CCCCXXXVIII.—*The Electrical Conductivities of Some Uni-univalent Salts in Benzonitrile. Evidence for the Incomplete Dissociation of Strong Electrolytes and the Applicability of the Law of Mass Action to their Dissociation.*

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In view of Debye and Hückel's theory and its recent developments, considerable significance attaches to the study of the conductivity of salts in non-aqueous solution. The earlier relevant data cannot be regarded as trustworthy, and it is only within the last few years that satisfactory measurements of conductivity in non-aqueous solution have been recorded (see Kraus and Bishop, *J. Amer. Chem. Soc.*, 1922, **44**, 2206; Morgan and Lammert, *ibid.*, 1924, **46**, 1117; Philip and Oakley, J., 1924, **125**, 1189; Frazer and Hartley, *Proc. Roy. Soc.*, 1925, *A*, **109**, 351; Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, **114**, 275; Walden, Ulich, and Busch, *Z. physikal. Chem.*, 1926, **123**, 429). The present investigation was undertaken with the object of providing additional accurate data in this field, more especially over a wide range of temperature (compare Philip and Oakley, *loc. cit.*; Walden, *loc. cit.*). Benzonitrile was chosen as solvent because (1) it is easily purified, (2) it is inert and not hygroscopic, and (3) its b. p. is fairly high. Moreover, it is desirable to examine a solvent less closely related to water than the alcohols which have been used in most of the accurate conductivity measurements in non-aqueous solutions. As solutes, potassium, sodium, and lithium iodides, lithium bromide, and silver nitrate were employed. The solubility of inorganic uni-univalent salts in benzonitrile is, with the exception of silver nitrate, not great, and the above are the only salts sufficiently soluble for the purpose. Among previous work on conductivities in benzonitrile, mention may be made of that of Walden on tetraethyl- and tetrapropyl-ammonium iodides (*Z. physikal. Chem.*, 1906, **54**, 189; **55**, 710) and of Dutoit on sodium iodide (*Z. Elektrochem.*, 1906, **12**, 643), all at 25°. The value of Λ_0 found by the author for sodium iodide at 25° is some 10% lower than Dutoit's, and the author's results yield a value for the mean ionic radius calculated from the Debye–Hückel theory of $3{\cdot}72 \times 10^{-8}$ cm., whereas Dutoit's give one of $6{\cdot}30 \times 10^{-8}$ cm.

EXPERIMENTAL.

Apparatus.—The bridge was set up as in the usual Wheatstone arrangement, the source of the current being connected to the sliding contact and the junction of the standard resistance with the cell. The sliding contact was earthed.

The bridge wire was of the drum type, 5 metres long, of 32 ohms resistance, and having an ebonite hood, made by Leeds and Northrup; it was calibrated by the method of Strouhal and Barus and had no appreciable error. The standard resistance was of the dial pattern, maximum resistance 11,110 ohms, accurate to 0·04%, made by Cambridge and Paul. The telephone was of 120 ohms resistance, made by Brown. The source of current was a valve oscillator made by the author and giving a pure sine-wave alternating current of frequency 1000 cycles per second. It was electromagnetically shielded from the bridge.

The condensers placed in parallel with the standard resistance in order to balance the capacity of the cell were (i) a step-up mica condenser of maximum capacity 1·0 microfarad, and (ii) a variable air condenser, of maximum capacity 0·001 microfarad, for fine adjustment: usually the air condenser alone sufficed.

The cells. Of the three cells used, two, one of lead glass and one of Pyrex (Cells P I and P II), were of the pipette type designed on the lines laid down by Washburn (*J. Amer. Chem. Soc.*, 1916, **38**, 2431). The platinum electrodes (3 cm. in diameter and 0·5 cm. apart) were grey-platinised. The capacity of each cell was about 20 c.c. The third cell (Cell III) was a stoppered, round-bottomed, Pyrex-glass bottle of about 20 c.c. capacity, the electrodes—two grey-platinised platinum discs 1 cm. in diameter and about 1 cm. apart—being sealed in through the sides. The cell constants of the pipette cells were 0·034014 and 0·041729, and of the other cell 0·19057. The pipette cells were used for all except the most concentrated solutions, since with small electrodes satisfactory minima were not obtained with solutions of low conductivity (compare Washburn, *loc. cit.*).

Temperature Control.—The thermostats were controlled by mercury–toluene gas-regulators and were constant to ± 0·01°. A layer of oil was placed on the surface of those at temperatures of 50° and above. The bath at 0° was maintained with distilled water and ice which had been washed with distilled water.

Determination of Cell Constants.—The constant of Cell III was determined at 25° with an *N*/100-potassium chloride solution prepared according to Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 312). The flask and small weighing bottle used were of hard glass and were steamed out before use. The water had a specific conductivity of 1×10^{-6} mho. The potassium chloride (A.R. quality) was recrystallised twice from conductivity water, fused in a platinum dish, and ground in an agate mortar. Two samples were prepared and both led to the same result for the cell constant. The constants of the two pipette cells could not be determined with this solution, since its conductivity was great enough to be outside the range of satisfactory minima. They were therefore obtained by intercomparison with Cell III. All three cells were filled with a solution consisting of 100 c.c. of *N*/100-potassium chloride and 900 c.c. of alcohol (Morgan and Lammert, *J. Amer. Chem. Soc.*, 1923, **45**, 1692); the ratio of the resistance of the cells so filled was the ratio of their cell constants, and, the constant of one of them being known, those of the others were readily calculated.

The ratio of the cell constants was found to be the same at all the temperatures used, and, since the dimensions of the pipette cells and Cell III were very different, this indicates that the constants of all of them were not appreciably altered by temperature. The values of the cell constants determined at 25° were therefore used for all the temperatures investigated; they were redetermined at frequent intervals and were found not to alter appreciably, except that of Cell P I which changed a little in the first month or so after manufacture.

Preparation of the Salt Solutions.—The solutions were made in 50 or 100 c.c. flasks with ground stoppers. If they were to be kept for any length of time, the stopper was covered by a cap and waxed. The flasks were specially selected not to have capillaries which might retain water. After thorough cleaning, they were washed repeatedly with conductivity water and then with redistilled absolute alcohol and placed upside-down in a steam oven to dry. They were rapidly removed to a desiccator containing phosphoric oxide, the desiccator was evacuated, and purified, dry air was admitted after the flasks had cooled.

All the solutions were made up by weight. The weight of dissolved salt was subtracted from the weight of solution, and from the resulting weight of pure solvent and the density of pure benzonitrile at the appropriate temperature the volume concentrations were calculated, *i.e.*, electrostriction was taken to be negligible. This assumption was found to be justified in the case of an *N*/100-silver nitrate solution, which was the highest concentration used.

The densities of benzonitrile at temperatures between 0° and 70° were found to be as follows :

Temp. ...	0°	25°	40°	50°	55°	70°
$d_{4^\circ}^{t^\circ}$	1·0222	1·0005	0·9872	0·9778	0·9739	0·9600

The stock solution was made by adding to a weighed amount of benzonitrile a small weighing bottle containing a weighed amount of the salt and shaking until the salt had dissolved. Potassium iodide was exceptionally slow in dissolving and sometimes had to be shaken over-night. The quantity of salt taken was of the order of 0·05—0·1 g. and was weighed to 0·01 mg., the method of oscillations being used.

The more dilute solutions were made by adding to flasks containing a weighed quantity of benzonitrile the requisite quantity of a more concentrated solution and weighing again. The weights were not reduced to *vacuo* since the same percentage error occurs both in the weight of pure solvent and in the weight of the previous dilution added, the resultant error being zero. No dilute solution was derived from a stronger solution which had previously been used for any other purpose. All the transferences were carried out in pipettes which had been cleaned and dried in the same way as the flasks, except that instead of cooling them in a vacuum desiccator, a stream of purified and dry air was drawn through them. When not in use, the ends of the pipettes were closed with rubber caps in order to prevent access of moist air. No pipette was used more than once in a series of dilutings, and a suitable guard was inserted between the mouth and the pipette. Experiment showed that the pouring of benzonitrile from one vessel to another in an ordinary room did not noticeably alter its conductivity.

Whetham's method of preparing solutions for conductivity measurements (*Phil. Trans.*, 1900, *A*, **194**, 321), in which successive portions of a concentrated salt solution are added from a weight pipette to a known volume of pure solvent in the cell, was inapplicable in the present work for the following reasons : (1) As will be explained later, it was necessary for the cell to have been filled with a concentrated solution before the more dilute solutions were measured. (2) Most of the salts investigated were so sparingly soluble in benzonitrile that large volumes of a stock solution would have had to be added in order to obtain the more concentrated solutions, thereby altering the effective constant of the cell.

The method used in the present work has none of the defects of the Ostwald–Arrhenius method, except the slight uncertainty as to the magnitude of the solvent correction.

Conductivity Measurements.—Before a series of measurements, the cells were cleaned with chromic–sulphuric acid mixture, washed with conductivity water, and warmed several times with conductivity water. They were then washed thoroughly with redistilled absolute alcohol and dried by being warmed to about 80° and having a current of purified dry air drawn through them. Cell III was dried by leaving it in a steam-oven and then allowing it to cool in a vacuum desiccator in the same way as the flasks used in making up the solutions. Between individual measurements in a single series of dilutions, the method of washing and drying the cell was the same, except that treatment with cleaning mixture and water was omitted. As recommended by Morgan and Lammert (*loc. cit.*, 1923), the electrodes were kept short-circuited during the process of cleaning and drying.

During the conductivity measurements, the bridge was approximately set and the current switched off for a minute; the fine setting was then made in about two seconds. This procedure was adopted in order to avoid errors due to the heating effect of the current. Perfect minima were always obtained, and the bridge could be set to 0·01% of its length.

With each salt at least two series of measurements starting from different stock solutions were made.

In the case of potassium iodide, a photochemical reaction took place which resulted in a minimum in the equivalent conductivity at high dilutions, but this was avoided by painting the cell with Brunswick black. It was also found that the conductivity of dilute potassium iodide solutions was not constant if the measurements were carried out beginning with the most dilute solution and working up to the most concentrated. If the measurements proceeded in the reverse order the conductivities were quite constant. This phenomenon was traced to adsorption on the electrodes. On immersion in a concentrated solution, an amount of electrolyte is adsorbed the removal of which does not noticeably alter the conductivity of the solution. The amount of adsorbed electrolyte does not vary appreciably with its concentration in the solution, and consequently in the more dilute solutions the electrolyte is neither further adsorbed on the electrodes nor given up to the solution. This latter point was proved by measuring the conductivity of the pure solvent in the cell, and then filling it with a concentrated solution, washing it in the way usual between two measurements, and measuring the conductivity of the pure solvent again. The two values thus obtained were identical. This observation is in agreement with the experience of Randall and Scott (*J. Amer. Chem. Soc.*, 1927, **49**, 636), who, in investigating the variation of cell constant with resistance and other factors, found that the quantity of electrolyte adsorbed did not vary appreciably with the concentration of the surrounding solution. All the measurements were therefore carried out in the dark and (except in the case of silver nitrate, where no trouble was experienced) beginning with the most concentrated solution and proceeding to the most dilute.

Solvent Correction.—The conductivity of the solvent was in all cases subtracted from the observed conductivity in order to obtain the conductivity due to the dissolved salt. The correction never amounted to more than 4%, and satisfactory agreement between the values for the conductivity of the dissolved salt was obtained even when the conductivity of the pure solvent varied by 100%, provided it did not exceed $1{\cdot}0 \times 10^{-7}$ mho.

Since the viscosity of an *N* 100-silver nitrate solution was the same as that of the pure solvent, it was unnecessary to apply a viscosity correction.

The molecular weights of the salts concerned have been taken as: potassium iodide 166·02; sodium iodide 149·92; lithium iodide 133·86; lithium bromide 86·86; silver nitrate 169·89.

Purification of Materials.—Benzonitrile. Benzonitrile (B.D.H.) was steam-distilled to remove the slight amount of carbylamine present. The distillate was washed with sodium carbonate to remove any benzoic acid, the benzonitrile extracted with ether, and the extract washed with water and dried over calcium chloride. After filtering, the ether was distilled off and the residue distilled under low pressure. The large middle fraction, b. p. 81°/22 mm., was then subjected to the following operations, being redistilled under diminished pressure after each: (1) shaken slowly with a mixture of anhydrous potassium carbonate and calcium chloride and filtered; (2) shaken very slowly with calcium chloride and decanted; (3) left over calcium chloride for some days and decanted. The benzonitrile then had a specific conductivity of $0{\cdot}5 \times 10^{-7}$ mho at 25°. Between two series of measurements it was treated as above, except that the steam-distillation was omitted. The distilling apparatus was washed with redistilled absolute alcohol and dried in the same way as the flasks used in making up the solutions.

Potassium and sodium iodides. The A.R. quality salts were recrystallised from conductivity water in a platinum basin and dried. Finally they were powdered in an agate mortar and electrically heated in a vacuum to 100° over phosphoric oxide, the drying agent remaining at room temperature. Analysis of the potassium iodide gave 76·4% iodine (calc., 76·4%), and of the sodium iodide 84·6% (calc., 84·7%). The sodium iodide did not turn at all yellow on keeping.

Lithium iodide. A sample of Kahlbaum's lithium iodide was slightly pink and contained free alkali. It was evaporated to dryness with freshly prepared hydriodic acid at about 50° in an electrically heated beaker in a desiccator containing caustic potash, and then recrystallised thrice from redistilled absolute alcohol.* It was perfectly colourless, gave no blue colour with starch, and its aqueous solution was neutral. The salt was dried by heating in a small hard-glass weighing bottle to 120° in the apparatus used for drying the potassium and sodium iodides and evacuating continuously for a week. In order to avoid transference of the very hygroscopic anhydrous lithium iodide, the weighing bottle was weighed empty, and the requisite amount of the damp salt added and dried as described above. The cap of the weighing bottle was then dropped on to it with a pair of forceps as it stood in the desiccator, and the covered bottle was removed, weighed, and dropped into a weighed quantity of pure benzonitrile to make up the stock solution. The material so prepared gave 94·7% iodine (calc., 94·8%), and contained no detectable alkali or free iodine.

Lithium bromide. The B.D.H. product, which was quite colourless and free from alkali, was recrystallised three times from redistilled absolute alcohol, and dried in the same way as the lithium iodide (Found : Br, 92·2. Calc., Br, 92·0%).

Silver nitrate. This was kindly provided by Dr. H. F. Harwood and had been purified for atomic-weight purposes. It was dried in the same way as the potassium iodide.

Alcohol. The absolute alcohol used for washing was redistilled in order to remove any electrolytic or high-boiling impurities.

Results.

The results of the conductivity measurements are given in Table I, v denoting the dilution (in litres). In the column headed Δ

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* Since lithium iodide is very soluble in alcohol, recrystallisation from this solvent is wasteful, and an attempt was made to precipitate it by the addition of ether, in which it is insoluble; but the liquid separated into two phases, one chiefly ether and the other a solution of lithium iodide in alcohol.

TABLE I.

Results of Conductivity Measurements.

	Series.	v.	Λ.	Δ.	Δ′.
KI, 0°.	d	803·1	27·50	+0·01	−0·05
	c	1,160	28·42	−0·01	±0·00
	d	2,078	29·61	+0·01	+0·08
	c	4,446	30·56	−0·01	+0·01
	d	7,639	31·00	±0·00	−0·06
	d	20,045	31·31	−0·13	−0·41
KI, 25°.	a	802·4	42·82	±0·00	−0·01
	b	907·2	43·39	+0·01	±0·00
	c	1,185	44·40	−0·05	−0·07
	a	3,256	47·60	±0·00	+0·08
	c	4,543	48·30	±0·00	+0·08
	b	8,806	49·29	+0·01	−0·03
	a	14,774	49·70	−0·08	−0·25
	a	39,188	50·45	+0·08	−0·34
KI, 40°.	a	813·2	52·64	+0·01	−0·01
	b	919·5	53·32	±0·00	−0·06
	c	1,201	54·67	−0·02	−0·13
	a	3,300	58·84	+0·01	+0·05
	c	4,604	59·83	+0·03	+0·11
	b	8,924	61·14	−0·02	−0·02
	a	14,973	61·60	−0·21	−0·40
	a	39,712	62·34	−0·06	−0·74
KI, 55°.	a	824·2	62·81	+0·01	±0·00
	b	932·0	63·60	±0·00	−0·45(?)
	c	1,218	65·39	−0·01	−0·16
	a	3,345	70·66	±0·00	+0·07
	c	4,667	71·86	+0·03	+0·11
	b	9,046	73·49	±0·00	−0·08
	a	15,177	74·09	−0·17	−0·53
	a	40,254	75·01	+0·05	−1·00
KI, 70°.	d	855·2	72·94	±0·00	±0·00
	c	1,235	76·09	+0·01	−0·06
	d	2,212	80·35	+0·01	+0·20
	c	4,734	83·95	−0·02	+0·05
	d	8,134	85·72	+0·02	−0·08
NaI, 0°.	b	466·5	24·40	+0·05	—
	a	474·2	24·39	±0·00	—
	c	508·3	24·55	−0·02	—
	a	876·8	25·82	−0·01	+0·05
	b	1,668	27·06	−0·01	±0·00
	a	5,270	28·56	+0·02	+0·01
	b	8,180	28·88	−0·02	−0·04
	c	17,450	29·28	±0·00	−0·13
	a	32,142	29·45	±0·00	−0·23
	a	59,488	29·46	−0·04	−0·42
NaI, 25°.	b	476·6	37·79	−0·05	—
	a	484·5	37·98	±0·00	—
	c	519·4	38·50	+0·05	—
	a	895·8	40·99	−0·01	−0·10
	b	1,704	43·03	−0·01	±0·00
	a	5,384	45·29	±0·00	+0·04
	b	8,358	45·85	+0·02	+0·03
	c	17,830	46·46	−0·01	−0·08
	a	32,841	47·01	+0·20	+0·05
	a	60,781	46·97	±0·00	−0·28

TABLE I (*contd.*).

	Series.	v.	Λ.	Δ.	Δ′.
NaI, 50°.	b	487·7	51·57	+0·01	—
	a	495·7	51·65	−0·01	—
	c	531·4	52·26	±0·00	—
	a	916·6	56·57	−0·04	−0·60
	b	1,744	60·23	±0·00	±0·00
	a	5,509	63·82	+0·01	+0·08
	b	8,551	64·57	±0·00	−0·09
NaI, 70°.	b	496·7	62·25	±0·00	—
	a	504·9	62·50	−0·01	—
	c	541·2	63·45	−0·04	—
	a	933·6	69·73	−0·02	−0·84
	b	1,776	74·42	+0·01	±0·00
	a	5,611	78·87	±0·00	±0·00
	b	8,710	80·35	+0·44	+0·66
LiI, 0°.	a	100·9	15·37	±0·00	—
	b	492·9	21·20	±0·00	±0·00
	a	923·3	23·27	−0·03	−0·30
	b	2,290	25·90	+0·01	−0·02
	a	4,549	27·10	±0·00	±0·00
	a	9,178	27·91	+0·05	−0·01
	b	9,513	27·70	−0·22	−0·28
LiI, 25°.	a	103·1	24·91	±0·00	—
	b	503·6	34·56	±0·00	−0·14
	a	943·3	38·14	−0·01	+0·04
	b	2,340	41·72	+0·03	+0·24
	a	4,648	43·18	−0·07	−0·01
	a	9,164	44·37	+0·11	±0·00
	b	9,719	44·00	−0·32	−0·46
LiI, 50°.	a	105·4	34·73	±0·00	—
	b	515·3	48·83	±0·00	−0·07
	a	965·2	53·82	−0·02	+0·01
	b	2,394	58·85	+0·03	+0·23
	a	4,756	60·88	−0·10	−0·17
	a	9,377	62·74	+0·45	−0·01
	b	9,945	61·97	−0·46	−0·89
LiBr, 0°.	a	487·5	7·10	−0·07	—
	c	552·6	7·52	+0·03	—
	a	982·8	9·39	+0·05	—
	b	1,949	12·15	−0·07	±0·00
	a	4,836	16·14	−0·01	−0·05
	b	8,146	17·85	+0·01	+0·03
	a	9,899	18·50	+0·13	+0·17
LiBr, 25°.	a	498·1	11·38	−0·02	—
	c	564·6	11·92	+0·03	—
	a	1,004	14·70	−0·06	—
	b	1,992	19·49	+0·03	±0·00
	a	4,941	25·47	−0·10	−0·13
	b	8,323	28·17	+0·04	+0·12
	a	10,114	29·25	+0·19	+0·45
LiBr, 50°.	a	509·7	15·52	−0·05	—
	c	577·7	16·39	+0·06	—
	a	1,027	20·16	+0·01	—
	b	2,038	27·33	+0·06	±0·00
	a	5,056	35·25	−0·10	−0·38
	b	8,516	39·24	+0·08	+0·26
	a	10,349	40·77	+0·40	+0·75

TABLE I (*contd.*).

	Series.	*v*.	Λ.	Δ.	Δ′.
LiBr, 70°.	a	519·1	18·72	±0·00	—
	c	588·4	19·85	+0·05	—
	a	1,046	24·55	±0·00	—
	b	2,076	32·51	+0·20	±0·00
	a	5,149	43·33	−0·37	−0·35
	b	8,674	48·44	+0·18	+0·34
	a	10,540	50·33	+0·58	+0·83
$AgNO_3$, 0°.	c	39·10	4·98	±0·00	—
	c	78·2	6·62	+0·05	—
	b	91·22	7·26	+0·35(?)	—
	a	104·6	7·07	−0·13	—
	c	156·4	8·12	−0·08	—
	a	598·0	13·60	−0·13	—
	b	709·2	14·92	+0·10	—
	a	3,119	22·46	+0·08	±0·00
	b	7,398	25·56	−0·07	−0·58
	a	11,432	27·58	+0·40	−0·01
	a	21,504	29·17	+0·05	+0·04
	a	40,400	30·11	−0·44	−0·11
$AgNO_3$, 25°.	c	39·86	7·50	−0·18	—
	c	79·72	9·86	+0·09	—
	b	93·20	10·55	+0·25	—
	a	106·8	10·62	−0·15	—
	c	159·4	12·30	−0·05	—
	a	611·0	20·57	−0·23	—
	b	724·6	22·18	+0·01	—
	a	3,276	34·72	+0·13	±0·00
	b	7,559	40·17	−0·16	−0·54
	a	11,680	42·88	−0·03	−0·09
	a	21,972	45·79	+0·08	+0·31
	a	41,278	47·28	±0·00	−0·01
$AgNO_3$, 40°.	b	94·46	12·48	+0·10	—
	a	108·3	12·77	−0·10	—
	a	619·2	24·75	−0·02	—
	b	734·3	26·49	+0·09	—
	a	3,320	41·92	+0·22	±0·00
	b	7,661	49·39	−0·26	−0·36
	a	11,837	52·83	−0·06	−0·13
	a	22,267	56·69	+0·45	+0·69
	a	41,833	58·07	−0·47	−0·30
$AgNO_3$, 55°.	b	95·75	14·36	+0·03	—
	a	109·7	14·90	−0·04	—
	a	627·7	28·91	−0·01	—
	b	744·4	30·73	−0·17	—
	a	3,365	49·48	+0·08	±0·00
	b	7,765	58·82	−0·03	+0·20
	a	11,999	62·98	+0·15	+0·32
	a	22,571	67·70	+0·63	+0·97
	a	42,404	68·62	−0·86	−1·03

are the differences between the observed points and a smooth curve drawn through them on a Λ–log *c* graph. Since the equation of this smooth curve is, except for the most concentrated solutions and for lithium bromide and silver nitrate, $\Lambda_0 = \Lambda + ac^n$, *a* and *n* being determined by Ferguson and Vogel's method (*Phil. Mag.*, 1925, **1**, 971), these differences are also the differences between the observed values and those calculated from this equation. Under Δ' are the differences between the observed points and a straight line drawn through them on a plot of Λ against $\sqrt{c}$, a positive sign before Δ indicating that the observed point is above the curve.

The values of the equivalent conductivity at even dilutions are given in Table II. Interpolation was carried out on a Λ–log c graph drawn with a flexible spline.

TABLE II.

Temp.	0°.	25°.	40°.	55°.	70°.	0°.	25°.	50°.	70°.
v.			Λ.				Λ.		
		Potassium Iodide.					Sodium Iodide.		
500	—	—	—	—	—	24·54	38·17	51·74	62·33
1,000	28·06	43·77	53·76	64·08	74·31	26·10	41·41	57·20	70·36
2,000	29·54	46·31	57·10	68·38	79·70	27·36	43·43	60·82	75·06
5,000	30·67	48·46	60·00	72·03	84·18	28·50	45·17	63·60	78·57
10,000	31·18	49·41	61·33	73·67	86·23	29·05	46·01	64·80	80·22
20,000	—	50·01	—	—	—	29·33	46·54	—	—
50,000	—	50·46	—	—	—	29·49	46·96	—	—
		Silver Nitrate.					Lithium Iodide.		
50	5·55	8·36	—	—	—	—	—	—	—
100	7·10	10·51	12·57	14·50	—	15·36	24·73	34·25	—
500	12·72	19·26	22·83	26·57	—	17·88	34·54	48·57	—
1,000	16·83	24·73	29·37	34·45	—	23·57	38·45	54·10	—
2,000	20·35	30·55	36·42	42·97	—	25·57	41·22	58·08	—
5,000	24·15	37·60	45·69	54·09	—	27·23	43·38	61·09	—
10,000	26·71	42·00	51·73	61·30	—	27·96	44·35	62·38	—
20,000	28·91	45·37	—	—	—	—	—	—	—

Temp.	0°.	25°.	50°.	70°.
v.		Λ.		
		Lithium Bromide.		
500	7·23	11·42	15·46	18·43
1,000	9·40	14·73	19·92	24·13
2,000	12·34	19·92	27·08	31·78
5,000	16·27	25·62	35·28	43·42
10,000	18·40	29·00	40·22	49·34

Viscosity Measurements.—An Ostwald viscometer was used. The measurements were made in a glass-sided thermostat, the temperature of which was constant to ± 0·01°. Drying tubes, attached to both ends of the viscometer, were found to be without effect on the time of flow. The viscometer was cleaned with alcohol and nitric acid, washed with water and alcohol, and dried in a warm bath by a current of purified dry air which was filtered from all dust particles by means of a Jena-glass filter. All the wash liquids and liquids to be measured were filtered similarly, since this method for removing dust motes has been found to be both convenient and very efficient. The time of flow was never less than 300 seconds, and readings were reproducible to $\frac{2}{5}$ sec. after emptying, cleaning, drying, and refilling the viscometer.

A correction was applied for the error at higher temperatures, arising from the fact that the coefficient of expansion of benzonitrile is greater than that of water, and hence that, whilst the volumes of benzonitrile and water placed in the viscometer were equal at the temperature at which they were measured, *viz.*, room temperature, they were not equal at other temperatures. The extra time of flow at 40° due to an additional 1 c.c. of water was determined, and, the effect of 1 c.c. of a liquid of a certain density being known, the effect of any volume of a liquid of any density could be calculated by simple proportion. The difference in volume of the benzonitrile and water in the viscometer was calculated from a knowledge of their densities at the temperatures involved, and the extra time of flow due to the larger volume of the benzonitrile was subtracted from its observed time of flow. The correction never amounted to more than 0·75% and averaged about 0·25%. The viscometer had previously been found by H. B. Oakley, of this department, to have a negligible deviation from Poiseuille's law. The values adopted for the viscosity of water were those of Bingham and White (1912).

The results obtained for the viscosity of benzonitrile at various temperatures were :

Temp.	0°	25°	40°	50°	55°	70°
$\eta \times 10^4$	194	124	100	87·6	82·6	66·6

Extrapolation to Λ_0.—Of the numerous formulæ that have been proposed for extrapolation to the equivalent conductivity at zero concentration (Λ_0) only two need now be considered.

(1) Kohlrausch's square-root law

$$\Lambda_0 = \Lambda + xc^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is important since it has been theoretically deduced by Debye and Hückel. The accuracy with which it applies to these benzonitrile solutions is illustrated by the differences in the last column of Table I. The range of dilution over which this equation holds is for potassium iodide $N/1000$ to $N/10{,}000$; for sodium iodide up to a concentration of $N/1000$; for lithium iodide up to $N/500$; and for lithium bromide and silver nitrate up to $N/2000$. This range is the same at all the temperatures at which experiments were carried out. In the case of potassium iodide at dilutions greater than 10,000 litres there is a definite deviation which may be due to experimental error. The values of Λ_0 and x obtained by this method are given in Table III, the unit of concentration being 1 g.-equiv. per litre.

TABLE III.

Values of Λ_0 and x (square-root law).

Temp.		0°.	25°.	40°.	50°.	55°.	70°.
KI	Λ_0 ...	32·76	52·12	64·83	—	78·22	91·95
	x	147·7	263·3	347·7	—	442·4	555·7
NaI	Λ_0 ...	30·45	48·11	—	68·28	—	84·58
	x	138·1	210·0	—	336·2	—	428·2
LiI	Λ_0 ...	29·98	47·33	—	66·99	—	—
	x	194·4	283·6	—	410·8	—	—
LiBr	Λ_0 ...	23·20	36·17	—	50·09	—	62·87
	x	488·0	744·5	—	1028	—	1380
$AgNO_3$	Λ_0 ...	33·30	52·18	64·78	—	77·50	—
	x	613·3	998·3	1318	—	1628	—

(2) Ferguson and Vogel's formula (*loc. cit.*)

$$\Lambda_0 = \Lambda + ac^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the best values of the constants a and n are determined by a graphical method, is logically the most satisfactory method of extrapolation. It has been applied except in the cases of silver nitrate and lithium bromide, where an equation of this form is not followed over a wide enough range to permit a satisfactory determination of a and n. In determining the constants in equation (2) the values of Λ at the series of concentrations (c) in geometrical progression were read off from plots of Λ against log c, instead of c, the latter being Ferguson and Vogel's practice. A common ratio of 1·5 was used. The range of concentration over which equation (2) is followed is for potassium iodide from the lowest concentrations measured up to $N/2000$, and for sodium and lithium iodides up to $N/1000$. The values of Λ_0 obtained from equation (2) and the values of the constants a and n are given in Table IV.

TABLE IV.

(Ferguson's method.)

	Values of Λ_0.			Values of n.			Values of a.		
Temp.	KI.	NaI.	LiI.	KI.	NaI.	LiI.	KI.	NaI.	LiI.
0°	32·15	30·51	29·29	0·632	0·484	0·634	320·6	125·3	456·4
25	51·11	47·57	45·99	0·637	0·600	0·658	607·8	396·3	710·7
40	63·83	—	—	0·615	—	—	723·6	—	—
50	—	66·79	64·38	—	0·687	0·711	—	1107	1397
55	76·73	—	—	0·626	—	—	978·4	—	—
70	89·98	82·34	—	0·631	0·726	—	1244	1805	—

The values to which both a and n appear to tend with increase of temperature for the iodides of the alkali metals are in the inverse order of atomic weight. At the lower temperatures there is no regularity, and that at the higher temperatures is perhaps merely fortuitous. This is in contrast with the finding of Ferguson and Vogel (*loc. cit.*, 1925) for electrolytes in water.

Discussion.

The Values of Λ_0.—For the iodides of the alkali metals Λ_0 increases with increasing atomic weight and volume. Frazer and Hartley (*loc. cit.*) observed the same phenomenon in methyl-alcoholic solutions. It must, therefore, be supposed that solvation or some form of interaction between solvent and solute occurs in these solvents as well as in water.

In Table V are given the ratios of the values of Λ_0 for the salts in benzonitrile at 25° to the corresponding values in water and methyl alcohol at 25°, and for potassium iodide at 0°, 25°, 40°, 55°, and 70° in benzonitrile to the values at the corresponding temperatures in nitromethane. The values in aqueous solution were obtained from the data of Kohlrausch ("Das Leitvermögen der Elektrolyte," 1916), in nitromethane from those of Philip and Oakley (*loc. cit.*), and in methyl alcohol from those of Frazer and Hartley (*loc. cit.*). In the last case, the values of Λ_0 of lithium iodide, lithium bromide, and sodium iodide were calculated from the ionic mobilities concerned, these salts not having been directly investigated. For the sake of consistency values of Λ_0 determined by the square-root law have been used throughout. The ratios of the viscosities of the solvents are also given.

TABLE V.

Solute.	Λ_0, PhCN.	Λ_0, H_2O.	Λ_0, MeOH.	$\frac{\Lambda_0, \text{PhCN}}{\Lambda_0, H_2O}$.	$\frac{\eta, H_2O}{\eta, \text{PhCN}}$.	$\frac{\Lambda_0, \text{PhCN}}{\Lambda_0, \text{MeOH}}$.	$\frac{\eta, \text{MeOH}}{\eta, \text{PhCN}}$.
KI	52·12	150·5	114·7	0·35		0·45	
NaI	48·11	127·0	106·7	0·38		0·45	
LiI	47·33	115·7	100·6	0·41	0·72	0·47	0·45
LiBr	36·17	117·1	95·1	0·31		0·38	
$AgNO_3$	52·18	133·8	112·9	0·39		0·46	

Values for potassium iodide in benzonitrile and nitromethane, and ratio of viscosities of solvents.

Temp.	Λ_0, PhCN.	Λ_0, $Me{\cdot}NO_2$.	$\frac{\Lambda_0, \text{PhCN}}{\Lambda_0, Me{\cdot}NO_2}$.	$\frac{\eta, Me{,}NO_2}{\eta, \text{PhCN}}$.
0°	32·76	91·3	0·36	0·43
25	52·12	123·8	0·42	0·51
40	64·83	145·6	0·45	0·53
55	78·42	169·4	0·46	0·54
70	91·95	194·4	0·47	0·59

If the motion of the ions is in accordance with Stokes's law, and if the ions are the same size in each solvent, the ratio of the values of Λ_0 of a given salt in two solvents should equal the ratio of the fluidities (*i.e.*, the inverse ratio of the viscosities) of the solvents. This is so for benzonitrile and methyl alcohol, and approximately so for benzonitrile and nitromethane, but for benzonitrile and water the values of Λ in the former are about half as great as would be expected from its viscosity. This can be explained by supposing that in the two non-aqueous solvents the extent of solvation or interaction between ion and solvent as suggested by Born (*Z. Physik*, 1920, **1**, 221) is the same, and in both cases greater than in water. That in this respect benzonitrile resembles methyl alcohol and that both differ from water affords yet further evidence of the unique position of water amongst liquids.

The Variation of Λ_0 *with Temperature.*—If the logarithm of Λ_0 for a given salt at different temperatures is plotted against the logarithm of the fluidity of the solvent, an unequivocally straight line results, from the slope of which it is found that Λ_0 varies as the *m*th power of the fluidity, where *m* for potassium iodide is 1·01, for sodium iodide 0·99, for lithium iodide 1·00, for lithium bromide 0·97, and for silver nitrate 1·01. It is clear that within the limits of experimental error Λ_0 is directly proportional to the fluidity of the solvent, and the constancy of the product $\Lambda_0\eta$ for a given salt is clearly shown in Table VI, which gives values of Λ_0 at 10° intervals from 0° to 70°, and of the product $(\Lambda_0)_{t^\circ}\cdot\eta_{t^\circ}$. The values of Λ_0 and η at temperatures at which they were not measured were interpolated graphically from plots of these quantities against temperature. Deviations from simple proportionality occur for all electrolytes at 60° and 70°.

TABLE VI.

	KI.		NaI.		LiI.		LiBr.		$AgNO_3$.	
Temp.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.
0°	32·1	0·62	30·5	0·59	29·3	0·57	23·2	0·45	33·3	0·64
10	39·5	0·63	37·1	0·59	35·8	0·57	28·3	0·45	40·6	0·65
20	47·2	0·63	44·0	0·59	42·5	0·57	33·4	0·45	48·3	0·65
30	55·2	0·64	51·3	0·59	49·6	0·57	38·7	0·44	56·4	0·65
40	63·6	0·64	58·9	0·59	56·8	0·57	44·2	0·44	64·8	0·65
50	72·3	0·63	66·8	0·59	64·4	0·57	50·1	0·44	73·2	0·64
60	81·1	0·62	74·5	0·57	72·3	0·55	56·5	0·43	81·7	0·62
70	90·0	0·60	82·4	0·55	—	—	62·9	0·43	—	—

Comparison of the Results with the Theory of Debye and Hückel.

According to the theory of Debye and Hückel (*Physikal. Z.*, 1923, **24**, 305) there is, in dilute solutions of strong electrolytes, a linear relation between equivalent conductivity and the square root of the concentration. The author's results (with the exception of those for extremely dilute potassium iodide solutions, which may be in error) are in agreement with this theory in so far as they yield straight-line plots of Λ against $\sqrt{c}$, as demonstrated by the fact that there are as many positive as negative differences in the last column of Table I; but the agreement with the equation $\Lambda_0 = \Lambda + ac^n$, where n is not 0·5, is still closer, as is evident from a comparison of the last two columns of Table I. However, the mean differences from the square-root law (1 part in 400 parts) and from equation (2) (1 part in 1000 parts) are both near to the possible accidental error of the measurements, and in addition there is the possibility of a slight systematic error, the magnitude of which could not be estimated from the data themselves. The true value of the index n therefore remains in doubt, for the somewhat superior fit of equation (2), in which there is an additional adjustable constant, may represent not a law of nature but merely the experimental error of the measurements. A comparison of the ranges of concentration over which the rival equations hold leads to no conclusion, since this range is approximately the same for both and the square-root law, according to Debye's theory, cannot be expected to hold in concentrated solutions owing to the approximations made in its deduction. At this point exception must be taken to Ferguson and Vogel's practice of testing the fit of their equation by comparing the consistency of the values of Λ_0 calculated from it with that of those calculated from the square-root law, using in both cases rounded values of Λ read off from a plot of Λ against c, *i.e.*, from the curve whose equation is $\Lambda_0 = \Lambda + ac^n$. The consistency of the values of Λ_0 so determined from their equation is a measure, not of its agreement with experiment, but of the skill with which a curve of the form $\Lambda_0 = \Lambda + ac^n$ has been drawn and its constants determined. Equation (2) is therefore represented in an unduly favourable light.

A similar situation occurs in methyl-alcoholic solutions, and here the view that the deviation of n from 0·5 is due to experimental error is favoured by the fact that the values of Λ_0 calculated from equation (2) definitely do not agree with Kohlrausch's law of the independent migration of ions, the validity of which can hardly be doubted, as closely as those calculated from the square-root law (Frazer and Hartley, *loc. cit.*; Vogel, *Phil. Mag.*, 1928, **5**, 199). On the other hand, it is difficult to believe that, although in general the values of n are within 20% of 0·5, this deviation, in aqueous as well as in non-aqueous solution, is in every case due to experimental error. Furthermore, certain regularities have been found in the author's data, based on values of Λ_0 calculated from equation (2), which do not always occur if those yielded by the square-root law are used (see later).

The author inclines to the opinion that deviations from the square-root law are magnified when judged by the difference between the value of n in equation (2) and 0·5, but that when this difference is large and the data are accurate there is a departure from the theory of Debye and Hückel. From the foregoing, the inadequacy both of plotting Λ against $\sqrt{c}$ and of determining n in equation (2) as a test of Debye's theory is apparent, and as a more certain test the slope of the Λ–$\sqrt{c}$ line and its calculation from the theory will now be considered.

The original Debye–Hückel theory (*loc. cit.*, p. **315**) gives the following derivation for the slope (x) of the straight line obtained by plotting Λ against $\sqrt{c}$ for uni-univalent electrolytes :

$$1 - f_\Lambda = (\Lambda_0 - \Lambda)/\Lambda_0 = (K_1 w_1 + K_2 b)\sqrt{2c} \quad . \quad . \quad (3)$$

$$K_1 = \frac{\varepsilon F}{6DRT}\sqrt{\frac{4\pi F^2}{DRT \times 10^3}}; \qquad K_2 = \sqrt{\frac{4\pi F^2}{DRT \times 10^3}}$$

where ε = the elementary charge of electricity;
D = the dielectric constant of the solvent at T° (Abs.);
F = the value of the faraday ($= N\varepsilon$, where N = Avogadro's number);
R = the gas constant per g.-mol.;
$w_1 = \frac{1}{2}(l_a/l_c + l_c/l_a)$, where l_a and l_c are the mobilities of the anion and kation, respectively;
and b = the mean radius of the anion and kation.

(The term $K_1 w_1$ gives the diminution in conductivity due to the dissymmetry of the ion atmosphere, and the term $K_2 b$ that due to electrophoresis and the viscous drag of the solvent.)

Writing $\Lambda_0 = \Lambda + x\sqrt{c}$, we have

$$1 - f_\Lambda = x\sqrt{c}/\Lambda_0 = x\sqrt{2c}/\Lambda_0\sqrt{2},$$

and combining this with equation (3), we obtain

$$b \times 10^8 = (x/\Lambda_0\sqrt{2} - K_1 w_1)/K_2 \times 10^{-8}. \quad . \quad . \quad (4)$$

Since b is unknown, Debye prefers to put his equation in this form, and to show that the values of b so determined are not inconsistent with our knowledge of their order of magnitude. The dielectric constant of benzonitrile has been taken as 26 at 25°. The mobilities of the anion and kation were obtained by the use of Kohlrausch's law of the independent migration of ions, and of the assumption that the mobility of the tetraethylammonium ion is given by the relation (Ulich, *Fortschritte d. Chemie*, 1926, **18**, No. 10; *Trans. Faraday Soc.*, 1927, **23**, 388)

$$\text{mobility} \times \text{viscosity of solvent} = 0{\cdot}295 \quad . \quad . \quad (5)$$

For tetraethylammonium iodide Λ_0 was obtained by extrapolating Walden's data (*Z. physikal. Chem.*, 1906, **54**, 189) by the square-root law. Values of the ionic mobilities thus obtained cannot be regarded as very trustworthy, but since l_a is approximately equal to l_c the term $\frac{1}{2}(l_a/l_c + l_c/l_a)$ is not sensitive to changes in l_a and l_c. For silver nitrate, the ionic mobilities were obtained from Koch's measurements of the *E.M.F.* of silver nitrate concentration cells in benzonitrile (this vol., p. 524). The approximate values of the ionic mobilities are: $N(C_2H_5)_4^{\cdot}$ 23·8, I′ 29·5, Br′ 18·4, NO'_3 27·9, Li˙ 17·8, Na˙ 18·6, K˙ 22·6, Ag˙ 24·3.

Inserting numerical values for benzonitrile at 25° in equation (4), we have

$$b \times 10^8 = (x/\sqrt{2}\Lambda_0 - 1{\cdot}439w_1)/0{\cdot}4035 \quad . \quad . \quad . \quad (6)$$

The values of Λ_0 used in calculating b from equation (6) are those obtained by extrapolation by the square-root law. Table VII gives the result of this calculation together with values of b calculated from the respective ionic mobilities on the assumption (1) that the only resistance to the motion of the ions at infinite dilution is the viscous drag of the solvent, and (2) that the magnitude of this drag is given by Stokes's law. This assumption is probably not strictly justified; however, a similar error occurs in equations (3), (4), and (6) since Debye (*Trans. Faraday Soc.*, 1927, **23**, 334) treats the term K_2b as being made up of two parts—one given by Stokes's law, and the other due to the fact that an external force acts on the elements of volume of the liquid (electrophoresis). For comparative purposes this error may therefore be neglected as a first approximation.

TABLE VII.

Values of the Mean Ionic Radius (b) *at 25° calculated from Debye and Hückel's Theory.*

Electrolyte.	$b \times 10^8$ (Debye and Huckel), cm.	$b \times 10^8$ (from ionic mobilities at infinite dilution and Stokes's law), cm.
KI	5·16	2·57
NaI	3·72	2·88
LiI	6·47	2·96
LiBr	32·4	3·63
$AgNO_3$	29·9	2·58

The following points may be noted: (1) The values of the mean ionic radii calculated from Debye and Hückel's theory are, except for lithium bromide and silver nitrate, of the correct order of magnitude. They are somewhat larger than in water and methyl alcohol. (2) Frazer and Hartley (*loc. cit.*) found a similar exceptionally large value of b for silver nitrate in methyl alcohol. Were it not for the fact that the value calculated from the ionic mobilities and Stokes's law is not large, one would be tempted to ascribe this large value to solvation and to link it up with the very great solubility of silver nitrate in benzonitrile. (3) For lithium iodide b is larger than for sodium iodide, but potassium iodide occupies an intermediate position; yet the values of b calculated from the ionic mobilities and Stokes's law are in the usual inverse order of atomic weight: $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$.

That only the order of magnitude of b and not its exact value is known independently of the theory renders this test much less convincing.

Onsager's Modification of the Debye–Hückel Theory.—Onsager (*Physikal. Z.*, 1926, **27**, 388; 1927, **28**, 277) has recently introduced a refinement into the Debye–Hückel theory by taking into account the Brownian movement of the ions. The final expression at which he arrives does not contain b, and does not require a knowledge of the individual ionic mobilities; when the numerical values of universal constants are inserted, it is, for uni-univalent electrolytes,

$$\Lambda = \Lambda_0 - \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{2/3}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{1/2}\eta}\right]\sqrt{2c} \quad . \quad . \quad (7)$$

For benzonitrile at 25° this becomes

$$\Lambda = \Lambda_0 - (0{\cdot}8475\Lambda_0 + 53{\cdot}14)\sqrt{2c} \; . \quad . \quad . \quad . \quad . \quad (8)$$

The great merit of equations (7) and (8) is that they contain no adjustable constants, and therefore provide a good test for the theory on which they are based. In the following table the slopes of the Λ–$\sqrt{c}$ lines calculated from equation (8) are given under "x, calc.," and the observed values under "x, obs." The values of Λ_0 used are those calculated by the square-root law, since according to equation (8) the law should hold: the use of values of Λ_0 determined by equation (2) makes very little difference.

Electrolyte.	KI.	NaI.	LiI.	LiBr.	$AgNO_3$.
x, calc.	137·5	132·9	131·9	118·5	137·8
x, obs.	263·3	210·0	283·6	744·5	998·3

For the three iodides the observed slope is about twice as great as the calculated, and for lithium bromide and silver nitrate some 7—8 times. The differences between the observed slopes for the various electrolytes are greater than those between the calculated slopes. It should be mentioned that the agreement of theory with observation is quite good in aqueous and methyl-alcoholic solutions.

Incomplete Dissociation and Applicability of the Law of Mass Action to the Dissociation of Strong Electrolytes.—Bjerrum (*Kgl. Danske Videnskap. Selsk. math.-fys. Medd.*, 1926, VII, 9) suggested that, in concentrated solutions of strong electrolytes, association of ions into electrically neutral doublets occurs. This is the factor which Onsager (*Physikal. Z.*, 1927, **28**, 277) considers accounts for a Λ–$\sqrt{c}$ slope greater than the theoretical. He writes, as an approximation,

$$\Lambda = \Lambda_0 - x\sqrt{c} - \Lambda_0 c/K,$$

where K is the dissociation constant of the electrolyte. However, he states that the mode of ionic association cannot be determined from the conductivity curve, and suggests an investigation of the viscosity and optical properties of the solution. He gives values for the dissociation constants of potassium and thallium nitrates and thallium chloride in water at one concentration only, calculated by comparing the values of Λ for these salts with that of potassium chloride at the same concentration, the last salt being assumed to be completely dissociated.

Fajans (*Trans. Faraday Soc.*, 1927, **23**, 357) has found evidence for the existence of undissociated molecules in concentrated solutions from refractometric data, but the concentrations at which he worked are so great that his results can hardly be said to conflict with the postulates of the Debye–Hückel theory.

Nernst (*Z. Elektrochem.*, 1927, **33**, 428) satisfactorily accounted for the heats of dilution of strong electrolytes in water, one of the most outstanding failures of the Debye–Hückel theory, by assuming incomplete dissociation governed by the law of mass action in addition to the effects due to the Debye–Hückel interionic attraction. He has recently shown (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1928, 4) that, if the greater decrease in equivalent conductivity with increasing concentration of certain electrolytes in water compared with that of potassium iodide and bromide be assumed to be due to incomplete dissociation, values of the degree of dissociation are obtained in approximate agreement with those calculated from the freezing-point depression, the effect of the interionic attraction being taken into account in this latter calculation.

It appears to the author that the law of mass action should be applicable to electrolytic dissociation if there is a sharp distinction between the type of interaction represented by an electrically neutral doublet (undissociated molecule) and that represented by an ion atmosphere of opposite sign surrounding a given ion (the interaction taken account of by the Debye–Hückel theory). The true degree of dissociation (α) is not given by the ratio Λ/Λ_0, since in this expression the decrease in conductivity due to the Coulomb forces between the ions (Debye effect) is not taken into account, and α has, therefore, been evaluated in the following way.

A graph was made of the theoretical relation between Λ and $\sqrt{c}$ deduced from Onsager's expression (8), using values of Λ_0 determined by equation (2). From this graph values of Λ (calculated) at a series of concentrations (c) were read off. The values of Λ (observed) used were those at round concentrations obtained from a plot of Λ against $\log c$. The ratio Λ (obs.)/Λ (calc.), at a given concentration c, gave the first approximation (α_1) to α. From this value of α_1, the concentration of ions $\alpha_1 c (= c')$ which was responsible for the observed conductivity was calculated. The ratio $\frac{\Lambda,\ \text{calculated for an ionic concentration } c}{\Lambda,\ \text{calculated for an ionic concentration } c'}$ gave the second stage (α_2) in the approximation to α. If the point having the co-ordinates Λ (obs.; total conc. $= c)/\alpha_1\alpha_2$ and $\sqrt{\alpha_2 c'}$ lay within the limits of experimental error on the theoretical Λ–$\sqrt{c}$ straight line, this method of successive approximation was not carried further. The degree of dissociation (α) at concentration c was then given by $\alpha_1\alpha_2$. In very dilute solutions one approximation was sufficient and only very rarely were more than two necessary. Although the theoretical slope is only slightly altered if values of Λ_0 determined by the square-root law instead of by equation (2) are used, considerably different values of α would be obtained for very dilute solutions, since in this region the differences between the theoretical and observed values are of the same order of magnitude as the differences in the intercepts on the axis of $\Lambda(\Lambda_0)$.

The results of this calculation are given in Table VIII, together with the values of the Ostwald dilution-law constant, $K = \alpha^2/(1-\alpha)v$, calculated from the values of α determined as above. In the cases of silver nitrate and lithium bromide, the theoretical values were calculated from the values of Λ_0 given by the square-root law, since it was impossible to apply equation (2) to these salts. The error caused by so doing is not large because the differences between the observed and calculated values of Λ are much greater for these salts than for the iodides of the alkali metals.

TABLE VIII.

Degree of Dissociation (100α) *of some Strong Electrolytes in Benzonitrile at* 25° ; *and Values of the Ostwald Dilution-law Constant.*

Electrolyte.	Dilution (litres).							
	20,000	10,000	5,000	2,000	1,000	500	100	
	Degree of dissociation (%).							
*KI	99·72	99·32	98·49	96·24	93·23	—	—	
*NaI	99·77	99·48	98·80	97·27	95·22	91·10	—	
LiI	—	99·24	98·23	95·53	91·40	85·05	70·45	
LiBr	—	82·62	73·73	58·33	43·66	34·50	—	
$AgNO_3$	88·56	82·45	74·46	61·37	50·78	41·14	23·09	
	Ostwald dilution-law constant (1000K).							Mean.
KI	17	14	13	12	13	—	—	13
NaI	21	19	16	17	19	19	—	19
LiI	—	13	11	10	10	10	17	12
LiBr	—	0·39	0·41	0·41	0·34	0·36	—	0·38
$AgNO_3$	0·3	0·4	0·4	0·5	0·5	0·6	0·7	0·5

* 100α = 100 at v = 50,000.

When allowance is made for the fact that in extremely dilute solutions α is so nearly 100% that a small error in it results in a relatively large error in $1 - \alpha$, and consequently in K, the constancy of K can be regarded as established.

By the foregoing method we have determined $K = c_{i+}c_{i-}/c$, where c_{i+} and c_{i-} are the concentrations of positive and negative ions and c is that of undissociated molecules. But strictly it is the expression $K' = \gamma_+ c_{i+}\gamma_- c_{i-}/\gamma_\mu c$, where the γ's are the respective activity coefficients, that should hold if the law of mass action applied to the equilibrium between ions and undissociated molecules. Since the activity coefficients involved have not been measured, γ_+ and γ_-, each of which for a uni-univalent electrolyte equals $\gamma_\pm$, have been calculated from the Debye–Hückel theory, and γ_μ has been assumed to be unity at all concentrations. This assumption is not strictly correct, but it is probable that the change in γ_μ with concentration is small compared with that in $\gamma_\pm$, and since γ_μ cannot be calculated, some assumption must be made about it. The equation of Debye and Hückel for the activity coefficient (*Physikal. Z.*, 1923, **24**, 185) is, for a uni-univalent electrolyte,

$$-\log_e \gamma_\pm = \frac{\varepsilon^2}{2DkT}\sqrt{\frac{4\pi\varepsilon^2}{DkT}\Sigma n_i} - \frac{2\pi\varepsilon^4 a}{(DkT)^2}\Sigma n_i \quad . \quad . \quad (9)$$

where k = Boltzmann's gas constant, n_i = the number of ions of the ith kind per c.c. of solution, a = the mean ionic diameter (taken as 6×10^{-8} cm.), and the other symbols are as already defined.

For benzonitrile at 25°, equation (9) becomes

$$-\log_{10} \gamma_\pm = 2{\cdot}66\sqrt{c} - 9{\cdot}12c \quad . \quad . \quad . \quad . \quad (10)$$

Table IX gives the values of the constant $K'(\times 10^3)$.

TABLE IX.

Electrolyte.	Dilution (litres). 20,000	10,000	5,000	2,000	1,000	500	100	Mean.
KI	16	13	11	9	9	—	—	11
NaI	20	17	14	13	14	12	—	14
LiI	—	11	9	8	7	6	8	8
LiBr	—	0·35	0·36	0·33	0·27	0·27	—	0·32
$AgNO_3$	0·31	0·36	0·40	0·40	0·40	0·41	0·41	0·40

The constancy of K' is approximately the same as that of K, and in the case of silver nitrate it is much greater. We may therefore say that the whole of the conductivity–concentration curve can be described by a dissociation governed by the law of mass action, the mobility of the resulting ions varying with their concentration, owing to the Coulomb forces between them, in the manner predicted by the Debye–Hückel–Onsager theory. In extremely dilute solutions dissociation is complete and the change in conductivity with concentration is determined entirely by the Coulomb forces between the ions.

The use of values of Λ_0 obtained from equation (2) in the foregoing calculation is justified since in this way the limiting value of the conductivity at zero concentration is found, no matter how many factors influence the variation of Λ with concentration and without any prejudices as to the nature of these factors, whereas the square-root law can be expected to give a correct result only when the sole factor influencing it is the Coulomb forces between the ions. That this regularity is found by the use of values of Λ_0 determined by equation (2) and not (in some cases) by using those given by the square-root law, indicates that here the deviation of the index n from 0·5 is not due merely to experimental error.

For the sake of comparison the following table is given, which contains values of $\alpha = \Lambda/\Lambda_0$ [Λ_0 being obtained from equation (2)] and the corresponding values of K for sodium iodide at 25°. To apply an activity correction to these values of K is illogical, since if the effect of interionic attraction is neglected in calculating α, it should also be neglected in calculating K. It is seen that K is definitely not constant.

v (litres) ……	50,000	20,000	10,000	5,000	2,000	1,000	500
100α ………	98·72	97·84	96·72	94·96	91·34	87·05	80·24
$1000K$ ……	1·5	2·2	2·8	3·6	4·7	5·8	6·5

Summary.

1. The conductivities of the iodides of lithium, sodium, and potassium, of lithium bromide, and of silver nitrate in benzonitrile have been measured over a range of dilution of from $N/500$ to $N/10{,}000$ or $N/50{,}000$, and over a range of temperature of from 0° to 70°.
2. The viscosity of benzonitrile over the same range of temperature has been measured.
3. Extrapolation to Λ_0 has been carried out by the square-root law and by Ferguson's method. The merits of the latter method have been discussed.
4. Over almost the whole range of temperature Λ_0 is directly proportional to the fluidity of the solvent.
5. The values of Λ_0 for a given salt have been compared with the values of Λ_0 for the same salt in aqueous, methyl-alcoholic, and nitromethane solution.
6. The slopes of the Λ–$\sqrt{c}$ straight lines are approximately twice as great as those calculated from the Debye–Hückel–Onsager theory.
7. The whole of the conductivity–concentration curve can be

described by a dissociation governed by the law of mass action, the mobility of the resulting ions varying with their concentration owing to the Coulomb forces between them, in the manner predicted by the Debye–Hückel–Onsager theory. In extremely dilute solutions dissociation is complete.

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