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The Conductance at 25° of Lithium Chloride, Sodium and Potassium Bromides and Potassium Iodide in Methanol, and of Lithium Chloride, Sodium Bromide and Potassium Iodide in Water

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The conductance of lithium chloride, sodium and potassium bromides and potassium iodide has been determined in anhydrous methanol by the direct current method, and as a check on the purity of the salts similar measurements with lithium chloride, sodium bromide and potassium iodide have been carried out in aqueous solution. The methanol data were extrapolated to zero concentration by two different methods; combined with the known limiting conductances for sodium, potassium and chloride ions recently determined in this Laboratory, they provide limiting conductances for lithium, bromide and iodide ions in this solvent. For the two bromides, the Kohlrausch rule is obeyed within experimental precision. As might be expected, the Walden rule fails completely to correlate the methanol data with those for water. The significance of the limiting conductance ratio for a pair of ions of like charge and sign in different solvents is discussed.

This research is a sequel to the earlier transference[1] and conductance measurements[2] for potassium and sodium chlorides in anhydrous methanol. Its purpose was to provide reasonably precise limiting conductances for lithium, bromide and iodide ions in this solvent.

Experimental

The measurements were effected by the direct current method[2,3] previously employed in this Laboratory, and are based on the Jones and Bradshaw 25° 0.01 Demal standard.[4] It was found that the silver–silver iodide probe electrodes gave somewhat larger bias potentials than was the case with chloride and bromide electrodes; such bias potentials were, however, independent of the current passing, and agreed within experimental precision (0.01 mv.) with the static bias measured in the absence of current. The preparation of the stock solutions, the dilution procedure, the technique of solution transfer to the cell (including the precautions taken to avoid evaporation losses) and the determination of solvent conductance have been previously described[2]; the only change in the methanol measurements lay in flushing the empty cell with methanol-saturated nitrogen before filling, thus eliminating the small evaporation correction previously employed.

Lithium Chloride.—Analar grade lithium nitrate was crystallized three times from water, making use of the difference in solubility between 0 and 60°. A concentrated, twice distilled solution of ammonium carbonate containing excess ammonia was added dropwise to the nitrate solution, and the precipitated carbonate was digested for several hours at 80°, filtered and washed until the washings were free from nitrate.[5] The carbonate was dissolved in three times distilled constant boiling hydrochloric acid, and the chloride was finally crystallized from slightly acid solution and centrifugally dried. The salt was fused in platinum in dry HCl, cooled in dry CO_2-free nitrogen, and weighed by means of a bottling apparatus. The product was neutral and spectroscopically pure.

Potassium Bromide.—Two methods of preparation were used. B. D. H. Analar grade KBr was three times crystallized from conductivity water containing a trace of HBr, and centrifugally dried. Alternatively, analytical grade constant boiling hydrobromic acid was three times distilled, only a 50% middle cut being retained in each distillation, and in this three times crystallized K_2CO_3 was dissolved leaving the solution slightly acid; the bromide was then recovered as outlined above. The salt was dried at 600° in purified nitrogen, and the resultant material was neutral and spectroscopically pure. Gravimetric analysis, in which the precipitation[6] was effected very slowly at a concentration of 0.01 N to minimize occlusion, gave (after allowing for the small solubility correction) 0.63370 ± 0.00003 for the KBr/AgBr ratio as compared with the theoretical 0.63375. Determinations of the conductance in aqueous solution showed no difference in the two methods of preparation, and the measured equivalent conductances were in good agreement with the earlier KBr data.[3d,7]

Sodium Bromide.—After a lengthy investigation, the procedure described below was adopted. Three times crystallized Na_2CO_3 was suspended in carefully purified methanol, and a slight excess of redistilled constant boiling hydrobromic acid was added; the solution was then concentrated under reduced pressure at temperatures below 40°, and the crystals (after being vacuum-dried) were dissolved at 40° in the minimum amount of methanol which had been slightly acidified with HBr. Carefully purified peroxide-free ether was then distilled in dropwise under an atmosphere of nitrogen until a crop of very fine crystals had formed, and the solution was then chilled to 0°; after standing, the crystals were filtered, washed in methanol and dried under vacuum. With reasonable precautions against exposure to moisture, it is possible in this way to obtain the anhydrous salt rather than the dihydrate (see below). The salt was heated to 600° in purified nitrogen, since it was found that this procedure gave results with samples prepared in this way identical with those obtained when the salt was fused in an atmosphere of HBr and subsequently cooled in nitrogen. The salt was finally weighed by means of a bottling apparatus. The material was neutral and spectroscopically pure. Electron diffraction patterns were notably sharp and corresponded to the correct lattice constant for NaBr in contrast to those obtained with samples containing appreciable amounts of chloride; we wish to thank Dr. F. C. Boswell of the Physics Department for making these measurements. Gravimetric analysis (see above) gave 0.54802 ± 0.00004 for the NaBr/AgBr ratio as compared with the theoretical 0.54800.

There are several points to be noted in the preparation of this salt. (1) Any procedure which yields the dihydrate, *e.g.*, recrystallization from aqueous solution, will in our experience yield on heating a slightly basic product even if the heating takes place in an atmosphere of HBr. For example, a 0.005 N aqueous solution gave at 25° $\Lambda = 122.35$ when salt prepared as outlined in the preceding paragraph was used. Some of the same preparation, after crystallization

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[1] J. A. Davies, R. L. Kay and A. R. Gordon, *J. Chem. Phys.*, **19**, 749 (1951).

[2] J. P. Butler, H. I. Schiff and A. R. Gordon, *ibid.*, **19**, 752 (1951).

[3] (a) H. E. Gunning and A. R. Gordon, *ibid.*, **10**, 126 (1942); (b) H. E. Gunning and A. R. Gordon, *ibid.*, **11**, 18 (1943); (c) G. C. Benson and A. R. Gordon, *ibid.*, **13**, 470 (1945); (d) G. C. Benson and A. R. Gordon, *ibid.*, **13**, 473 (1945).

[4] G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1870 (1933).

[5] G. Jones and B. C. Bradshaw, *ibid.*, **54**, 138 (1932).

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

[7] G. Jones and C. F. Bickford, THIS JOURNAL, **56**, 602 (1934).

from acidified conductivity water, gave for this concentration $\Lambda = 122.45$. (2) Recrystallization is ineffective in eliminating chloride—a common impurity. Thus when to an aqueous solution of standard NaBr, NaCl corresponding to 0.6% by weight of the bromide was added, the resultant crystals, weighed as NaBr gave $\Lambda = 123.00$ for 0.005 *N*. After allowing 0.10 unit for hydrolysis during crystallization, the increase of 0.55 unit, if ascribed to sodium chloride as an impurity, would correspond to a sodium chloride content of the crystals of almost exactly 0.6%. (3) The anhydrous salt, even when normal precautions against exposure to light are taken, is unstable. For example, a standard preparation of the salt four days old showed an increase in conductance in aqueous solution as compared with the results obtained from the same batch when first prepared varying from 0.13 unit at 0.005 *N* to 0.18 unit at 0.0005 *N*. For this reason, a fresh sample of salt was prepared for each stock solution. In contrast, with methanol as solvent, the difference in conductance between freshly prepared and old samples of the salt was but little above experimental error.

Potassium Iodide.—B. D. H. Analar grade constant boiling hydriodic acid was four times distilled in an atmosphere of nitrogen, only the middle fraction being retained with each distillation. To this was added three times crystallized potassium carbonate, centrifugally dried. The resultant solution, which was distinctly acid and contained a considerable amount of free iodine, was concentrated at 30° under reduced pressure, and the dark red crystals formed were vacuum dried. To prepare a solution, the salt was heated in purified nitrogen; the product was pure white, neutral and spectroscopically free from impurities. Conductance measurements on 0.002 *N* aqueous solutions prepared from samples heated to various temperatures up to fusion showed that the measured Λ within experimental precision (0.01 unit) was independent of the temperature of heating, provided this was 400° or more; with lower temperatures, the measured conductance was slightly but significantly lower.

It was found that the salt was stable when kept in a desiccator as long as the crystals contained considerable amounts of hydriodic acid and iodine. Preparations which had lost acid and iodine resembled samples prepared by recrystallization of the Analar grade salt from aqueous solution, *i.e.*, the measured conductance tended to be high and to increase with the age of the salt; the discrepancy was relatively slight at 0.005 *N* but became greater with decreasing concentration—in one extreme case to as much as 0.15 unit at 0.0005 *N*. As with NaBr, stabilized and unstabilized samples in methanol solution showed only slight differences in conductance, amounting at most to a few hundredth's of a per cent.

Solvents.—The methanol was prepared as previously described.[2] Its water content was 0.005% by Fischer titration[8] and all conductances have been corrected for this[2]; its specific conductance was from 3 to 5 $\times 10^{-8}$, and its density 0.78657 at 25°, corresponding to 0.78656 for the anhydrous material. The conductivity water, which was equilibrated with atmospheric CO_2,[4] had a specific conductance of 0.7 $\times 10^{-6}$.

Densities.—For aqueous solutions, the data of "International Critical Tables" were employed. For methanol, the densities of the solutions were determined by means of Shedlovsky and Brown[9] type pycnometers. For the small concentration ranges involved, these can be represented within experimental precision by $G = 0.78657 + Bx$, where x is the weight fraction of the salt and B is 0.81 for LiCl, 0.77 for NaBr and 0.71 for KBr and KI.

Results

The results are summarized in Tables I and II. Here C is the concentration in equivalents per liter, and Λ_0' is the Shedlovsky[10] function $(\Lambda + 2\sigma C^{1/2})/(1 - \vartheta C^{1/2})$ where $\sigma = 30.09$, $\vartheta = 0.2289$ for water, and $\sigma = 78.07$ $\vartheta = 0.9004$ for methanol.[11] Owing to the large number of individual measurements, only mean values for round concentrations are printed; the Λ for each run was corrected for the slight difference of concentration involved by means of the Shedlovsky function as discussed by Benson and Gordon,[3c] and such concentration corrections amounted at most to one or two hundredth's of a conductance unit in Λ_0'. Each entry is the mean of at least four and in general of eight or more independent measurements each with a different solution and involving three or more different preparations of the salt; the mean absolute deviation of the individual results from the average as printed varies from somewhat less than 0.01 conductance unit for the more concentrated solutions to about 0.02 unit for the most dilute.

Table I

Conductance in Aqueous Solution at 25°

$10^4 C$	LiCl Λ	LiCl Λ_0'	NaBr Λ	NaBr Λ_0	KI Λ	KI Λ_0'
5	113.13	115.07	126.28	128.28	148.42	150.54
10	112.39	115.13	125.47	128.30	147.60	150.59
20	111.33	115.20	124.36	128.37	146.48	150.71
30	110.56	115.30	123.56	128.47	....	....
50	109.34	115.46	122.34	128.68	144.38	151.08

Table II

Conductance in Methanol Solution at 25°

$10^4 C$	Λ	$\Lambda_0' - EC \log C$	$\Lambda_0' - BC$	Λ	$\Lambda'_0 - EC \log C$	$\Lambda_0' - BC$
		LiCl			NaBr	
1	89.74	92.13	92.22	99.19	101.67	101.76
2	88.70	92.08	92.22	98.11	101.61	101.74
5	86.65	91.99	92.21	96.04	101.58	101.76
10	84.52	92.08	(92.31)	93.80	101.63	101.77
20	81.74	92.45	(92.49)	90.86	101.95	101.78
30	79.73	92.86	....	88.80	102.40	101.75
50	76.73	93.74	....	85.66	103.28	(101.36)
		KBr			KI	
1	106.34	108.88	108.96	112.52	115.12	115.15
2	105.26	108.85	108.97	111.43	115.10	115.15
5	103.10	108.78	108.97	109.29	115.10	115.15
10	100.71	108.74	108.96	106.94	115.16	115.16
20	97.51	108.88	108.96	103.74	115.37	115.16
30	95.19	109.12	108.94	101.50	115.76	(115.27)
50	91.80	109.83	(108.90)	98.16	116.63	(115.43)

Measurements in Aqueous Solution.—To take the aqueous measurements first, since these were undertaken primarily to test the purity of the salts: the lithium chloride data can be represented within 0.01 unit by $\Lambda_0' = 115.03 + 88C$, Shedlovsky's measurements[12] for his four most dilute solutions (after correcting to the Jones and Bradshaw standard) correspond within similar limits to $\Lambda_0' = 115.04 + 94C$, *i.e.*, our data lie about 0.02 unit below his curve except for our highest concentration where the discrepancy is 0.05 unit. Krieger and Kilpatrick's individual results[13] show somewhat greater scatter than do Shedlovsky's or ours, but up to 0.01 *N* can be represented by $\Lambda_0' = 114.99 + 95C$. Our results are thus intermediate, agreeing closely with Shedlovsky's at our lower concentrations and with Krieger and Kilpatrick's at our highest.

The sodium bromide conductances can be represented, once again within 0.01 unit, by $\Lambda_0' = 128.26$

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[8] K. Fischer, *Z. angew. Chem.*, **48**, 394 (1935).

[9] T. Shedlovsky and A. S. Brown, This Journal, **56**, 1066 (1934).

[10] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[11] The dielectric constant of methanol selected is 31.52 (G. Akerlof, This Journal, **54**, 4126 (1932)) and the viscosity is taken as 0.005445 poise (G. Jones and H. J. Fornwalt, *ibid.*, **60**, 1683 (1938)).

[12] T. Shedlovsky, This Journal, **54**, 1411 (1932).

[13] K. A. Krieger and M. Kilpatrick, *ibid.*, **59**, 1878 (1937).

$+ 234C + 65C \log C$. The presence of a logarithmic term for the sodium salt is somewhat surprising and may be spurious, since the data may also be represented with a maximum deviation of 0.02 unit by $\Lambda_0' = 128.21 + 90C$. From the Kohlrausch rule, if Benson and Gordon's[3d] Λ_0 are selected (149.85, 126.45 and 151.64 for KCl, NaCl and KBr, respectively) Λ_0 for NBr should be 128.24. Shedlovsky, Brown and MacInnes' values for the two chlorides[10] (149.86 and 126.45) combined with Jones and Bickford's result[7] for KBr, give 128.22, while Harned and Owen's "best" values[14] (149.85, 126.50 and 151.67) give 128.32. About all that can be said of the results reported here for NaBr is that they are as consistent with existing data as can be hoped.

The KI measurements correspond within 0.01 unit to $\Lambda_0' = 150.47 + 121C$, a relation which also represents Longsworth's data[15] for 0.005 N and 0.01 N within the same limits, and his result for 0.02 N within 0.02 unit. The most extensive measurements, however, are those of Owen and Zeldes,[16] who report $\Lambda_0' = 150.34 + 121C$. Their results are based on differential potentiometric analysis of stock solutions, prepared from samples of the salt which had undergone prolonged drying at 60°. They also found in other measurements where the solutions were prepared gravimetrically from the fused salt that the conductances were 0.05% higher, which would correspond to $\Lambda_0' = 150.42 + 121C$. The discrepancy between this second series and the data of Longsworth and ourselves (0.03%) is somewhat greater than the apparent precision of the measurements, but nevertheless suggests, in our opinion, that the analysis may have been in error. That Owen and Zeldes do not mention the apparent "aging" effect we have found may be due to the fact that at their lowest concentration—0.0014 N—it is not as noticeable as at lower concentrations, particularly if their stock solutions were made up from freshly prepared samples of the salt.

Measurements in Methanol Solution.—A glance at the methanol results in Table II shows that except for KI, there is a minimum in Λ_0' more pronounced than was the case with KCl and NaCl.[2] Extrapolation by the Shedlovsky and Brown method,[9] *viz.*, plotting $(\Lambda_0' - \Lambda_0)/C$ against log C for a Λ_0 which will yield a plot linear in log C, leads to the values of the coefficients in the extended Onsager–Shedlovsky equation[9,10] given in

$$\Lambda_0' = \Lambda_0 + BC + EC \log C \qquad (1)$$

Table III; the last column of Table II shows that an equation of this form does represent the data adequately over considerable ranges of concentration except for LiCl. The size of the coefficients, however, raises the question whether we have here more than a fortunate piece of curve fitting. As an alternative, we have extrapolated by another method, suggested by Shedlovsky[17]; this has been generally employed for weak electrolytes, but for strong electrolytes has not (we believe) received the attention it deserves. For the latter, Shedlovsky writes

$$\Lambda = \Lambda_0 - (A\Lambda/\Lambda_0) \times C^{1/2} \qquad (2a)$$

where A is written for the Debye–Onsager limiting law coefficient, $\vartheta\Lambda_0 + 2\sigma$. To a first approximation, this is obviously equivalent to writing

$$\Lambda = \Lambda_0 - AC^{1/2} + (A^2/\Lambda_0) \times C \qquad (2b)$$

i.e., in contrast to eq. 1, the coefficient of the term linear in C is no longer disposable. By an obvious rearrangement, (2a) may be written

$$1/\Lambda_0 = 1/\Lambda - AC^{1/2}/\Lambda_0^2 \equiv F(\Lambda) \qquad (3)$$

If $F(\Lambda)$ for an assumed Λ_0 be plotted against some function of the concentration, its limiting value should be $1/\Lambda_0$, and a consistent Λ_0 can then be found by a short series of approximations. Dr. Shedlovsky, with whom we had the pleasure of discussing the problem, suggests $C \log C$ as a suitable function of concentration for purposes of extrapolation, and the resulting plots are shown in Fig. 1; for the lower concentrations, they are sensibly linear and, at worst, the uncertainty of the

TABLE III

COEFFICIENTS FOR EQUATIONS 1 AND 3

	LiCl	NaBr	KBr	KI
Λ_0, eq. 1	92.22	101.76	108.96	115.15
B	1870	2110	1510	1010
E	700	750	575	335
Λ_0, eq. 3	92.19	101.75	108.93	115.15
Λ_0, mean	92.20	101.76	108.95	115.15

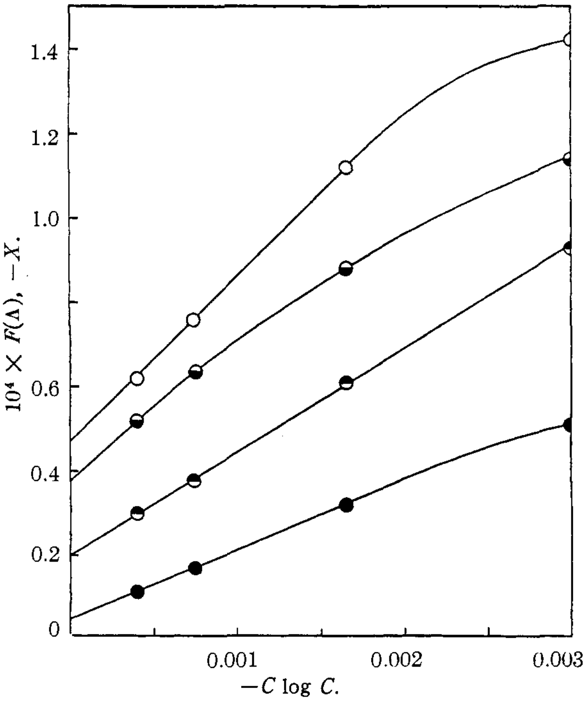

Fig. 1.—Extrapolation by means of equation 3; ○, LiCl, X = 108.00; ◒, NaBr, X = 97.90; ◓, KBr, X = 91.60; ●, KI, X = 86.80.

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(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 590.

(15) L. G. Longsworth, reported in D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 339.

(16) B. B. Owen and H. Zeldes, *J. Chem. Phys.*, **18**, 1083 (1950).

(17) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

extrapolation amounts at most to a few hundredth's of a per cent. in $1/\Lambda_0$. As is evident from Table III, the two methods of extrapolation lead to essentially the same results.

Discussion

One test may be applied at once to the data of Table II. The difference between the values of Λ_0 for KBr and NaBr is 7.19 units, and this agrees within experimental precision with the corresponding difference[2] for the two chlorides—7.17 units; since transference measurements[1,2] have shown that the limiting chloride conductances for KCl and NaCl also obey the Kohlrausch rule, we believe this supplies additional evidence in favor of the limiting ion conductances given in Table IV. It must however be noted that here, as with KCl and NaCl, our results are in serious disagreement with the earlier data of Frazer and Hartley[18]; they report for LiCl, NaBr, KBr and KI Λ_0 to be 90.90, 101.5, 109.35 and 114.85, respectively; the deviations between the two sets of results are entirely random, and we can offer no explanation for this curious situation.

TABLE IV

LIMITING ION CONDUCTANCES AND ION CONDUCTANCE–VISCOSITY PRODUCTS IN WATER AND METHANOL

	Li^+	Na^-	K^+	Cl^-	Br^-	I^-
$\lambda^0_\pm$, H_2O	38.68	50.10	73.50	76.35	78.14	76.97
$\lambda^0_\pm$, CH_3OH	39.82	45.22	52.40	52.38	56.55	62.75
$\lambda^0_\pm\eta$, H_2O	0.346	0.448	0.658	0.683	0.699	0.689
$\lambda^0_\pm\eta$, CH_3OH	0.217	0.246	0.285	0.285	0.308	0.342

Table IV also gives for comparison the limiting ionic conductances in water,[19] and also the ionic conductance–viscosity products for the two solvents; as might be expected for small ions, the Walden rule fails completely.[20] As an alternative, one might expect that ion conductance ratios might prove more tractable, particularly if the ions to be compared were of the same sign and charge and (as is the case here) of the noble gas type; in the ratio there should be some cancellation of viscosity effects, the cancellation being more complete the more nearly Stokes' law was obeyed. In fact, if one assumes Stokes' law, change in the ratio with change in solvent or temperature should be a measure of the change in ratio of the effective radii of the two ions in question. On the basis of any simple electrostatic picture of solvation, one would expect the effective radius of the moving entity to depend on the charge, sign and crystallographic radius of the ion, the effective dipole moment of the solvent, the temperature (if some sort of Boltzmann factor were involved) and perhaps on the dielectric constant. Thus an ion conductance ratio should be a function of solvent and temperature, and such dependence for different pairs of symmetrical ions of the same valence type should be of the same general nature, regardless of the particular solvent property or properties selected as significant.

Table V gives values of the logarithm of the limiting ion conductance ratio, $\Delta \log \lambda_0$, at 25 and 45° in water[21] and at 25° in methanol. For the cations, it will be seen that the ratio of the slower to the faster ion increases with rise in temperature (as might be expected) and with decrease in dielectric constant, the relative increase with rise in T or fall in D being greatest for the slowest ion. For Cl^-/Br^-, there is again an increase in ratio with rise in temperature in aqueous solution, but on passing to methanol, the trend is reversed, while with Cl^-/I^-, the faster ion at 25° in aqueous solution is the slower at 45° and is again the faster in methanol. We believe these results support the often expressed view that solvation cannot be treated as a purely electrostatic problem, but that other types of ion–solvent interaction are involved as well.

TABLE V

Δ LOG $\lambda^0_\pm$ FOR PAIRS OF IONS OF LIKE CHARGE AND SIGN

	H_2O, 25°	H_2O, 45°	CH_3OH, 25°
Li^+/K^+	−0.2788	−0.2513	−0.1191
Na^+/K^+	− .1664	− .1470	− .0640
Cl^-/Br^-	− .0101	− .0070	− .0333
Cl^-/I^-	− .0035	+ .0010	− .0785

Since even with a relatively simple quantity such as a limiting conductance ratio, there is a marked difference in behavior between anions and cations, it seems evident that attempts to correlate equivalent as distinct from ionic conductance with solvent properties are doomed to failure. If so, additional transference data are required, and for this reason, if for no other, the development of new and generally applicable transference techniques[22,23] is important.

In conclusion, we wish to express our thanks to the National Research Council of Canada for a grant in aid of this research, for the award of a Studentship and of a Fellowship to R. E. J. and for similar awards to J. P. B.

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[18] J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* (*London*), **A109**, 351 (1925).

[19] For consistency, the values for Li^+ and I^- were obtained by difference from the Λ_0 of this paper; the others are from (3d).

[20] See in particular: Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

[21] The values chosen for Li^+ and I^- at 45° are those of Harned and Owen,[14] the others from (3d).

[22] (a) D. A. MacInnes and B. R. Ray, THIS JOURNAL, **71**, 2987 (1949); (b) D. A. MacInnes and M. O. Dayhoff, *J. Chem. Phys.*, **20**, 1034 (1952).

[23] A. R. Gordon and R. L. Kay, *ibid.*, **21**, 131 (1953).