

The Electrical Conductivity and Fluidity of Strong Solutions

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XI. *The Electrical Conductivity and Fluidity of Strong Solutions.* By W. S. TUCKER, B.Sc.

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It may be fairly assumed that when solutions are of such concentration that the molecules of dissolved substance occupy a relatively large volume, the ions produced will interfere with each other's movements. If the ionisation factor be calculated from the ratio of the molecular conductivity to that at infinite dilution, we get a result which fails to take into account this interference, and therefore cannot be regarded as reliable.

In Prof. Callendar's association theory of strong solutions* the depression of freezing point and elevation of boiling point can be foretold by associating with each molecule and ion a certain constant number of water molecules. With the data at his disposal he obtains good agreement between the experimental values and his calculated values for cane sugar up to any concentration, and for solutions of potassium, sodium and magnesium chlorides. For the strong solutions of calcium chloride discrepancy occurs, most probably owing to unsatisfactory ionisation data.

The experiments here described were made to find whether there is any relation between conductivity and fluidity.

Certain experiments have already been performed by Lyle and Hosking† with sodium chloride, and later by Hosking‡ with lithium chloride, but they did not work with so many strong solutions, nor did they cover the same ranges of temperature.

Calcium chloride solution, with its low cryohydrate point and its extreme solubility, forms a very good solution to work on. Moreover, it can be highly supercooled. This can be illustrated by taking a solution slightly above cryohydrate strength and cooling it.

Referring to the curves shown in Fig. 1, crystals of the salt $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ should separate out at P, but the solution supercools to Q. The addition of a fragment of ice causes rise to R, giving the approximate freezing point. Ice now separates

* Callendar, "Proc." Roy. Soc., A, Vol. 80, 1908, p. 466.

† Lyle and Hosking, "Phil. Mag.," May, 1902, p. 487.

‡ Hosking, "Phil. Mag.," May, 1904, p. 469.

from R to S. At S fresh crystals presumably of the salt make their appearance, causing a rise to T, probably above cryohydric point; but separation of these crystals quickly brings the solution to the constant temperature of the cryohydric point.

A supercooling of $15^{\circ}\text{C}.$ can be obtained with proper precautions, when the crystals are dissolved in their own water of crystallisation.

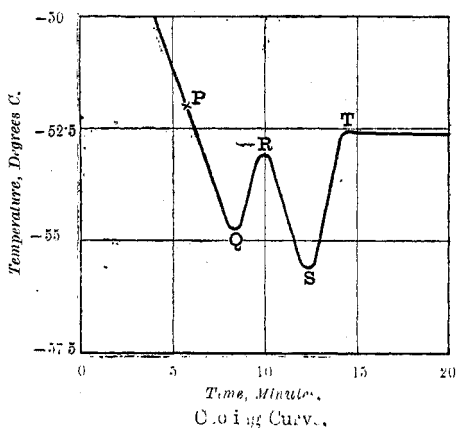
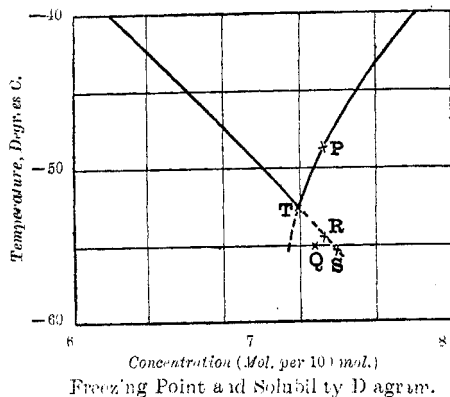


FIG. 1.

The feature of the method here described is the simultaneous observation of temperature, viscosity and resistance. The electrolytic cell and viscometer are immersed in the solution for which they are employed, and both are bound to the bulb of a platinum thermometer, which serves also as a stirrer.

Measurement of Conductivity.

The electrolytic cell C is a flattened tube drawn out into a flat jet. It contains a platinised-platinum electrode, P, whose dimensions are 25 mm. by 5 mm. The second electrode, also of platinised-platinum, forms a cylindrical sheath, Q, round the bulb of the thermometer T. (See Fig. 2.)

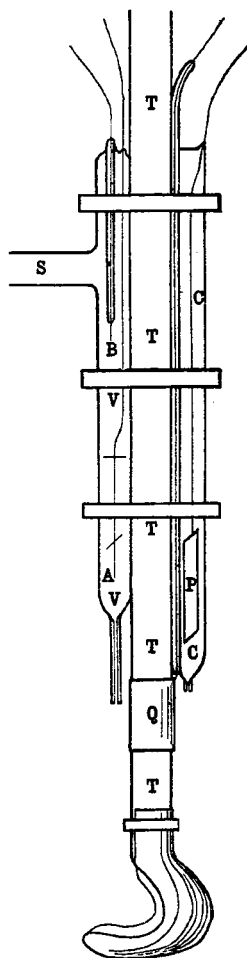


FIG. 2.—APPARATUS FOR DETERMINING VISCOSITY AND CONDUCTIVITY.

The thermometer is mounted on a frame to which a vertical oscillatory motion is imparted. This motion is caused by a connecting rod attached to a large pulley driven by a motor.

As the thermometer oscillates it draws through the liquid a platinum scoop, which acts as an efficient stirring arrangement.

The resistance was measured by that modification of Kohlrausch's method described by Fitzpatrick,* in which a high-speed double commutator and a moving-coil galvanometer replace the coil and telephone. An accuracy of 1 part in 2,000 could be thus obtained, and was greater than that possible with the viscosity apparatus.

A preliminary experiment was made which showed that the oscillatory motion of the cell and the consequent motion of the liquid in it did not affect the resistance readings. Such oscillatory motion ensured the temperature of the liquid in the jet being exactly that of the liquid in the bath.

In the observations taken the concentration was expressed in gram-molecules per 100 molecules of water. This concentration remains constant with change of temperature, and was employed by Prof. Callendar in his Paper on strong solutions.

The capacity of the cell was found by the use of a standard solution employing Kohlrausch's results.

The molecular weight of the anhydrous salt is taken as 110.92.

Measurement of Viscosity.

The viscosity is measured by a modification of Poiseuille's method. The tube through which the flow occurs is a uniform jet about 2 cm. long drawn out from a piece of quill tubing, V, as shown by the diagram, Fig. 2. Connection can be made by means of the side-tube S with an aspirator or with a compressed air reservoir. When the tube is immersed in the solution, the latter can be drawn in or driven out at will.

The viscometer is plunged into the solution to a certain depth, and the time of inflow is measured and compared with that of water under the same conditions.

During the experiments the viscometer is invisible, hence the levels of the liquid when flowing into the tube are indicated by electrical means.

Two fine platinum wires A and B serve as contacts and are insulated from one another. As the liquid rises within the tube it makes circuit with Q and A through the liquid and the motion of a galvanometer is noted. A second motion is pro-

* B.A. "Report," 1886, p. 328.

duced when contact with B is made. Thus the passing of the levels can be accurately timed.

The assumption is now made that the rate of influx of the solution is proportional to the hydrostatic pressure, and inversely proportional to the viscosity.

The accuracy of this assumption was checked by an experiment with pure water, whose viscosity has been accurately found by Thorpe and Rodger.*

Two experiments are performed.

1. The water is run into the tube under its own pressure, the initial and final differences in level being H and h_1 respectively. It can be shown that

$$\frac{H}{h_1} = e^{\frac{K}{a} \frac{\rho}{\eta} t_1} = e^{mt_1},$$

where ρ is the density, η the viscosity, t the time of inflow, K a constant depending on the dimensions of the jet, and a the area of the wider portion of the tube.

2. An external pressure P is applied by means of the aspirator, and this acting with the hydrostatic pressure accelerates the rate of inflow. The expression then becomes

$$\frac{\frac{P}{\rho} + H}{\frac{P}{\rho} + h_1} = e^{mt_2},$$

where t_2 is time of inflow.

Readjustments are made so that $h_1=0$, and H becomes H_1 ,

giving $1 + \frac{\rho H_1}{P} = e^{mt_2}$,

from which $\rho = \frac{P}{H_1} \{e^{mt_2} - 1\}$;

but $m = \frac{1}{t_1} \log_e \frac{H}{h_1}$,

hence $\rho = \frac{P}{H_1} \left\{ e^{\frac{1}{t_1} \log_e \frac{H}{h_1} t_2} - 1 \right\}$.

With the apparatus used a value of the density of water was obtained with an error of less than 1 per cent. This result justifies the use of the method, since no higher accuracy was

* Phil. "Trans.," 1894, A, p. 1.

attempted. The viscosities of the solutions used in the extreme cases are as 1 : 40.

Water is taken as a standard liquid of known viscosity.

Variation of Conductivity and Fluidity with Concentration at Constant Temperature.

The following table shows the results obtained for solutions of different concentrations all at the temperature of 16.77°C.

This temperature was approximately that of the room. To ensure its constancy the solution was contained in a cylindrical Dewar vessel, which, however, was not silvered. The temperature of the contents was brought to the above exact value by presenting to the walls of the vessel a warm or cool surface, and the liquid was stirred to secure uniformity of temperature. The vessel was then screened from further radiation.

TABLE I.
Temperature 16.77°C.

(1) Concentration. (n) Mol. per 100 mol. of water.	(2) Density. Grammes per cubic cm.	(3) Resistance. Ohms.	(4) Conductance. (C) Ohms ⁻¹ × 10 ⁻⁴ .	(5) Viscosity. C.g.s. units.	(6) Fluidity. (F) C.g.s. units.	(7) $\frac{1}{n} \cdot \frac{C}{F}$ × 10 ⁻⁴
0	0.9988	0.01081	92.50	...
0.927	1.0434	2,032	4.921	0.0121	82.64	6.424
2.757	1.1293	915.4	10.93	0.0161	62.11	6.38
4.106	1.1793	782.5	12.78	0.0199	50.25	6.19
5.436	1.2313	766.8	13.04	0.0251	39.84	6.02
7.252	1.2933	845	11.83	0.0371	26.95	6.05
8.429	1.3308	968.5	10.32	0.0486	20.58	5.95
9.363	1.3569	1,074	9.31	0.0602	16.61	5.99
10.11	1.3788	1,179	8.479	0.0706	14.16	5.93
10.65	1.3960	1,278	7.823	0.0818	12.22	6.01
11.22	1.4063	1,435	6.969	0.0989	10.11	6.14
*16.66	1.5210	3,220	3.106	0.3320	3.012	6.18

* Melted crystals supercooled about 13°C.

The meaning of the last column is difficult to interpret, but is worth quoting. It will be seen that while the concentration alters from 4 to 16 molecules, while fluidity changes to 16 times its value and conductivity suffers a fourfold change, the quantity $\frac{1}{n} \cdot \frac{C}{F}$ only varies about 3 per cent.

A similar treatment of Lyle and Hosking's results for sodium

chloride and Hosking's results for lithium chloride suggests a similar conclusion. The data supplied, however, are inadequate, since the solutions are generally more dilute.

Curves connecting C and n , F and n , and $\frac{C}{F}$ and n are plotted in Fig. 3.

From the fluidity and conductivity curves no evidence is given of a vanishing of these quantities at higher concentrations.

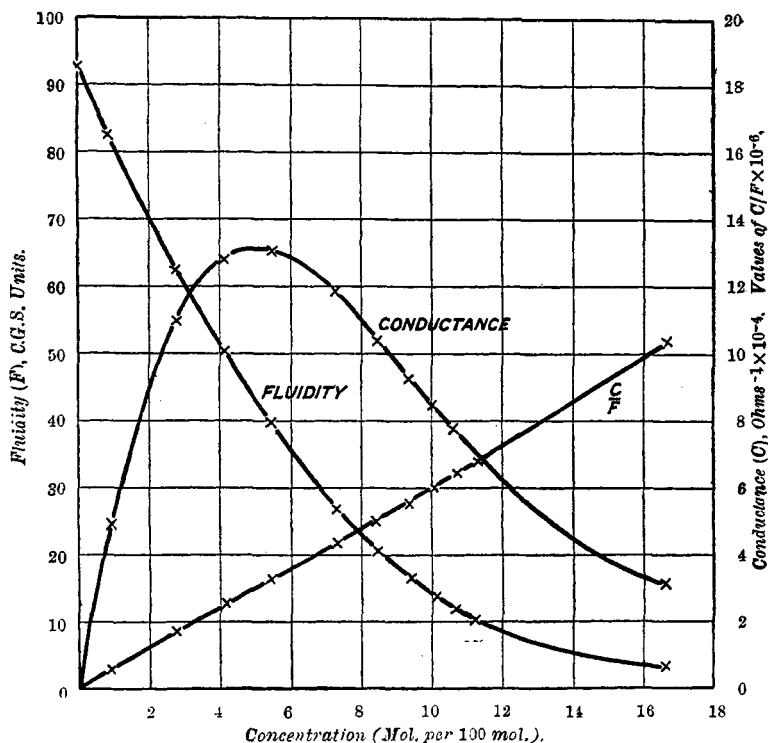


FIG. 3.

The above authors quoted such a vanishing of both quantities for sodium chloride at 10.74 normal, and for lithium chloride at 16-normal concentration.

Both these results are obtained by extrapolation.

[Since this Paper was first submitted, the results obtained by Bousfield and Lowry* with strong solutions of sodium

* Bousfield and Lowry, "Phil. Trans.," 1905, Vol. 204, p. 253.

hydrate have been examined. The relations between conductivity, fluidity and concentration expressed as a ratio of weights of solid to solvent are shown in Fig. 3A.

The linear relation between $\frac{C}{F}$ and n for strong solutions is again shown.]

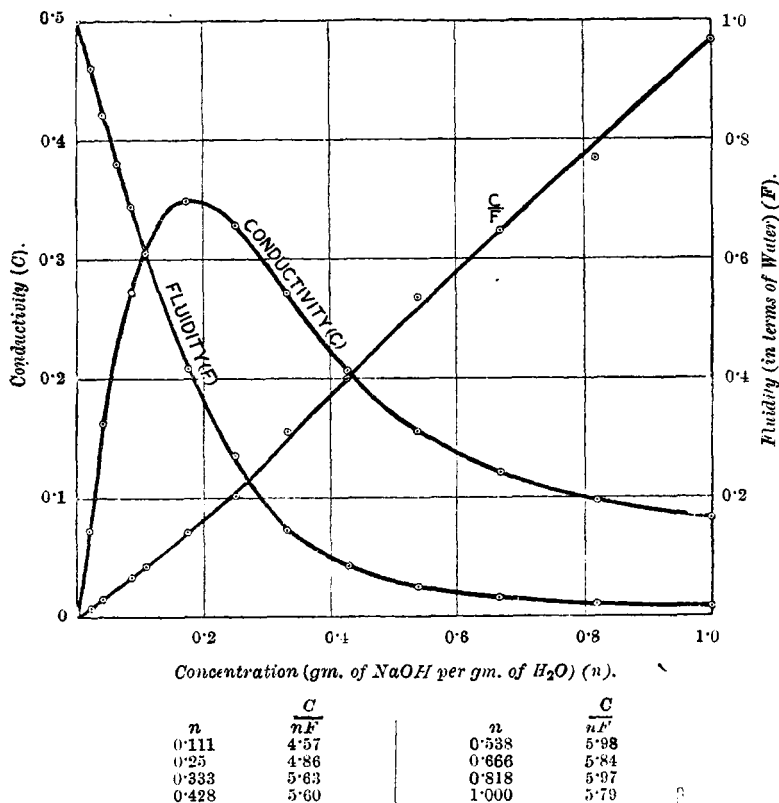


FIG. 3A.—PROPERTIES OF NaOH SOLUTIONS (BOUSFIELD AND LOWRY).

Variation of Fluidity and Conductivity with Temperature.

The same apparatus was used as before, except that the electrode P in the electrolytic cell was slightly moved.

The temperatures above that of the air were obtained by surrounding the Dewar cylinder by a second larger Dewar cylinder containing water.

This was heated by a current of steam.

For temperatures below that of the air, ice was added to the water, and below 0°C . a mixture of ice and salt was employed. Finally, for temperatures below -10°C . liquid air was used. After cooling to the desired temperature the excess of liquid air was boiled off by passing a current of air through it. During the observations the mean of the initial and final temperatures gave the temperature quoted.

In the viscosity-temperature experiment the solution of strength 7.252 molecules was taken. A preliminary experiment was made to determine the densities at the various temperatures employed. For this purpose an accurate mercury thermometer, reading to 50°C . by $\frac{1}{10}$ deg. divisions, was employed. The mercury was replaced by the solution and the volume of the bulb was accurately found by weighing the mercury.

The co-efficient of expansion for a range of nearly 100°C . is nearly constant, its mean value between 0°C . and 50°C . being 0.000455.

The following table gives the relation between fluidity and temperature :—

TABLE II.
Concentration 7.252 molecules per 100 molecules of water.

(1) Temperature. $^{\circ}\text{C}$.	(2) Density.	(3) Viscosity.	(4) Fluidity. C.g.s. units.
85.22	1.259	0.01438	69.55
70.61	1.266	0.01678	59.59
56.79	1.275	0.01849	54.09
37.15	1.282	0.02666	37.51
23.70	1.290	0.03544	28.22
16.77	1.293	0.0418	23.92
-0.15	1.301	0.0726	13.77
-5.51	1.303	0.086	11.56
-8.85	1.305	0.1007	9.94
-15.19	1.308	0.1338	7.475
-19.07	1.309	0.1569	6.372
-30.45	1.314	0.2628	3.806
-40.16	1.323	0.5919	1.689

At the same time, readings of resistance were taken from which the conductivity for the same solution was obtained. These are included in Table III. (p. 120), together with results for the other solutions.

Columns (1) and (4) of Table II. and (1) and (2) of Table III. are plotted in Fig. 4, while columns (1) and (3) of Table III. are plotted in Fig. 5.

TABLE III.

(1) Temperature. °C.	(2) Specific conduc- tivity of solu- tion 7.252 mol.	(3) Values of $\frac{\text{conductivity}}{\text{concentration}}$ at the concentrations given.								
		0.927	2.13	5.436	7.252	8.22	9.363	10.11	10.65	11.22
39.72	2,280	1,034	922	455	314.0	250.1	198.0	166.7	150.3	132.4
31.74	2,000	909	808	398	276.0	217.0	170.2	144.0	143.4	112.2
27.67	1,858	853	742	371	256.0	200.0	157.6	130.5	119.2	103.4
23.69	108.0	92.0
19.74	1,598	739	628	320	220.0	170.0	143.6	110.0	...	85.1
15.78	1,457	677	558	295	201.0	153.3	121.0	100.0	88.3	77.7
11.70	1,340	617	...	268	185.0	142.1	106.6	89.5	...	69.0
9.00	492
5.79	...	522	57.1
4.09	111.5	86.0
3.81	...	505	...	222
-0.14	997	455	400	203	137.5	103.0	77.7	62.6	54.6	...
-4.37	880	180	121.4	89.6	68.3	54.6
-8.28	774	...	340	159.5	106.6	78.9
-10.24	316	554.0
-12.20	683	142	94.2	69.2
-16.14	600	124.2	82.7	59.4
-20.17	512	107.8	70.7	50.8
-24.11	435	97	60.0	43.0
-27.99	369	79.3	50.9	35.7
-31.88	307	67.1	42.5
-33.94	26.3
-35.84	246	34.0
-39.78	199	27.5
-43.65	149	20.5
-47.55	114	15.7
-51.5	81.9	11.0

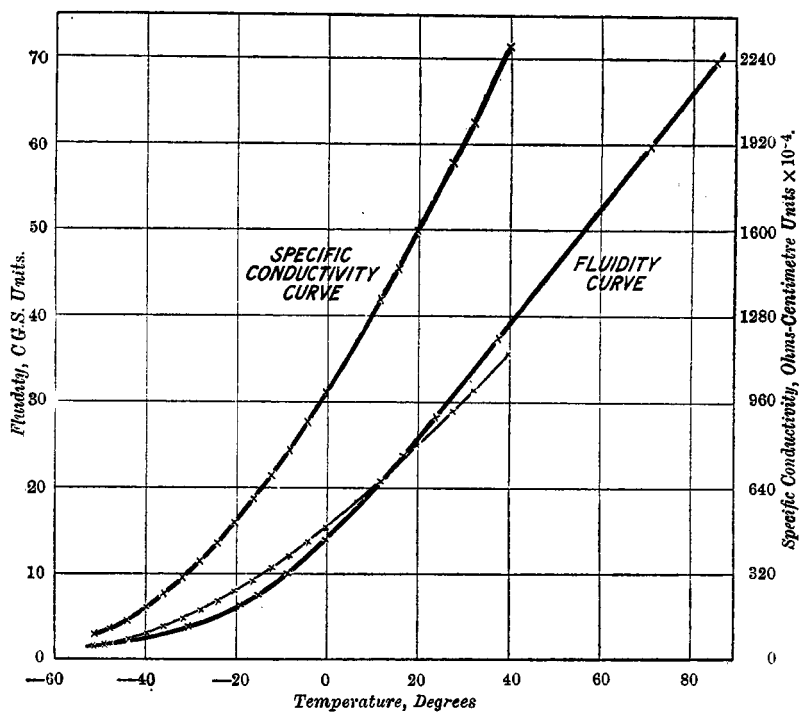


FIG. 4.

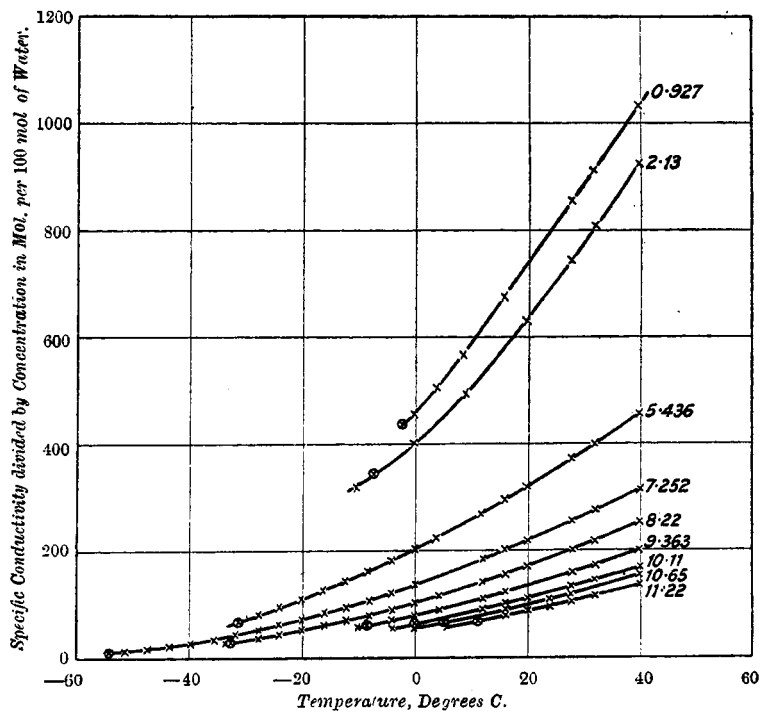


FIG. 5.

Fig. 4 has a third curve, the ordinates for conductivity being halved, so that its variation with temperature can be more readily compared with that of fluidity.

The variation of conductivity with concentration and temperature is clearly shown in Fig. 5.

Very dilute solutions give a straight line relation, which is gradually modified to a curve of increasing curvature, as the concentration increases. The ratio $\frac{\text{conductivity}}{\text{concentration}}$ has here no definite meaning, since the denominator deals with a ratio of masses, but the latter has the advantage of not changing with temperature, and in this way the curves can be separated. They are very similar to the molecular conductivity curves.

It will be seen that there is no evidence of a disappearance of conductivity at a definite temperature, such as has been suggested by Lyle and Hosking for sodium chloride solutions and by Hosking for solutions of lithium chloride. The risk in extrapolation from above -20°C. to obtain such a vanishing point is clearly shown by the lower curves of Fig 5.

The above results also agree in this matter with those of Kunz,* who worked with sulphuric acid at low temperatures. As distinct from sulphuric acid, however, these properties of calcium chloride solutions exhibit no marked breaks in continuity with concentration at the temperatures above referred to. We thus have no evidence, within the limits of accuracy of the above observations, of the existence of many different hydrates.

The author wishes to thank Prof. Callendar and Dr. S. W. J. Smith for their valuable suggestions and helpful interest in the work, which was carried out at the Imperial College of Science.

ABSTRACT.

In adopting Callendar's association theory of strong solutions ("Proc." Roy. Soc., A., Vol. LXXX., p. 466) some difficulty is experienced in getting the strongest solutions of electrolytes to conform to the laws laid down. This is attributed to the inaccuracy of the ionisation data, which are derived from observations on electrical conductivity. It may be supposed that the viscosity of the solution will affect its conductivity, and the author carried out a series of experiments to determine if there were any definite relation between conductivity and fluidity in the case of calcium chloride solutions.

* Kunz, "Compt. Rend.," Vol. CXXXV., p. 788, 1902.

The feature of these determinations is the simultaneous observation of viscosity, electrolytic resistance and temperature.

Solutions were contained in an unsilvered Dewar cylinder, which permitted a slight adjustment of temperature if necessary.

A platinum thermometer records the temperature, and is caused to oscillate in the solution by a stirring mechanism.

In so doing it draws a platinum scoop through the liquid and thus acts as an efficient stirrer. The conductivity cell and the viscometer were bound to the thermometer by rubber bands. While the thermometer oscillates the readings of electrical resistance were measured by means of the rotating commutator and bridge. The viscometer was in the form of a capillary pipette, which was immersed in the solution a known depth. The levels of the inflowing liquid were indicated electrically, and hence the rates of inflow could be accurately estimated and compared with that of water. Viscosities correct to less than 1 per cent. were obtained.

Isothermal Observations.—Perfectly smooth curves for conductivity and fluidity were obtained, even when the supercooled melted crystals were included. No definite connection between conductivity, fluidity and concentration can be derived if the latter is expressed in terms of volume, but if concentration is expressed as a ratio of masses—molecules of solute to 100 molecules of solvent—the ratio conductivity C /fluidity F stands in linear relation to the concentration n when the latter exceeds one-fourth its maximum value. In spite of the enormous variations of the quantities in this ratio C/nF has values differing at most only 2 per cent. from the mean.

Examination of similar results by Bousfield and Lowry for sodium hydrate give striking agreement with this conclusion. However, owing to the dependence of C and F on linear dimensions, this relation is difficult to interpret.

Variations with Temperature.—One solution of nearly cryohydric strength was examined at temperatures from 40°C . to -50°C . The same tube and apparatus were employed, and for lower temperatures liquid air was used as a cooling agent. The failure of the fluidity-temperature and conductivity-temperature curves to exhibit the same variations was clearly shown.

Conductivities of various solutions were examined from 40°C . to their freezing points and the curves C/n and temperature plotted. The increasing curvature with concentration is shown and the error involved in applying the ratio, molecular conductivity to that at infinite dilution, obtained at one temperature, to indicate ionisation at another temperature, is quite apparent.

Moreover, within the limits of accuracy employed no indication is given of the existence of different hydrates.

The results obtained above suggest that no reliance can be placed on ionisation data derived from electrical conductivity observations.

DISCUSSION.

Prof. C. H. LEES remarked that the observations should be extended to see whether other strong solutions gave a simple relation between the fluidity and the resistance.

Mr. F. P. WORLEY thought the ratio of the conductivity to the concentration when the latter was expressed as so many gramme molecules of salt per 100 of water had a rather doubtful meaning.

Mr. F. E. SMITH asked if Mr. Tucker had got any explanation of the fact that he found the cryohydric point $2\frac{1}{2}$ deg. higher than previously found.

The AUTHOR, in reply, stated that Morse and Fraser, working on the osmotic pressure of sugar solutions, found it bore a simple relation to the concentration per 100 molecules of water and not to the volume concentration. In reply to Mr. F. E. Smith, Roozeboom had used an alcohol thermometer in determining the cryohydric point. He might also have got it too low, due to supercooling.