LVIII. The electrical conductivity and fluidity of solutions

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It is generally admitted that this assumption is illegitimate as an assumption, but (at any rate in the case of an infinitely rare gas) true in fact. But is Mr. Burbury prepared to charge with inconsistency all those that hold these views?

It need hardly be said that I am very grateful to Mr. Burbury for the kind interest he has always taken in my work. Criticism, in particular, is always of special value to anyone who, like myself, has not worked at a subject for long. But in the present instance, although it is only with the greatest diffidence that I have ventured to try to maintain my position against Mr. Burbury's criticism, I cannot persuade myself that these criticisms have any true foundation.

J. H. JEANS.

LVIII. *The Electrical Conductivity and Fluidity of Solutions.*
By RICHARD HOSKING, 1851 *Exhibition Science Research Scholar**.

THE present paper describes experiments carried out in the Cavendish Laboratory, Cambridge, during the year 1903 and the Michaelmas Term 1902; and these experiments are the continuation of work performed in the Physical Laboratory, Melbourne, and described in the *Philosophical Magazine* for May 1902 †, in a joint paper by Professor Thomas R. Lyle and myself.

One of the main results of the Melbourne work was to show that both the Specific Molecular Conductivity and the Fluidity of the solutions used became zero at the same temperature, viz., $-35^{\circ}5$ C.

This result was based on the form of the curves representing the temperature variations of both these quantities between 100° C. and 0° C.; but it is interesting to find that Kohlrausch ‡ quite independently arrived at the conclusion that in the case of dilute aqueous solutions, all conductivities would cease at practically the same temperature, viz., -39° C.

Another general result was that the fluidity-concentration isothermals and the conductivity-concentration isothermals all cut the axis of zero fluidity and conductivity respectively at the same point, representing a concentration of 10.74 normal. It was felt that these, and other conclusions arrived

* Communicated by Prof. J. J. Thomson, F.R.S.

† *Phil. Mag.* May, 1902, p. 487.

‡ *Sitz. Akad. Wiss. Berlin*, Oct. 31st, 1901.

at, needed further investigation, and with that object mainly in view the experiments described in the present paper were undertaken.

As solutions with high concentrations would be necessary to test one of these points, lithium chloride was chosen as the salt to be used.

The method of experimenting was practically unaltered, but there were slight variations which will be briefly indicated, The dilatometer described in the joint paper was again used for measuring the specific gravity of my solutions at all the temperatures.

Viscosity.

The glischrometer was changed back to the original form described in an earlier paper (Phil. Mag. March 1900, p. 274), which was more likely to give accurate values for viscosity; and the viscosity of my solutions was found in the way there described.

In this new glischrometer the following constants were determined, correct at 0° C.

Corrected length of capillary tube = 5·4391 cms.

Mean radius of the capillary tube = 0·011592 cms.

Working volume of each limb = 3·8441 c.cms.

and in the formula

$$\eta_t = \alpha \times \rho \times h \times T - \beta \frac{\delta}{T} (1 + 2\gamma t)$$

the values for $\log \alpha$ and $\log \beta$ came out as $\bar{7} \cdot 521643$ and $\bar{2} \cdot 44902$.

Resistance.

The cell in which the electrical resistances were measured was similar to that described in the joint paper, and its capacity was determined by measuring in it the resistance of a standard solution of sulphuric acid (20 per cent. by weight). The value obtained for the capacity was 136·43 cm.⁻¹ at 18° C.

The modified arrangement of Kohlrausch's method *, by which a double commutator and a moving coil galvanometer are used instead of the coil and telephone, was employed to determine the resistances. Our previous arrangement was very similar, the magneto-alternator being used instead of the dry cells and one set of sectors on the commutator.

The commutator was driven by a water-motor, and could

* Phil. Trans. A. cxciv. p. 330 (1900).

be kept rotating at constant speed by controlling the water-supply with a long lever fixed to the tap.

The unit of resistance used throughout was the ohm, and the unit of concentration the number of gramme equivalents of salt per cubic centimetre of solution.

The conductivity of the water used for making up the solutions was found to be 4.9×10^{-6} at 18° C.

General Arrangement of Apparatus.

The bath contained the dilatometer, glischrometer, electrolytic cell, thermometer, and stirrer; and these were all held rigidly from above. It was enclosed in an iron jacket with glass windows at the front and back, and was heated from below by a large burner or small controlling flame as required.

Telescopes were used for reading the thermometer, observing the coincidence of meniscus and line in the glischrometer, reading the dilatometer as well as setting it, and for viewing the scale reflected from the mirror of the galvanometer.

The limbs of the glischrometer were connected by rubber tubing to the manometer and compressed-air cylinder through three-way taps, and each could be put in connexion with pressure or atmosphere independently.

An accuracy of 1 in 1000 was aimed at throughout, and corrections to stop-watch, manometer readings, and thermometers were carefully ascertained.

The temperature of the bath was kept constant within $\frac{1}{10}^{\circ}$ C. while the necessary readings were being taken, and the stirring was very efficient.

The lithium chloride was obtained pure. It was completely soluble in a mixture of ether and alcohol, and gave no residue when dissolved in water.

The solutions were not made up to any particular strength, but were obtained by diluting a stock solution. The densities of the solutions were measured in the dilatometer while the viscosities and resistances were being measured in the glischrometer and cell respectively.

Results.

With pure water in the dilatometer and glischrometer a set of readings was taken every 10° , from 0° C. to 100° C., and the values for the density thus obtained were correct within 0.01 per cent., and those for viscosity agreed within 0.1 per cent. with those originally obtained by me.

Eight solutions were made up, and these will be referred to in the following pages as solutions 1, 2, 3, . . . 8.

The following table will give an idea of their composition and properties at 15° C.; where density means specific gravity 15/4, concentration means $\frac{\text{gm.-equivalent}}{\text{litre}} = n$, and normal solution = 42.48 gms. per litre.

Solution.	Density.	Concentration.	Viscosity.	Fluidity.	Resistance.	Sp. Mol. Conduct.	C/F.
Water...	0.9992	.....	.01143	87.5	27.6×10^6	92.5	1.057
1.....	0.9992	0.00645	.01144	87.4	242700	87.1	0.997
2.....	1.0016	0.1030	.01152	86.8	17210	76.9	0.886
3.....	1.0115	0.5203	.01220	82.0	4000	65.6	0.800
4.....	1.0234	1.0125	.01308	76.5	2281	59.1	0.772
5.....	1.0665	2.937	.01718	58.2	1055	44.0	0.756
6.....	1.1107	5.02	.02331	42.7	887	31.0	0.719
7.....	1.1611	7.36	.03640	27.5	953	19.6	0.715
8.....	1.2319	10.71	.00805	12.4	1440	8.8	0.710

Viscosity and fluidity are given in absolute measure. Resistance is given in ohms = R, and

$$\text{sp. mol. cond.} = C = \frac{x(1-gt)}{n \times 10^{-3} \times R},$$

where x is the capacity of the cell and $(1-gt)$ is the temperature correction for the expansion of the glass.

Instead of Water we may write Solution of infinite dilution. In resistances of 1 and 2, conductivity of the water is allowed for.

The temperature of the bath, while readings were being taken, was generally within one or two tenths of a degree of the even temperatures 0°, 10°, 20°, &c., &c.; so that in calculating the values of the viscosity, resistance, and density at these even temperatures from their values at the actual temperatures observed, the amount of error introduced was extremely small.

It is the smoothed values, obtained in this way, which are collected in the following tables, A, B, and C, and we may take the actual observations of solution 5 as typical of all, and reproduce them here also.

Solution 5. (Actual observations.)

Weight of solution in dilatometer (corrected) = 5.4123 gms.

Bath.		Glischrometer.			Bath.	Glischro- meter.	Dilato- meter.	Cell.
Temp. (Cent.).	Vari- ation.	Time (secs.).	Pressure (cms.).	Viscosity	Mean Temp.	Viscosity	Dilatr. (divs.).	Resist. (ohms)
{ 0.15	-0.00	556.0	143.9	.02646	0.15	.02644	24.0	1545.3
{ 0.15	-0.00	551.0	144.9	.02642				
{ 9.70	-0.02	421.0	142.6	.01984	9.71	.01982	29.2	1196.2
{ 9.72	+0.06	421.4	142.2	.01980				
{ 20.00	-0.00	333.1	139.2	.01529	20.00	.01527	36.9	948.8
{ 20.00	-0.00	334.1	138.5	.01526				
{ 30.30	-0.00	302.3	122.9	.01222	30.35	.01220	46.9	776.2
{ 30.40	-0.00	301.7	122.7	.01217				
{ 40.06	-0.00	250.0	123.4	.01011	40.06	.01009	58.0	658.5
{ 40.06	-0.00	249.2	123.2	.01006				
{ 50.20	-0.00	219.4	118.7	.00850	50.20	.00850	71.3	566.6
{ 50.19	-0.02	218.6	119.0	.00849				
{ 59.68	-0.00	197.2	114.2	.00732	59.68	.00731	85.3	499.5
{ 59.68	-0.00	196.4	114.5	.00731				
{ 69.98	+0.02	177.6	110.6	.00635	70.02	.00633	101.7	441.5
{ 70.07	+0.06	177.0	110.3	.00631				
{ 79.92	+0.04	157.4	110.4	.00558	79.95	.00558	119.0	397.2
{ 79.97	-0.00	155.8	111.5	.00558				
{ 89.83	-0.08	189.2	82.0	.00499	89.80	.00499	157.3	361.5
{ 89.77	-0.00	187.4	82.8	.00499				
{ 95.10	+0.10	177.6	82.9	.00472	95.15	.00472	148.4	343.7
{ 95.20	+0.10	179.8	81.9	.00473				

TABLE A.—Density of LiCl Solutions.

Temp.	Water.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	.9999	1.0003	1.0026	1.0131	1.0253	1.0694	1.1142	1.1654	1.2368
10	.9997	0.9999	1.0023	1.0124	1.0243	1.0676	1.1119	1.1626	1.2334
18	.9986	0.9986	1.0012	1.0110	1.0229	1.0658	1.1099	1.1601	1.2309
20	.9983	.9983	1.0009	1.0106	1.0225	1.0653	1.1094	1.1596	1.2301
30	.9958	.9958	.9980	1.0083	1.0197	1.0623	1.1064	1.1565	1.2267
40	.9923	.9923	.9947	1.0045	1.0162	1.0590	1.1032	1.1533	1.2232
50	.9882	.9882	.9905	1.0003	1.0121	1.0552	1.0996	1.1500	1.2196
60	.9834	.9834	.9855	.9958	1.0076	1.0509	1.0957	1.1462	1.2159
70	.9779	.9779	.9803	.9905	1.0028	1.0464	1.0918	1.1422	1.2120
80	.9719	.9719	.9747	.9849	.9972	1.0416	1.0876	1.1381	1.2080
90	.9656	.9656	.9683	.9790	.9915	1.0366	1.0830	1.1340	1.2039
100	.9586	.9586	.9614	.9728	.9856	1.0312	1.0781	1.1298	1.1998

TABLE B.—Viscosity of LiCl Solutions.

Temp.	Water.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	·01794	·01802	·01806	·01894	·02025	·02652	·03558	·05576	·1290
10	·01309	·01310	·01320	·01397	·01497	·01965	·02652	·04150	·0937
18	·01060	·01061	·01070	·01133	·01212	·01600	·02169	·03365	·0739
20	·01009	·01012	·01020	·01075	·01154	·01527	·02070	·03204	·0699
30	·00802	·00804	·00810	·00859	·00920	·01228	·01664	·02562	·0540
40	·00659	·00659	·00668	·00706	·00758	·01012	·01366	·02112	·0431
50	·00554	·00554	·00561	·00595	·00636	·00853	·01156	·01751	·03552
60	·00472	·00472	·00479	·00510	·00542	·00728	·00995	·01482	·02957
70	·00408	·00408	·00414	·00441	·00474	·00632	·00865	·01289	·02508
80	·00358	·00358	·00363	·00390	·00417	·00558	·00764	·01133	·02161
90	·00319	·00319	·00323	·00346	·00368	·00496	·00686	·01003	·01885
100	·00287	·00287	·00292	·00308	·00325	·00444	·00617	·00895	·01660

TABLE C.—Resistance of LiCl Solutions.

Temp.	LiCl Solutions.							
	1.	2.	3.	4.	5.	6.	7.	8.
0° C.	370500	25870	5974	3360	1552	1291	1398	2240
10	275200	19460	4513	2568	1186	995	1070	1652
18	227300	16050	3740	2131	990	830	891	1336
20	217700	15350	3588	2033	949	796·9	853·4	1274
30	177200	12520	2931	1661	781·1	655·8	699·5	1006
40	147600	10590	2462	1402	659·0	552·7	585·2	819
50	126100	8985	2112	1205	568·1	476·9	500·3	680
60	109200	7810	1840	1052	496·5	417·5	434·8	578
70	96500	6910	1629	931·3	441·5	369·4	384·0	500
80	86040	6190	1460	836·6	396·9	331·3	342·3	436
90	77980	5585	1323	759	360	301·5	308·9	386
100	71080	5080	1210	693	330	278·0	281·5	348

Knowing the molecular concentrations of our solutions at any one temperature, say 18° C., we can calculate them for the other temperatures from the alteration in the density as we heat or cool the solutions.

Professor Kohlrausch kindly supplied me with the figures connecting the density of lithium chloride solutions at 18° C. (18/4) with the concentration; and these were used in determining the concentration of my solutions at 18° C., and, by means of Table A, the concentration at the other temperatures as well. These concentrations, in grammes-equivalents per litre, are given in Table D.

Table E gives the fluidity values obtained by inverting the values in Table B; and Table F, by using the values for R in Table C, and for n in Table D, gives the values for the

TABLE D.—Concentration (n) of LiCl Solutions.

Temp.	LiCl Solutions.							
	1.	2.	3.	4.	5.	6.	7.	8.
0° C.	·00646	0·1032	0·5211	1·0144	2·945	5·04	7·38	10·75
10	·00646	0·1031	0·5207	1·0154	2·940	5·03	7·37	10·72
18	·00645	0·1030	0·5200	1·0120	2·935	5·02	7·35	10·70
20	·00645	0·1030	0·5198	1·0116	2·934	5·02	7·35	10·70
30	·00643	0·1027	0·5186	1·0088	2·925	5·00	7·33	10·67
40	·00641	0·1023	0·5167	1·0054	2·916	4·99	7·31	10·63
50	·00638	0·1019	0·5145	1·0013	2·906	4·97	7·29	10·60
60	·00635	0·1014	0·5122	0·9968	2·894	4·96	7·26	10·57
70	·00632	0·1008	0·5095	0·9921	2·882	4·94	7·24	10·53
80	·00628	0·1002	0·5066	0·9866	2·868	4·92	7·21	10·50
90	·00624	0·0996	0·5035	0·9810	2·854	4·90	7·19	10·46
100	·00619	0·0989	0·5004	0·9750	2·840	4·88	7·16	10·43

TABLE E—Fluidity (F) of LiCl Solutions.

Temp.	Water.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	55·73	55·50	55·37	52·80	49·38	37·71	28·10	17·93	7·75
10	76·40	76·33	75·76	71·38	66·80	50·89	37·71	24·10	10·67
18	94·35	94·25	93·40	88·26	82·50	62·50	45·89	29·72	13·33
20	99·11	98·81	98·00	93·02	86·65	66·49	48·31	31·21	14·30
30	124·7	124·4	123·4	116·4	108·9	81·43	60·09	39·03	18·52
40	151·7	151·7	149·7	141·6	131·9	98·84	73·21	47·31	23·20
50	180·4	180·4	178·2	168·1	157·2	117·2	86·50	57·11	28·15
60	211·9	211·9	208·8	196·0	184·3	137·4	100·5	67·32	33·82
70	245·1	245·1	241·5	226·8	211·0	158·2	115·6	77·58	39·87
80	279·4	279·4	275·5	256·4	240·0	179·2	130·9	88·26	46·28
90	313·5	313·5	309·6	289·0	271·8	201·6	145·8	99·70	53·05
100	348·4	348·4	343·0	324·6	307·7	225·2	162·0	111·70	60·24

TABLE F.—Sp. Mol. Cond. (C) of LiCl Solutions.

Temp.	Infinite Dilution.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	60·60	57·0	51·13	43·82	40·03	29·85	21·23	13·22	5·66
10	81·4	76·8	67·99	58·05	52·42	39·12	27·60	17·31	7·70
18	98·9	93·1	82·52	70·14	63·26	46·95	33·15	20·84	9·54
20	103·4	97·2	86·31	73·15	66·33	49·00	34·53	21·77	10·01
30	127·6	119·8	106·1	89·75	81·41	59·70	42·08	26·61	12·72
40	153·4	144·2	125·9	107·2	96·78	70·98	50·1	31·9	15·67
50	180·0	169·5	149·0	125·5	113·1	82·64	58·2	37·5	18·87
60	209·6	196·6	172·3	144·7	130·1	94·9	66·8	43·3	22·33
70	239·2	223·6	195·7	164·4	147·7	107·3	75·7	49·2	25·9
80	269·6	252·6	219·8	184·5	165·3	119·8	84·8	55·3	29·8
90	299·7	280·4	245·2	204·8	183·2	132·7	93·6	61·5	33·6
100	330·6	309·8	271·5	225·3	201·9	145·6	100·0	67·7	37·6

TABLE G.—Ratio $\frac{C}{F}$ for LiCl Solutions.

Temp.	Infinite Dilution.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	1·087	1·027	·923	·830	·811	·791	·756	·739	·734
10	1·066	1·006	·897	·811	·784	·768	·732	·720	·711
18	1·048	·988	·883	·795	·767	·751	·716	·703	·703
20	1·044	·983	·881	·786	·766	·748	·715	·699	·700
30	1·023	·962	·860	·771	·749	·733	·703	·684	·687
40	1·011	·950	·841	·757	·734	·718	·684	·676	·675
50	·998	·937	·831	·747	·719	·704	·673	·657	·670
60	·989	·928	·825	·738	·706	·691	·664	·642	·660
70	·976	·915	·810	·725	·700	·678	·655	·634	·650
80	·965	·904	·798	·719	·690	·669	·648	·628	·644
90	·956	·895	·792	·709	·675	·658	·646	·618	·633
100	·948	·888	·791	·695	·658	·646	·638	·608	·624

specific molecular conductivity, in units, already mentioned.

Table G gives the values for the ratio $\frac{C}{F}$.

It will be necessary to explain how the figures in the first columns of Tables F and G are obtained, and for this purpose we must examine closely the other figures in Table G. It will be seen that for each solution the decrease in the value $\frac{C}{F}$ is the same for equal rises in temperature: thus between 0° and 10° we have decreases of ·022 throughout, and between 80° and 90° decreases of ·008 as an average.

If we assume that for a solution of infinite dilution the same values apply, and if we have values of the fluidity of such a solution, and the absolute value for the conductivity at any one temperature, we can calculate the values for $\frac{C}{F}$ at all temperatures. Now Kohlrausch has determined the value for C_∞ at 18° C., namely 98·9, and the fluidities will be those of water, so that having $\frac{C}{F}$ at 18° C. equal to 1·048, we can build up the first column by adding or subtracting the proper differences or those which exist in solution 1—which amounts to practically the same thing.

We can now fill up the first column in Table F, for we have both values of $\frac{C}{F}$ and of F for a solution of infinite dilution, so that we know the values of C_∞ at all temperatures between 0° and 100° C.

Experiments were made on two solutions in which the

temperatures were carried down below 0° C., and the figures for these solutions, which we shall call numbers 9 and 10, are here given. It will be seen that the lowest temperature reached was $-15^{\circ}20$ C.

Solution 9.

Temp.	Variation.	Density.	Concentration.	Viscosity	Fluidity.	Resistance.	Sp. Mol. Cond.	C/F.
15.20	-0.00	1.0500	2.266	.01530	65.36	1197	50.30	.768
0.20	-0.00	1.0517	2.270	.02346	42.62	1733	34.68	.811
-8.00	-0.00	1.0527	2.272	.03125	32.00	2217	27.08	.847

Solution 10.

Temp.	Variation.	Density.	Concentration.	Viscosity	Fluidity.	Resistance.	Sp. Mol. Cond.	C/F.
15.00	-0.00	1.1530	6.74	.03256	30.71	933.2	21.69	.706
0.40	+0.04	1.1570	6.76	.04913	20.35	1346	14.99	.737
- 7.15	-0.00	1.1584	6.76	.06293	15.89	1676	12.04	.758
-12.00	+0.04	1.1595	6.77	.07441	13.44	1964	10.26	.763
-14.50	-0.00	1.1599	6.78	.08125	12.06	2154	9.34	.759
-15.20	+0.20	1.1601	6.79	.0837	11.95			

In these experiments, the bath was of methylated spirits surrounded by a freezing mixture of crushed ice and salt, and the bath was kept well stirred in the ordinary way.

Discussion of the Results.

Let us consider the temperature variations of fluidity and conductivity, as represented by our ten solutions, or eleven if we include the solution of infinite dilution.

It will be seen at once that the fluidity increases more rapidly than the conductivity, the former increasing its value sixfold, and the latter fivefold, in being heated through 100° from 0° C., and this applies whether the solutions be weak or dilute.

If we represent the results algebraically, we find that both the fluidity and conductivity values can be expressed by equations of the same form, and that they are proportional to the m th power of the temperature measured from a fixed point below the 0° C., which is the same for all solutions.

This temperature is calculated to be $-48^{\circ}\cdot10$ C. Thus for the solutions in Table E we have the equation $F = \frac{T^m}{a}$, where m and a are different constants for the different solutions, and T is the temperature measured from $-48^{\circ}\cdot10$ C.

For the solutions in Table F, we have similar equations, as $C = \frac{T^n}{b}$; and of course in Table G, the temperature variations are represented by $\frac{C}{F} = \frac{a/b}{T^{m-n}}$.

The values for the constants $a, b, m, n, a/b, m-n$, have been calculated, and are collected in the following table.

The formula here used is that known as Slotte's, and was found by Thorpe and Rodger to represent better than any other the results of their experiments on viscosity.

Values of Constants.

Solution.	m .	n .	$m-n$.	a .	b .	a/b .
8	1.8631	1.7016	0.1615	182.00	130.13	1.3986
7	1.6456	1.4841	0.1615	33.290	24.050	1.3841
6	1.5853	1.4256	0.1597	16.650	11.847	1.4054
5	1.5933	1.4306	0.1627	12.723	8.555	1.4873
4	1.6325	1.4579	0.1756	11.392	7.091	1.6065
3	1.6230	1.4763	0.1467	10.163	6.950	1.4620
2	1.6357	1.4960	0.1397	10.165	6.403	1.5874
1	1.6500	1.5257	0.1243	10.705	6.442	1.6665
Inf. Dilution.	1.6440	1.5291	0.1149	10.416	6.145	1.6950

The following table, which gives the values for $\frac{C}{F}$ calculated

Calculated values of $\frac{C}{F}$.

Temp.	Infinite Dilution.	LiCl Solutions.							
		1.	2.	3.	4.	5.	6.	7.	8.
0° C.	1.086	1.025	.926	.829	.814	.792	.757	.741	.748
10	1.063	1.002	.900	.806	.787	.770	.735	.718	.726
18	1.048	.990	.884	.791	.770	.752	.720	.703	.710
20	1.043	.982	.881	.787	.766	.748	.716	.700	.707
30	1.027	.964	.864	.772	.748	.732	.701	.685	.692
40	1.013	.951	.849	.758	.732	.717	.687	.672	.678
50	1.001	.939	.837	.746	.718	.705	.676	.660	.667
60	.989	.927	.825	.736	.706	.694	.665	.650	.657
70	.979	.918	.815	.726	.695	.684	.656	.640	.647
80	.970	.909	.806	.718	.685	.675	.648	.632	.639
90	.962	.900	.798	.710	.676	.667	.640	.625	.631
100	.954	.892	.790	.702	.668	.660	.633	.619	.624

from the formulæ by using the above constants, may be compared with Table G, the observed values for $\frac{C}{F}$, and the calculated values for G and F represent the observed values with the same degree of accuracy.

If we treat these results graphically, as we have done in figures 1 and 2, where the ordinates represent temperatures

Fig. 1.

and the abscissæ the fluidity and conductivity respectively, we see that here, too, from the form of the curves above the points representing the lowest temperatures reached by experiment, the curves if continued all cut the axis representing zero fluidity and zero conductivity respectively at this same temperature of $-48^{\circ}10$ C.

On examining the figures previously obtained for sodium-chloride solutions, it was found that they could be represented by the same form of equation, which contains this temperature $-48^{\circ}10$ C. as the starting point, and it is very probable that low temperature experiments would lead to this temperature, and not $-35^{\circ}5$ C., being fixed at the point at which, apart

from solidification, the fluidity and the conductivity of these solutions would have zero value.

Fig. 2.

Let us calculate out the values of the ratio $\frac{C_n}{C_a}$ in Table F. For the weaker solutions the numbers will measure the ionization coefficients, and we can see how these alter with change of temperature.

Ionization Coefficients.

Temperature.	1.	2.	3.	4.	5.	6.
0° C.....	·940	·814	·723	·661	·493	·350
10	·943	·835	·713	·644	·481	·339
18	·941	·834	·709	·640	·475	·335
20	·940	·835	·708	·641	·474	·334
30	·939	·832	·705	·638	·468	·330
40	·940	·821	·699	·631	·463	·327
50	·942	·828	·697	·628	·460	·323
60	·938	·822	·690	·621	·453	·319
70	·935	·818	·687	·618	·449	·316
80	·937	·815	·684	·613	·444	·314
90	·936	·818	·683	·610	·443	·312
100	·937	·821	·682	·611	·440	·302

In solution 1, the ionization remains constant at all temperatures, but for the other solutions there is a very marked decrease with rise of temperature, and this becomes greater the stronger the solution.

Referring back to Table E, it will be seen that for solution 1 there has been no change in fluidity by the addition of the salt to the water. It is only when the fluidity becomes smaller by the addition of the salt that there is the diminishing of the ratio $\frac{C_n}{C_a}$ with rise of temperature, so that the diminution of $\frac{C_n}{C_a}$ may be due to two causes, the re-combination of the ions and the retarding influence of the molar viscosity; and the latter influence may be felt in much weaker solutions than one has generally supposed.

I have at the beginning of this paper briefly referred to the work of Kohlrausch in connexion with the zero conductivity of dilute solutions. His conclusions were arrived at from a study of the temperature variations of conductivity of dilute solutions between 0° and 34° C. The question of a lower limit to the conductivity has since been attacked by Bousfield and Lowry*, who show that the conductivity of dilute solutions and the viscosity of water tend towards the same limiting temperature, and over the range of temperature (from 5° to 34° C.) the temperature variations can be expressed by the same kind of curve. They, however, doubt the existence of the zero at the point indicated by Professor Kohlrausch and Professor Lyle and myself.

Neither Kohlrausch nor Bousfield and Lowry used Slotte's form of equation to represent their results, and it has been shown by Thorpe and Rodger† that this is the one which gives the best values, where a wide range of temperature is involved, for viscosity; and it is probably the best form of equation to use in connexion with conductivity results.

Kunz‡ conducted some low-temperature experiments with strong sulphuric-acid solutions and solutions of other substances, and decided that in these cases no zero conductivity existed at the temperature supposed.

Kohlrausch§ has recently studied the temperature variations of ionic mobilities, and has here introduced the idea that ions in solutions are surrounded by watery atmospheres carried along with them, and the resistance the ions

* Bousfield & Lowry, Roy. Soc. Proc. p. 42, June 19, 1902.

† Thorpe & Rodger, Phil. Trans. 1894.

‡ Kunz, *Compt. Rend.* vol. cxxxv. p. 788 (1902).

§ Kohlrausch, *Sitz. Ber. d. Berlin. Akad.* p. 572 (1902).

have to overcome is mainly friction between this atmosphere and the solvent water.

In a later paper, Kohlrausch* has explained more fully his previous paper, and has sketched out the new view of the mechanics of electrolysis, according to which the moving ion carries with it a mass of adhering solvent, and the electrical resistance of an ion is a frictional resistance which increases with the dimensions of the atmosphere surrounding it.

One of the conclusions he arrives at is that the resistance of an ion expressed in mechanical units must be of the same order of magnitude as the mechanical resistance of a molecule of the solvent.

The velocity of the ions will depend on the viscosity of the medium through which they pass, and on the size of the ionic atmosphere; and the conductivity of the solution will depend on the viscosity of the medium, the size of the ionic atmosphere, and the fraction of dissociated ions in solution.

The lithium ion, which moves very slowly, may be considered as the centre of a larger atmosphere than the fastly moving chlorine ion, and probably with rise of temperature the atmospheres will approach the same size, as Kohlrausch has observed that with rise of temperature the velocity of the ions tend to become equal.

If we examine our weakest solution, we shall see that here the conductivity does not keep pace with the molar fluidity as the temperature is raised, although there is no combination of the ions. It looks as if the atmosphere around the negative ion is increasing rapidly, while that around the positive ion remains constant or diminishes slowly.

If for our solution at infinite dilution we take the value $\frac{C}{F} = 1.048$ at 18°C ., and consider the atmosphere of the Cl ion to have unit radius, that of the Li ion will have $\sqrt{2}$ times this radius at the temperature 18°C ., because the Cl ion moves twice as fast, and the retardation will depend on the square of the radius.

Now $\frac{C}{F}$ at $100^\circ = .946$. The ratio has decreased in the proportion $1.048 : .946$ or 1.11 to 1 . This decrease is due to the increase of the atmosphere of the ions, and as these atmospheres tend to become equal, if we assume that at 100° they are equal, the radius of each will be 1.29 , so that the Cl has increased its atmosphere by $.29$, and the Li has diminished its by $.12$.

* Kohlrausch, Roy. Soc. Proc. Feb. 17, 1903.

In solution 1, there is no combination of the ions as the temperature rises, so that here, too, any change in the value of $\frac{C}{F}$ will indicate a change in the ionic atmospheres. Here also the decrease is from 1.11 to 1. For this solution, F has the same values as for the solution just considered, but C has smaller values throughout because there are fewer carriers of electricity, although the atmospheres work out to have the same values as in the other solution throughout.

Solution 2 has the same increase for the radii of the atmospheres if the ionization coefficients in our table have the physical meaning which that name should imply, but here the atmospheres at any particular temperature are smaller by one per cent. If, however, the atmospheres remain of constant radius for all solutions, at any particular temperature, the figures under 2 in the table of ionization coefficients must be increased by 1 per cent. throughout to have their physical meaning.

Fig. 3.

For the stronger solutions the ratio 1.11 to 1 remains throughout, but there is nothing to indicate how the ionic atmospheres vary with the concentration.

In the present paper I have confined myself to the temperature variations of fluidity and conductivity. The fluidity-concentration and conductivity-concentration isothermals are also interesting, but I shall not discuss them here. There are indications, however, that all the isothermals will cut the axis of zero conductivity and fluidity at the same point representing concentrations of about 16 normal. I intend making further experiments on strong solutions to test this point.

Fig. 4.

The curves connecting the variables F and n , and C and n , are given in figs. 3 and 4 respectively, each curve being the isothermal for the temperature indicated on it.

I wish, in conclusion, to thank Professor Thomson for the interest he has taken in this investigation.

Cavendish Laboratory,
March 14, 1904.