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The conductance of aqueous solutions of calcium chloride at temperatures from 15° to 45°C has been determined by the direct-current method previously used for potassium chloride, sodium chloride, and potassium bromide. The results for 25° are in excellent agreement with those of Shedlovsky and Brown. At all temperatures the data can be represented by the extended Onsager-Shedlovsky equation, as in the case of the 1–1 salts. In contrast to the 1–1 salts, however, the contribution of the logarithmic term passes through a minimum with increasing temperature, and then rises. The limiting conductance has been determined for calcium ion; the temperature coefficient of the ionic conductance is large in comparison with those for univalent ions.

THIS research concerns the conductance of dilute aqueous solutions of calcium chloride at temperatures from 15° to 45°C; it is a natural complement to the work previously reported[1,2] from this laboratory on the conductance of the 1–1 salts potassium chloride, sodium chloride, and potassium bromide, and yields as well values of the limiting conductance and temperature coefficient for calcium ion when combined with the revised data for chloride ion reported in the accompanying paper.[3]

The measurements were carried out by the direct-current method previously described.[1] The only significant variation in technique lay in the determination of the solvent correction. Here, the correction was determined by adding to a weighed sample of the conductivity water to be used in making up the calcium chloride solution, a weighed amount of a 0.01N KCl solution so that the resulting concentration was approximately $5 \times 10^{-6}N$ in KCl, i.e., the conductance of the solution was caused in roughly equal amounts by the added salt and by the water. The specific conductance was then determined in a cell similar in all respects to that used in the calcium chloride measurements; by subtracting from the observed specific conductance, the known amount caused by the potassium chloride, the solvent

correction was obtained at once. This method was found to give remarkably reproducible results, and had the advantage that both solution and solvent conductances were determined under as nearly identical conditions as possible.

The solutions were made by gravimetric dilution of stock solutions prepared as described in the preceding paper;[4] all weights have been reduced to vacuum, and in converting from mass to volume concentrations, the density data in *International Critical Tables*[5] have been used. Bath temperatures were set by means of a platinum resistance thermometer with National Bureau of Standards certificate, whose calibration has been checked repeatedly in this laboratory at the ice and Glauber's salt points.

Earlier measurements in this laboratory have been based on Jones and Prendergast's 0.01 Normal standard;[6] the reasons for selecting this rather than the more generally used Jones and Bradshaw[7] 0.01 Demal standard have been discussed in reference 1. We have been informed by

TABLE I.

10^4C	97.232	99.136	99.421	99.454	98.929
Λ	120.55	120.42	120.43	120.41	120.45
Λ_0'	138.17_3	138.22_1	138.26_0	138.24_3	138.23_3
$\Lambda_0'\ c_{=0.01}$	138.25_7	138.24_7	138.27_8	138.26_0	138.26_5

[1] H. E. Gunning and A. R. Gordon, J. Chem. Phys. 10, 126 (1942).

[2] H. E. Gunning and A. R. Gordon, J. Chem. Phys. 11, 18 (1943).

[3] G. C. Benson and A. R. Gordon, J. Chem. Phys. 13, 473 (1945).

[4] A. G. Keenan, H. G. McLeod, and A. R. Gordon, J. Chem. Phys. 13, 466 (1945).

[5] *International Critical Tables*, Vol. 3, p. 72.

[6] Grinnell Jones and M. J. Prendergast, J. Am. Chem. Soc. 59, 731 (1937).

[7] Grinnell Jones and B. C. Bradshaw, J. Am. Chem. Soc. 55, 1780 (1933).

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Dr. B. B. Owen,[8] however, that while Jones and Prendergast's hundredth Normal and tenth Normal standards are slightly more self-consistent than are the Demal when tested by Shedlovsky, Brown, and MacInnes' Eq. (7), the actual experimental results[9] of Shedlovsky, Brown, and MacInnes indicate no significant superiority of the Normal standards over the Demal; we have therefore used the Jones and Bradshaw $0.01D$ standard at 25° for purposes of calibration.

Owing to the large number of measurements, we have recorded in Table III not the results of individual runs but averages for a number of experiments carried out at approximately round values of the concentration. The method by which these averages were obtained (and incidently an idea of the self-consistency of the data) may be illustrated by taking the entry for $0.01N$ solution at 25° as an example. The first line of Table I gives the actual concentrations in equivalents per liter for a number of measurements near this concentration; the solution in each is the result of a dilution from a different stock solution. The second line of the table gives the observed equivalent conductance, corrected for solvent conductance, and the third line the corresponding Λ_0' (see Eq. (1) below). From a large scale plot of all the data for this temperature, a value of $d\Lambda_0'/dC$ at $C=0.01$ was determined; for the narrow range of concentration involved, this could be taken as constant for the table. From the difference in concentration from $0.01N$, and the known value of $d\Lambda_0'/dC$ viz., 304, it was then possible to calculate the Λ_0' for $C=0.01$ corresponding to each of the observed values of Λ_0' in the third line. The results are entered in the fourth line of the table, the mean of the entries being $138.26_2 \pm 0.00_8$; this corresponds to

TABLE II.

	15°	25°	35°	45°
Λ_0	108.40	135.85	165.48	197.11
t_-°	0.5666	0.5620	0.5573	0.5525
ϑ	0.4844	0.4942	0.5052	0.5177
3σ	85.87	110.49	138.08	167.93
B	472	529	615	894
D	147	144	155	270

[8] B. B. Owen, private communication.
[9] T. Shedlovsky, A. S. Brown, and D. A. MacInnes, Trans. Am. Electrochem. Soc. **66**, 165 (1934).

TABLE III.

10^4C	15°C Λ_{obs}	Λ_{calc}	10^4C	25°C Λ_{obs}	Λ_{calc}
5	105.30	105.30	5	131.90	131.90
10	104.05	104.04	10	130.32	130.33
20	102.35	102.36	20	128.20	128.18
30	101.11	101.12	30	126.61	126.60
50	99.28	99.26	50	124.23	124.24
70	97.89	97.86	70	122.47	122.45
100	96.24	96.25	100	120.38	120.38
	35°C			45°C	
5	160.58	160.57	5	191.09	191.07
10	158.64	158.62	10	188.65	188.66
20	155.97	155.95	20	185.34	185.36
30	153.98	153.99	30	182.94	182.94
50	151.03	151.05	50	179.34	179.33
70	148.84	148.82	70	176.65	176.61
100	146.21	146.21	100	173.43	173.47

$\Lambda = 120.38 \pm 0.01$, which is the value entered in Table III.

The results are summarized in Table III as a function of the concentration in equivalents per liter. As Shedlovsky and Brown[10] have shown, a suitable analytic representation may be obtained by the use of the Onsager-Shedlovsky equation, just as in the case of the 1–1 salts:[9,11]

$$(\Lambda + 3\sigma\sqrt{C})/(1 - \vartheta\sqrt{C})$$
$$= \Lambda_0' = \Lambda_0 + BC + DC \log C, \quad (1)$$

where for a 2–1 electrolyte ϑ and σ are given by[12]

$$\vartheta = (4.5734 \times 10^6/(DT)^{\frac{3}{2}})/$$
$$(1 + t_-^\circ + 0.8165(1 + t_-^\circ)^{\frac{1}{2}}), \quad (2)$$

$$\sigma = 50.435/\eta(DT)^{\frac{1}{2}}, \quad (3)$$

where D is the dielectric constant, η the viscosity of water, and t_-° is the transference number of the chloride ion at infinite dilution. Since t_-° can only be computed from λ_-° for chloride ion if Λ_0 is known, the extrapolation to infinite dilution by means of Eq. (1) requires a short series of approximations. The final values of Λ_0, and the corresponding t_-° (obtained from these and the revised values of λ_-° listed in Table III of the accompanying paper[3]) are summarized in Table II.

[10] T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. **56**, 1066 (1934).
[11] A. R. Gordon, J. Chem. Phys. **7**, 221 (1939).
[12] The values of the universal constants used to compute the coefficients ϑ and σ are those recommended by Manov, Bates, Hamer, and Acree (J. Am. Chem. Soc. **65**, 1765 (1943)). The dielectric constants are those of Wyman (Phys. Rev. **35**, 623 (1930)) and the viscosities are from *International Critical Tables*, Vol. 6, p. 234.

TABLE IV.

	15°	25°	35°	45°
$(\lambda_+{}^\circ)_{\frac{1}{2}Ca^{++}}$	46.98	59.50	73.26	88.21
$d \ln \lambda_+{}^\circ / dT$	0.0252_5	0.0221_0	0.0196_0	0.0176_5

The table also gives the values of ϑ and σ and of the coefficients B and D of Eq. (1); the latter are, of course, entirely empirical, and are chosen to give the best fit with the data. That Eq. (1) does give an excellent representation is evident from the columns headed Λ_{calc} in Table III, the differences between "observed" and "calculated" being in general no greater than the precision of the measurements.

Although the physical interpretation of the coefficients[13] B and D of Eq. (1) is a matter of uncertainty, a comparison of the results obtained here with those for the 1–1 salts (see Table I of reference 3) is nevertheless of interest. In the first place, the values for calcium chloride are much greater, i.e., the deviation of the conductance from the limiting Onsager equation is greater than for potassium chloride, potassium bromide, and sodium chloride. Secondly, B and D for calcium chloride, though large, are not such as to cause Λ_0' to pass through a minimum[14] at any concentration investigated; in other words, a plot of the data of Table III against the square root of the concentration would lie everywhere above the Onsager limiting slope. Conductances which lie below the limiting slope at moderately low concentrations, as in the case of potassium and silver nitrate in aqueous solution,[15] have been interpreted as evidence for ion association in solution; on this basis, calcium chloride is as

[13] L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932).

[14] It should be noted that the use of Eq. (1) necessitates a minimum for Λ_0' at a concentration given by $\ln C = -(2.303B+D)/D$. For calcium chloride at 15°, this concentration is $0.00023N$, at which Λ_0' is 0.015 conductance unit less than Λ_0; for higher temperatures, this concentration is still lower. Similarly, with potassium and sodium chlorides at 15°, the minimum Λ_0' occurs at approximately $0.0005N$, and is less than the corresponding Λ_0 by 0.01_5 unit in both cases.

[15] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932). The minima for the two nitrates occur, however, at concentrations much higher than those discussed in footnote 13—approximately $0.0025N$; moreover, the minimum Λ_0' for the potassium and silver salts are approximately one-quarter and one-tenth of a conductance unit less than the corresponding Λ_0; see reference 11.

"strong" an electrolyte as potassium and sodium chlorides. Finally it should be noted that the contribution of the logarithmic term for a given concentration passes through a minimum with increasing temperature; this is in contrast to the behavior of the 1–1 salts, for which its importance, both absolutely and relatively, decreases rapidly with rising temperature.

The most extensive precise measurements on the conductance of calcium chloride solutions in the literature are those of Shedlovsky and Brown[10] at 25°C. A comparison of the smoothed entries in their Table VI with the 25° data in our Table III shows that the agreement between the two sets of measurements is most satisfactory; in only one instance is the discrepancy as great as 0.03 conductance unit.

The values of the limiting ionic conductance for calcium ion are given in Table IV; they were obtained from the Λ_0 of Table II and the known values of $\lambda_-{}^\circ$ for chloride ion (see Table III of reference 3). The table also lists the temperature coefficient of the conductance for calcium ion; the values were obtained by differentiation of a cubic equation fitted to $\ln \lambda_+{}^\circ$ for the four temperatures. A comparison of these values with those for the univalent ions[3] shows that calcium ion has a larger temperature coefficient than sodium ion although it is from 15 percent to 20 percent faster. Such temperature coefficients have been interpreted[16–18] as a measure of the energetics of the transport process; it is evident, however, that the statement that large slow ions must naturally have larger activational energies of transport and consequently larger temperature coefficients than small fast ions is an oversimplification. The evidence obtained here and in the earlier papers[1,2] indicates that the Kohlrausch rule can only be true if the ions to be compared are of the same charge and sign, and this is, after all, not surprising.

[16] H. Eyring, J. Chem. Phys. **4**, 283 (1936).
[17] H. S. Taylor, J. Chem. Phys. **6**, 331 (1938).
[18] M. J. Polissar, J. Chem. Phys. **6**, 833 (1938).