The ionization decreases in all cases steadily with rising temperature, the decrease being more rapid the higher the temperature and the greater the valence-product of the ions of the salt.

The freezing point lowerings caused by most of the same salts were also determined; and from each of these lowerings the mol number i (that is, the number of mols resulting from one formula weight of salt) was calculated and compared with the mol number derived from the conductivity by the well-known expression, $i = 1 + (n - 1)(\Lambda/\Lambda_0)$. Between the two i values considerable differences, far exceeding the experimental error (often of 5–10 per cent. in 0.05–0.2 normal solution), were found to exist, of which we are able to offer no explanation.

BOSTON, July, 1909.

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THE CHANGE OF THE EQUIVALENT CONDUCTANCE OF IONS WITH THE TEMPERATURE.

BY JOHN JOHNSTON.

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In connection with a research on the electrical conductivity of salts of higher ionic type,[1] it was necessary to determine the value of the equivalent conductance (Λ_0) at infinite dilution at eight temperatures ranging from 0° to 156°. The conductance values obtained by actual measurement in extremely dilute solutions are not reliable, unless they are made with great care in a specially constructed apparatus, by means of which access of air or other impurity to the solution is prevented. Even in the case of 0.002 normal solutions it is often difficult to obtain completely concordant results. Recourse was therefore had to extrapolation from higher concentrations, using the function which has been previously employed in this laboratory, *viz.*, $1/\Lambda = 1/\Lambda_0 + K\,(C\Lambda)^{n-1}$, where Λ is the equivalent conductance at the concentration C, and K is a constant. A value of n was chosen so that the graph obtained by plotting the values of $1/\Lambda$ against those of $(C\Lambda)^{n-1}$ was nearly a straight line, and two other graphs corresponding to neighboring values of n on opposite sides of the first line were also drawn. The value of $1/\Lambda_0$ is obtained by determining the most probable point at which these three graphs cut the $1/\Lambda$ axis.

For the salts of simpler type it had been found that lines very nearly straight were obtained with values of n not far different from 1.45; but for the salts of higher types it appears to be impossible to obtain a straight line between the concentrations 0.1 and 0.002 normal, no matter what

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[1] THIS JOURNAL, 31, 987 (1909).

value is assigned to n. As an example the curves for potassium ferrocyanide at 25° are reproduced in Fig. 1.[1]

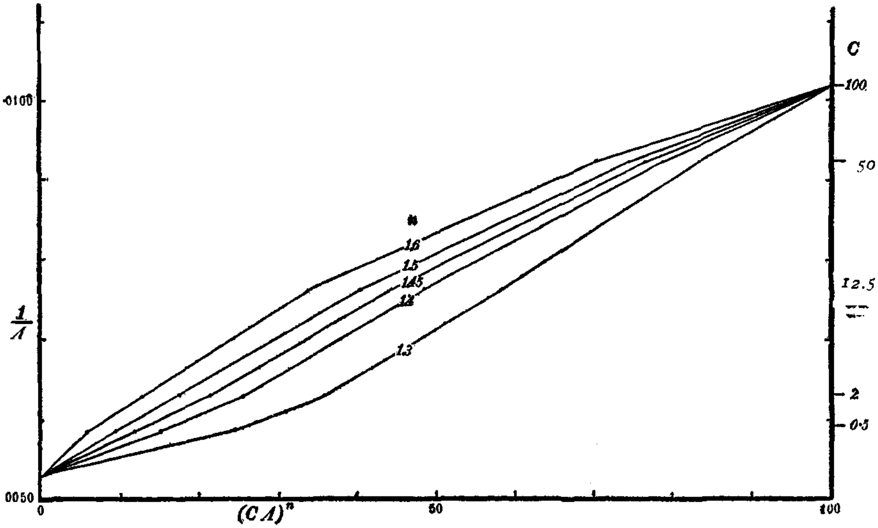

Fig. 1.

It is evident from this figure that values of n of 1.5 or 1.6 give curves convex to the horizontal axis; that when n is 1.3, the graph is mainly concave, while for the intermediate values of n there is double curvature. It is evident, too, that the point of inflexion lies at greater concentrations for the lower values of n, which makes it probable that double curvature exists even when n is 1.5 or 1.6, though in that case the point of inflexion would be near the vertical axis and the Λ_0 value would not be affected thereby to a great extent. It is also probable that this double curvature is present in the graphs of salts of simple ionic type: but there again it would exert only a small influence, since the ionization is greater and consequently the amount of extrapolation necessary is smaller.

A comparison of the Λ_0 values at 18° obtained by this graphical method with those of Kohlrausch, which are based on unusually accurate measurements extending to 0.0001 normal, shows that the former are uniformly higher than the latter,[2] which is what we should expect if double curvature

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[1] In order to make the various curves comparable, the value of $(C\Lambda)^{n-1}$ for the highest concentration (0.100 N) was made equal to 100 for each value of n and the other values were proportionally varied by multiplying by the appropriate factor. For the sake of clearness, the adjoining points are connected by straight lines.

[2] The following values illustrate this:

	KCl.	K_2SO_4.	$Ba(NO_3)_2$.
Kohlrausch	130.1	132.8	116.9
Johnston	130.5	134.6	118.3

existed and had not been taken into account in producing the graphs. The values given in Table 2 are therefore doubtless somewhat too large, especially for the salts of higher ionic types; so finally, by assuming that the temperature coefficients derived from Table 2 were correct, they were brought into agreement with the values commonly accepted.

First of all, however, in order to secure uniformity, I redetermined by graphical extrapolation Λ_0 values for all the salts whose conductivities have been measured at a series of temperatures in this Laboratory,[1] excluding those in which the Λ_0 could be obtained by combining other Λ_0 values, and also the acids and bases HCl, HNO_3, NaOH and $Ba(OH)_2$, which are for the present purpose less important.

These values, though derived independently, differ little, if at all, from those previously published. Table 1 contains these newly determined values of Λ_0, together with the values given for the bases and acids[2] in the previous publication.

TABLE 1.—VALUES OF Λ_0 DERIVED DIRECTLY FROM THE CONDUCTIVITY DATA.

Salt.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
KCl	81.9	130.5	...	...	...	414	...	625
KNO_3	81	126.4	145	220	299	385	480	576
NaCl	...	109.1	...	...	...	362	...	555
NH_4Cl	...	130.6	...	...	...	415	...	628
$AgNO_3$	...	116.1	...	...	...	367	...	570
$NaC_2H_3O_2$	...	78.1	...	...	...	285	...	450
$\frac{1}{2}K_2SO_4$	...	134.6	...	...	...	447	...	715
$\frac{1}{2}K_2C_2O_4$	80.6	128.3	149	232	324	424	537	653
$\frac{1}{2}Ba(NO_3)_2$	...	118.3	...	...	...	384	...	600
$\frac{1}{2}Ca(NO_3)_2$	71.1	113.8	132	205	286	374	475	578
$\frac{1}{3}K_3C_6H_5O_7$	77.5	127	147	230	329	429	...	....
$\frac{1}{3}La(NO_3)_3$	77.8	125	147	229	320	425	555	685
$\frac{1}{4}K_4Fe(CN)_6$	100	163	189	294	417	540	...	....
HCl	...	379	...	...	...	850	...	1085
HNO_3	...	377	421	570	706	826	945	1047
NaOH	...	216	...	...	...	594	...	835
$\frac{1}{2}Ba(OH)_2$	...	222	256	389	...	645	...	847

Since the Λ_0 values obtained by the graphical method are much affected by experimental errors, it was sought to improve the individual values for each salt by plotting them against some function of the temperature. After several functions had been tried, it was found that, when the logarithms of the Λ_0 values were plotted against the logarithms of the fluidity of water corresponding to each temperature, the resulting graph was a straight line, and hence could be used advantageously for interpolation. It was found that the corresponding graphs for the logarithms

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[1] See THIS JOURNAL, 30, 335, *et seq.* (1908).

[2] *Carnegie Publication*, No. 63, pp. 137, 174, 262 (1907).

of the conductances of the separate ions (Λ_K, etc.) are also straight lines; and, as it is much more convenient to use these values than the Λ_0 values for the salts, such graphs were employed.

To obtain such values, the conductances of K^+ and Cl^- were first derived for potassium chloride from the data of Table 1 with the help of the transference numbers for this salt. The best values of the latter are probably those of Jahn[1] and Bogdan.[2] For the transference number of the cation at 18° at a dilution of 120 liters (which for this purpose is equivalent to infinite dilution), a value of 0.497 was found. From this follows $\Lambda_K = 64.8$ and $\Lambda_{Cl} = 65.7$ at 18°. Further, the experiments of Jahn at the three temperatures 0°, 18° and 30° show that with increasing temperature the transference numbers always approach 0.5; so in default of exact knowledge of the transference number at 100°, the probable assumption is made that it is 0.5, when $\Lambda_K = \Lambda_{Cl} = 207$ at 100°.[3]

In equalizing the experimental errors and studying the effect of temperature on the conductance, the relation of the latter to fluidity was found most helpful, as stated above. The results on the viscosity (η) of water at temperatures up to 100° given by Thorpe and Rodger[4] were used, the values being calculated from the formula given by them,

$$\eta = \frac{5.9849}{(43.252 + t)^{1.5423}}$$

which may also be written in the form

$$\log \varphi = 1.5423 \log (43.252 + t) - 0.7771,$$

where φ is the fluidity (equal to $1/\eta$). On calculating by means of this formula the viscosity of water at 128°, the value 0.00215 is obtained, which is identical with the value interpolated from the results of de Haas.[5] At 156° the formula gives 0.00170, while extrapolation from the data of de Haas gives 0.00178. The mean of these two results was adopted.[6]

With values of $\log \Lambda_K$ as ordinates and of $\log \varphi$ as abscissae, the points for potassium-ion at 18° and at 100° were laid down on a large scale, and were joined by a straight line which was produced in both directions.

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[1] *Z. physik. Chem.*, **58**, 645 (1907).

[2] *Ibid.*, **37**, 673 (1901).

[3] Bein (*Z. physik. Chem.*, **27**, 1 (1898) has made transference experiments at temperatures up to about 75°; his results at the lower temperatures do not agree very well with those of Jahn, while at the higher temperatures there is some uncertainty in the corrections to be applied. At the highest temperature, 76°, Bein obtained the values 0.490, 0.489, 0.482, 0.492 as the transference number of potassium ion On account of this uncertainty the procedure given above was preferred.

[4] The values of the fluidity at the temperatures in question are:

0°.	18°.	25°.	50°.	75°.	100°.	128°.	150°.
56.24	95.35	112.2	182.5	263.1	353.3	465.4	575

[5] See *Landolt-Börnstein-Meyerhoffer Tabellen*, pp. 76–77.

[6] This was done because the value 0.00178 seemed to be somewhat high, since, when it was used, all the graphs curved a little downwards beyond 128°.

From this plot the values of log Λ_K corresponding to each of the other temperatures in question were taken off. Then, taking as an example the case of KNO_3, these values of Λ_K were subtracted from the original Λ_0 values for KNO_3 given in Table 1; the logarithms of the resulting rough values of Λ_{NO_3} were plotted as before against log φ and the best straight line drawn through all the points. The conductance values for chloride-ion and for the other ions were obtained in a similar manner, except that the graphs for hydrogen-ion and for hydroxide-ion are curves, in consequence of which the accuracy of the interpolation is not so great. Their graphs were the only ones that exhibited noticeable deviation from linearity. In what follows, unless the contrary is expressly stated, these two exceptional ions are not included in the discussion. The results for all the ions are brought together in Table 2.

TABLE 2.—VALUES OF THE EQUIVALENT CONDUCTANCES OF THE SEPARATE IONS.

Ion.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
K	40.5	64.8	74.8	115.3	159	207	264	319
Na	26	43.4	50.8	81.6	116	155	202	248
NH_4	40.4	64.8	74.9	115.4	160	208	265	320
Ag	32.7	54	63.1	100	142	187	244	297
$\frac{1}{2}Ba$	33.4	56.3	66.1	107	153	205	268	330
$\frac{1}{2}Ca$	30.6	52.1	61.4	100.3	145	195	257	319
$\frac{1}{3}La$	37	63.7	75.4	124.5	181	246	326	406
Cl	41.2	65.7	75.6	116	160	208	265	319
NO_3	40.5	62	70.9	105	141	179	223	264
$C_2H_3O_2$	20.3	34.6	40.8	66.6	96.3	130	171	211
$\frac{1}{2}SO_4$	42.3	69.7	81.3	128	181	240	311	380
$\frac{1}{2}C_2O_4$	39	63.8	74.3	117	164	216	279	340
$\frac{1}{3}C_6H_5O_7$	37	62.1	72.6	117	166	221	....	...
$\frac{1}{4}Fe(CN)_6$	60.4	98.6	115	180	253	333	....	...
H	240[1]	314	350	465	565	644	722	777
OH	105[1]	172	192	284	360	439	525[1]	592

That this method of interpolation is justified as an empirical one by the results is shown by the fact that, if we compare the values of Λ_0 in Table 1 for all the salts for which Λ_0 was determined at each temperature with those obtained by adding together the appropriate values of the ionic conductances, the differences are irregular, and, with one or two exceptions, are within much less than 1 per cent. of the Λ_0 value.

The equivalent ionic conductances at 18° as tabulated above do not differ much from those given by Kohlrausch,[2] whose values are probably the most reliable at present, because, since his measurements were extended to solutions of very small concentration, relatively less extrapolation was necessary, with a proportionately increased accuracy of the Λ_0

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[1] Relatively inexact values.

[2] Kohlrausch, *Z. Elektrochem.*, 13, 333 (1907).

values. On this account, in giving a table of definitive values, it seemed better so to amend Table 2 as to bring the values at 18° in accord with those of Kohlrausch. For several of the ions considered here, however, no data are given by Kohlrausch; in these cases, the values adopted were such as seemed most probable from a comparative study of the values of Λ_0 at 18°.[1] The values at 18° served as a basis from which those at the other temperatures were calculated with the aid of the temperature coefficients deduced from the values of Table 2 and given in Table 4.

TABLE 3.—THE EQUIVALENT CONDUCTANCE OF THE SEPARATE IONS.

Ion.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
K	40.4	64.6[2]	74.5	115	159	206	263	317
Na	26	43.5[2]	50.9	82	116	155	203	249
NH_4	40.2	64.5	74.5	115	159	207	264	319
Ag	32.9	54.3[2]	63.5	101	143	188	245	299
$\frac{1}{2}$Ba	33	55[2]	65	104	149	200	262	322
$\frac{1}{2}$Ca	30	51[2]	60	98	142	191	252	312
$\frac{1}{3}$La	35	61	72	119	173	235	312	388
Cl	41.1	65.5[2]	75.5	116	160	207	264	318
NO_3	40.4	61.7[2]	70.6	104	140	178	222	263
$C_2H_3O_2$	20.3	34.6	40.8	67	96	130	171	211
$\frac{1}{2}SO_4$	41	68[2]	79	125	177	234	303	370
$\frac{1}{2}C_2O_4$	39	63[2]	73	115	163	213	275	336
$\frac{1}{3}C_6H_5O_7$	36	60	70	113	161	214	...	...
$\frac{1}{4}Fe(CN)_6$	58	95	111	173	244	321	...	...
H	240	314	350	465	565	644	722	777
OH	105	172	192	284	360	439	525	592

From the method of drawing the graphs, it is obvious that the relation between ionic conductance (Λ) and fluidity (φ) is given by the equation

$$\log \Lambda = m \log \varphi + \log k_1; \text{ or } \Lambda = k_1 \varphi^m, \ldots\ldots\ldots\ldots (1)$$

where m and k_1 are constants for each ion. The values of m and $\log k_1$ for the various ions are given in the second and third columns of Table 4.

The relation between the fluidity and the temperature function θ (which is equivalent to $43.25 + t$, t being the temperature above zero centigrade), as obtained from the expression given by Thorpe and Rodger for the change of viscosity of water with the temperature, has the form

$$\varphi = k_2 \theta n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

k_2 and n being constants (n having the value 1.542). Hence the relation between Λ and θ has the form

$$\Lambda = \theta^p / k \text{ or } \log \Lambda = p \log \theta - \log k. \ldots\ldots\ldots\ldots (3)$$

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[1] The question of the choice of Λ_0 values at 18° will be fully discussed in a later publication from this laboratory. Cf. also THIS JOURNAL, 31, 746.

[2] Kohlrausch, *loc. cit.*

The values of p and of $\log k$ for each ion are given in the fourth and fifth columns of Table 4. With their aid the value of Λ at any temperature can be readily derived.

TABLE 4.—VALUES OF THE CONSTANTS IN THE EQUATIONS (1) AND (3).

($\theta = 43.25 + t$; $n = 1.542$.)

	$\log \Lambda = m \log \varphi + \log k_1$.		$\log \Lambda = p \log \theta - \log k$.		
Ion.	m.	$\log k_1$.	p.	$\log k$.	$p-n$.
K	0.887	+0.054	1.368	0.635	−0.174
Na	0.97	−0.281	1.495	1.034	−0.047
NH_4	0.891	+0.045	1.374	0.647	−0.168
Ag	0.949	−0.143	1.463	0.88	−0.079
$\frac{1}{2}$Ba	0.986	−0.212	1.521	0.978	−0.021
$\frac{1}{2}$Ca	1.008	−0.286	1.554	1.069	+0.012
$\frac{1}{3}$La	1.03	−0.253	1.588	1.053	+0.046
Cl	0.88	+0.074	1.357	0.609	−0.185
NO_3	0.807	+0.194	1.245	0.432	−0.297
$C_2H_3O_2$	1.008	−0.455	1.554	1.238	+0.012
$\frac{1}{2}SO_4$	0.944	−0.037	1.456	0.768	−0.086
$\frac{1}{2}C_2O_4$	0.931	−0.043	1.436	0.766	−0.106
$\frac{1}{3}C_6H_5O_7$	0.972	−0.146	1.499	0.901	−0.043
$\frac{1}{4}Fe(CN)_6$	0.929	+0.139	1.433	0.582	−0.109

From the above equations it follows that

$$\Lambda/\varphi = k_3\theta^{p-n} = k_3\,\theta^{n(m-1)}. \tag{4}$$

Now, if the assumption is made that change of fluidity directly causes a proportional change in the conductance, the magnitude of the factor $p - n$ (or of $m - 1$) is a measure of the influence of secondary specific factors characteristic of the separate ions—an influence which may well be due in part to changes in hydration. A consideration of the last column

TABLE 5.—VALUES OF $\Lambda/\varphi \times 1000$.

Ion.	Λ at 0°.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
K	40.4	718	678	665	630	603	584	565	553
Na	26	463	456	454	449	442	440	435	433
NH_4	40.2	715	677	665	630	605	586	567	554
Ag	32.9	584	569	565	551	543	533	527	519
$\frac{1}{2}$Ba	33	580	578	575	573	569	568	562	561
$\frac{1}{2}$Ca	30	533	535	536	539	540	541	541	544
$\frac{1}{3}$La	35	620	640	640	650	660	665	670	675
Cl	41.1	729	686	672	633	606	587	568	553
NO_3	40.4	717	648	628	572	534	504	476	456
$C_2H_3O_2$	20.3	361	363	364	365	366	367	367	367
$\frac{1}{2}SO_4$	41	734	714	707	685	671	662	651	644
$\frac{1}{2}C_2O_4$	39	685	661	654	633	616	608	592	583
$\frac{1}{3}C_6H_5O_7$	36	640	630	625	620	615	605	..	..
$\frac{1}{4}Fe(CN)_6$	58	1030	1000	990	950	930	910	..	..
H	240	4270	3300	3120	2550	2150	1820	1550	1350
OH	105	1870	1800	1710	1560	1370	1240	1130	1030

of Table 4, in which the values of $p - n$ are tabulated, shows that the influence of these secondary factors is in most cases comparatively small. This is also shown by Table 5, which contains the values of Λ/φ for the various ions at a series of temperatures; besides which, for purposes of comparison, the values of Λ at 0° are given in the second column.

A consideration of the results in Table 5 suggests that with increasing temperature there is a normal decrease (arising from physical causes) which is a function of the conductance of the ion.[1] Thus this decrease is large and nearly constant for the four ions K^+, NH_4^+, Cl^-, and $C_2O_4^{--}$, having an approximately equal and fairly high conductance at 0°; it is less for Ag^+ ion, and still less for Na^+ ion in correspondence with their smaller conductances, and it has disappeared altogether in the case of $C_2H_3O_2^-$ ion, which has the least conductance; the decrease is, moreover. exceptionally large in the case of the highly conducting H^+ and OH^- ions, and larger in the case of the former. The fact that some ions (Ba^{++}. Ca^{++}, La^{+++}, $SO_4^=$, $Fe(CN_6^{==})$ form exceptions to this principle in the respect that their conductance does not undergo the normal decrease may be explained by a decrease in their hydration with increasing temperature.[2] (The NO_3^- alone forms an exception in the opposite direction, exhibiting, as it does, an abnormally large decrease.) This suggestion is, of course, only of the nature of a hypothesis; but it is one which can be further tested with the aid of additional experimental data.

The relation expressed by equation (1) above appears to be applicable also to solutions in other solvents. Dutoit and Duperthuis[3] published recently some results on the conductance at zero concentration of sodium iodide in a number of solvents at a series of temperatures lying between 0° and 80°; these Λ_0 values they obtained from their conductivity data by applying the Ostwald dilution law, which holds at high dilutions for the solutions in question. In addition the authors give data (in part from the work of Thorpe and Rodger) on the viscosities of the pure solvents at the temperatures in question. The various values are reproduced in Table 6, in which, however, fluidities, instead of viscosities, are given.

On plotting, as before,[4] the values of log Λ_0 against those of log φ,

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[1] That the temperature coefficient of the conductance of ions is in general closely related to the value of the conductance itself has been clearly established by Kohlrausch (see *Sitzungsber, königl. preuss. Acad.*, **26**, 572–580 (1902), and also *Z. Elektrochem.*, **14**, 129 (1908)).

[2] That these multivalent ions are largely hydrated at low temperatures is indicated by the abnormally small values of their equivalent conductance. See Noyes, *Carnegie Institution Publication*, No. **63**, p. 336 (1907).

[3] *J. chim. phys.*, **6**, 726 (1908).

[4] In these solvents, however, it was necessary to use the Λ_0 value for the salt sodium iodide instead of that for either of the ions, since the transference numbers are unknown. Although, considered from an exact mathematical standpoint, the functions for these two cases can not both be of this same form, yet they seem to be

TABLE 6.—VALUES OF Λ_0 FOR SODIUM IODIDE IN VARIOUS SOLVENTS, AND OF φ FOR THE PURE SOLVENTS.

	Ethyl Alcohol.		Propyl Alcohol.		Isobutyl Alcohol.	
$t°$.	Λ_0.	φ.	Λ_0.	φ.	Λ_0.	φ.
0	27.95	56.5	11.85	26.15	5.48	12.44
10	33.83	68.96	15.68	34.8	7.77	18.03
20	40.52	84.03	20.28	45.02	10.81	25.6
30	47.87	101	25.73	57.12	14.87	34.92
40	56.13	120.8	32.42	72.36	19.54	47.15
50	66.24	143.3	40.33	90.02	25.6	62.16
60	77.25	168.9	48.93	110.5	32.02	80.72
70	.....	......	58.26	133.7	38.73	102.8
80	.....	......	......	......	45.33	128.4

	Isoamyl Alcohol.		Acetone.		Pyridine.	
0	4.49	12.03	127.5	253.8	42.1	73.53
10	5.95	17.13	142.7	280.9	50.4	88.5
20	7.8	23.64	159	309.6	59.15	104.4
30	10.06	31.95	176	341.2	68.1	120.6
40	12.7	42.55	192.9	373.2	77.86	138.1
50	15.79	55.55	......	......	88.23	156.5
60	19.24	71.43	......	......	98.76	175.8
70	22.75	89.28	......	......	109.65	196.8
80	28.3	111.1	......	......	120.9	216.5

the graphs proved again to be straight lines. The deviations from linearity are small and irregular, except at the two highest temperatures in the case of isobutyl alcohol; this divergence is probably due to some experimental error, since the concordance is otherwise so good. For each of the solvents, therefore, the relation between Λ_0 and φ has as before the form $\log \Lambda_0 = m \log \varphi - \log k$. The values of m and of $\log k$ are brought together in Table 7.

TABLE 7.—VALUES OF THE COEFFICIENTS IN THE EQUATION $\log \Lambda_0 = m \log \varphi - \log k$.

Solvent.	m.	$\log k$.
Ethyl alcohol..................	0.935	0.192
Propyl alcohol................	0.974	0.303
Isobutyl alcohol..............	0.955	0.308
Isoamyl alcohol...............	0.806	0.213
Acetone......................	1.086	0.507
Pyridine.....................	0.99	0.228

This table shows that, notwithstanding the diversity of character of the solvents, the coefficient m does not differ greatly from unity (except in the case of isoamyl alcohol); in other words, for any one solvent, under varying conditions of temperature, the conductance at zero concentration

approximately so in practice, as shown by the results obtained in aqueous solutions, owing no doubt to the fact that the exponent m is nearly unity and varies little with the nature of the ion.

is very nearly proportional to the fluidity of the solvent. This is shown perhaps more clearly by Table 8, containing the values of Λ_0/φ.

TABLE 8.[1]—VALUES OF $\Lambda_0/\varphi \times 1000$.

t°.	Ethyl alcohol.	Propyl alcohol.	Isobutyl alcohol.	Isoamyl alcohol.	Acetone.	Pyridine.
0	495	453	440	373	502	572
10	491	451	431	347	508	570
20	482	451	422	330	514	567
30	474	450	426	315	516	565
40	465	448	414	299	517	564
50	462	448	412	284	...	564
60	457	443	397	269	...	562
70	...	436	377	255	...	557
80	...	...	353	255	...	558

Summary.

In this article are presented (in Table 1) newly derived values of the equivalent conductance (Λ_0) at zero concentration between 0° and 156° for the salts previously investigated in this laboratory up to the latter temperature. On the assumption, which is doubtless nearly correct, that at the higher temperatures the equivalent conductance of potassium-ion and chloride-ion are equal, values for the equivalent conductances of the separate ions were calculated for eight different temperatures between 0° and 156°. These values are presented in Table 3 above.

A consideration of the results has shown that the equivalent conductance (Λ) in aqueous solutions of each of these ions (except hydrogen-ion and hydroxide-ion) through the range of temperature in question, is a function of the fluidity (φ) of water of the form $\Lambda = k\varphi^m$ where m is a constant for each ion, varying between 0.81 and 1.03 for the different ions (see Table 4). The graph is therefore linear when the values of log Λ for any one ion are plotted against those of log φ; and such a plot can be used to advantage as a method of obtaining by interpolation the value of Λ for a given ion at any temperature.

It has been further shown by combination of this result with the known functional relation between the fluidity of water and the temperature that the relation between Λ and the temperature t may be expressed by the equation $\Lambda = (1/k)(t + 43.25)^p$. Values of the constants p and of log k have been given in Table 4, thus enabling one to calculate the conductance for any ion at any temperature.

Values of the ratio Λ/φ have also been given (in Table 5) for the various ions at the various temperatures. Consideration of these values seems to show: (1) that with increasing temperature there is a decrease in this ratio arising from physical causes which is a function of the conductance of the ion, the decrease being greater when the conductance is greater;

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[1] Cf. Dutoit and Duperthuis, *loc. cit.*, p. 729.

and (2) that the exceptional behavior of some ions, especially those of higher valence, is to be attributed to a change in their state of hydration with the temperature.

Finally, making use of the data of Dutoit and Duperthuis, it is shown that analogous relations hold for solutions of sodium iodide in six organic solvents of diverse character

In conclusion, I desire to express my thanks to Prof. A. A. Noyes for valuable suggestions in connection with the preparation of this paper.

ON THE NATURE OF PRECIPITATED COLLOIDS.

[SECOND PAPER.]

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In a previous article[1] by one of us, evidence has been given to show that precipitated iron or aluminium hydroxides may be regarded as solid solutions of water in the oxide or in some lower hydrate. In that article, a method was described for determining the composition of the so-called saturated solution of water in the oxide. Briefly the method consisted in slowly drying the moist precipitated hydroxides in the air, at intervals placing them over pure water in a closed vessel immersed in a thermostat for twenty-four hours or more.

In the drying process, a point was reached where the material began to gain in weight when placed over water and the composition at the point where gain in weight first occurred, was that of the saturated solution. The water removed up to this point was considered mechanical water and the water remaining in the oxide was regarded as dissolved. The reasons for this conclusion will be found in the first paper. The results obtained showed that the composition of the "saturated solutions" was practically independent of the method of preparation but varied with the temperature as is the case in general with saturated solutions. It was found that the point where the residues began to take up water, or in other words, the point where mechanical water was removed, could be determined approximately by the mechanical condition of the residues which were moist and somewhat waxy or pasty up to this point and were dry and powdery when more water was removed. This fact was of the greatest assistance in carrying out determinations, for the precipitates could be dried till nearly all the mechanical water was removed before testing them over water in the thermostat for loss or gain in weight.

The errors in the results obtained were considerable. This was partly because the tests for gain or loss in weight showed only the limits be-

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[1] THIS JOURNAL, 30, 1388.