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A Reinvestigation of the Conductance of Aqueous Solutions of Potassium Chloride, Sodium Chloride, and Potassium Bromide at Temperatures from 15° to 45°C

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The conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide has been redetermined by the direct-current method at temperatures from 15° to 45°C. It is found that on the whole the present measurements satisfactorily confirm the earlier work reported from this laboratory; however, there were apparently slight errors in the temperature scale at 35° and 45° corresponding to a few hundredth's of a percent in the conductance. Revised values of the conductance, of the limiting ionic conductance and its temperature coefficient, and of the coefficients in the Onsager-Shedlovsky equation are tabulated.

IN the course of the work reported in the preceding paper¹ we have reinvestigated the conductance of potassium chloride, sodium chloride, and potassium bromide in aqueous solution at temperatures from 15° to 45°C by the direct-current method. The apparatus and technique were the same as were previously employed.¹⁻³ Bath temperatures were fixed directly with the platinum resistance thermometer which is temperature standard for this laboratory; its calibration by the U. S. National Bureau of Standards has been checked repeatedly at the ice and Glauber Salt points. As in the case of calcium chloride,¹ the measurements are based on the Jones and Bradshaw⁴ 0.01 Demal standard

at 25° rather than on the Jones and Prendergast⁵ 0.01 Normal standard previously employed; this has the effect of decreasing all the conductances 0.021 percent as compared with those previously reported.

We find that the earlier measurements for 35° and 45° correspond in general to temperatures slightly more than 0.01° too high; the exceptions are the sodium chloride data² for 35° (for which the previous temperature was approximately 0.02° too high) and the potassium bromide results³ at 45° where the previous temperature was approximately 0.01° too low. To save space, Table I gives the values of the constants in the Onsager-Shedlovsky equation

$$(\Lambda + 2\sigma\sqrt{C})/(1 - \vartheta\sqrt{C}) = \Lambda_0 + BC + DC \log C, \quad (1)$$

TABLE I.

	15°	25°	35°	45°
ϑ	0.2249	0.2289	0.2335	0.2387
2σ	46.76	60.18	75.20	91.44
Λ_0 , KCl	121.07	149.85	180.42	212.41
B , KCl	217	154	150	158
D , KCl	76	32	16	6
Λ_0 , NaCl	101.18	126.45	153.75	182.65
B , NaCl	210	107	137	159
D , NaCl	73	3	2	0
Λ_0 , KBr	122.81	151.64	182.24	214.17
B , KBr	105	108	143	165
D , KBr	6	0	0	0

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¹ G. C. Benson and A. R. Gordon, *J. Chem. Phys.* **13**, 470 (1945).

² H. E. Gunning and A. R. Gordon, *J. Chem. Phys.* **10**, 126 (1942).

³ H. E. Gunning and A. R. Gordon, *J. Chem. Phys.* **11**, 18 (1943).

⁴ Grinnell Jones and B. C. Bradshaw, *J. Am. Chem. Soc.* **55**, 1780 (1933).

TABLE II.

10°C	0	5	10	20	50	100
Λ for potassium chloride						
15°	121.07	119.40	118.72	117.78	116.04	114.31
25°	149.85	147.76	146.92	145.76	143.56	141.27
35°	180.42	177.85	176.81	175.38	172.68	169.84
45°	212.41	209.30	208.05	206.33	203.07	199.62
Λ for sodium chloride						
15°	101.18	99.61	98.98	98.10	96.47	94.86
25°	126.45	124.51	123.74	122.66	120.64	118.53
35°	153.75	151.33	150.38	149.04	146.55	143.94
45°	182.65	179.71	178.54	176.93	173.88	170.70
Λ for potassium bromide						
15°	122.81	121.19	120.54	119.66	118.00	116.28
25°	151.64	149.57	148.75	147.61	145.46	143.20
35°	182.24	179.68	178.66	177.26	174.62	171.86
45°	214.17	211.06	209.83	208.12	204.90	201.52

⁵ Grinnell Jones and M. J. Prendergast, *J. Am. Chem. Soc.* **59**, 731 (1937).

TABLE III.

	15°	25°	35°	45°
(λ_-°) Cl $_-$, KCl	61.41	76.35	92.21	108.92
(λ_-°) Cl $_-$, NaCl	61.43	76.35	92.22	108.88
(λ_-°) Br $_-$, KBr	63.15	78.14	94.03	110.68
(λ_+°) K $_+$, KCl	59.66	73.50	88.21	103.49
(λ_+°) Na $_+$, NaCl	39.75	50.10	61.53	73.77
(λ_+°) H $_+$, HCl	300.6	349.82	397.0	441.4

which represent the revised data within experimental precision; the values of the theoretical coefficients ϑ and σ are those previously employed.^{4,2} Table II gives the conductance, computed by Eq. (1), for a few round values of the concentration C in moles per liter. When the altered calibration and (at 35° and 45°) the correction for temperature are born in mind, it will be noted that as far as dependence of conductance on concentration is concerned, these results are practically indistinguishable from those previously reported.

Table III gives the revised values of the ionic conductances at infinite dilution. The entries for chloride, potassium, and sodium ions were obtained from the Λ_0 of Table I and the limiting transference numbers.^{6,7} It will be noted that the agreement between λ_-° for potassium chloride and sodium chloride at 35° is closer than was previously reported, but that for 45° it is slightly worse; at all temperatures, however, it is within the precision of the transference measurements. The λ_-° for bromide ion were obtained by dif-

⁶ R. W. Allgood, D. J. Le Roy, and A. R. Gordon, J. Chem. Phys. **8**, 418 (1940).

⁷ R. W. Allgood and A. R. Gordon, J. Chem. Phys. **10**, 124 (1942).

TABLE IV.

	$d \ln \lambda_{\pm}^\circ / dT$			
	15°	25°	35°	45°
Cl $_-$	0.02340	0.02020	0.01765	0.01570
Br $_-$	0.02285	0.01980	0.01730	0.01535
K $_+$	0.02235	0.01950	0.01705	0.01500
Na $_+$	0.02445	0.02180	0.01930	0.01695
H $_+$	0.01655	0.01385	0.01155	0.00970

ference from the Λ_0 for KBr and the λ_+° for K $_+$. The table also includes for comparison λ_+° for hydrogen ion, obtained from the conductance measurements of Shedlovsky⁸ and of Owen and Sweeton⁹ and the values of λ_-° for chloride ion; these differ from those of Owen and Sweeton by 0.3-conductance units at 15° and 35° and by 0.6-conductance units at 45°; the discrepancy is caused by the transference numbers Owen and Sweeton employed. Table IV gives the temperature coefficients for the limiting ionic conductance; these were obtained by differentiating cubic equations fitted to the values of $\ln \lambda^\circ$ for the four temperatures.

When allowance is made for the change in calibration, the revised data in Tables II, III, and IV differ in general from those previously reported by but little more than the precision¹⁰ of the measurements; our present values nevertheless are, we believe, the more reliable, and are moreover self-consistent in the temperature.

⁸ T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).

⁹ B. B. Owen and F. H. Sweeton, J. Am. Chem. Soc. **63**, 2811 (1941).

¹⁰ For a discussion of the correlation of the results obtained by the direct-current method with those given by the more usual alternating-current bridge, see references 1, 2, and 3.