundary method on calcium chloride solutions are those of Longworth⁸ at 25°C. His values of t_+ however, are uniformly about 0.001

less than those reported here. While the measurements on calcium chloride are not quite as reproducible as those for potassium and sodium chlorides, this discrepancy is nevertheless definitely greater than the apparent precision of either set of measurements. Thus Longworth in his Table V gives for $0.02N$, $t_+=0.4226$ and $t_-=0.5776$, whose sum is unity within the precision of the measurements. From our Table I, the mean t_+ for $0.02N$ is 0.4234 and the mean t_- (from both iodate and paratoluene sulphonate boundaries) is 0.5768, the sum once again being unity within the same limits. Although Longworth does not specifically say so, his measured transference numbers presumably were independent of the current, so that as far as internal evidence is concerned, it is difficult to make a decision as to the relative accuracy of the two sets of data. Even more puzzling is the fact that the conductances reported in the accompanying paper⁹ are in satisfactory agreement with those of Shedlovsky and Brown,⁵ and that the same is true of e.m.f. measurements on calcium chloride solutions carried out here and those of Shedlovsky and MacInnes;¹¹ this would seem to eliminate any serious divergence in technique in the preparation of the solutions in the two laboratories. It therefore seems evident that a final decision on this point can only come from a further independent investigation.

In conclusion we wish to express our thanks to Canadian Industries Limited for the grant to one of us (A.G.K.) of a fellowship.

⁹ G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 470 (1945).

¹⁰ G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 473 (1945).

¹¹ T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **59**, 503 (1937).