267. *Studies on Hydrogen Cyanide. Part VIII. The Conductivity of Electrolytes in Anhydrous Hydrogen Cyanide. Some Uni-univalent Salts at* 18°.

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As a general principle, the Nernst–Thomson rule, which relates the dissociating power of a medium and its dielectric constant, is fairly well obeyed, although the chemical nature of both solute and solvent must be taken into account to explain apparent anomalies. Owing to its high dissociating power, water has so far held a unique position among the great variety of solvents in which the Debye–Hückel–Onsager theory has been tested. Hydrogen cyanide is a medium of markedly different chemical type from water and has a much higher dielectric constant. In view of its relatively high dipole moment ($2 \cdot 5 \times 10^{-18}$ e.s.u.; Lutgert, *Z. physikal. Chem.*, 1931, **14**, *B*, 27) and of the fact that solvates with inorganic salts are known (unpublished work in this laboratory) it is to be expected that, as in water, the ions are surrounded by a somewhat closely attached sheath of oriented solvent molecules. Further evidence of the existence of this solvent sheath is given by work on the "salting-in" of hydrogen cyanide by various salts (Gross, Schwarz, and Iser, *Monatsh.*, 1930, **55**, 287, 329). The high dielectric constant and ion solvation lead to the expectation that hydrogen cyanide will be at least as powerful a dissociating medium as water. A study of conductivity in this solvent appeared, therefore, to be of much interest in relation, not only to the physical theory, but also to the chemical nature of hydrogen cyanide. It may be expected that the dilution range in which the limiting equation of the Debye–Hückel–Onsager theory is obeyed will be more readily attainable than is the case for many non-aqueous solvents.

Previous work on solutions of electrolytes in hydrogen cyanide includes measurements of freezing points, solubility, and conductivity. Lespieau (*Compt. rend.*, 1905, **140**, 855) showed from f.-p. measurements that potassium iodide and nitrate are almost completely dissociated, and recent measurements of f. p. in this laboratory (unpublished) have led to the same conclusion for potassium bromide and iodide and lithium chloride. Centnerszwer (*Z. physikal. Chem.*, 1901, **39**, 217) measured the conductivities of potassium iodide and trimethylsulphonium iodide at 0° over the concentration range 0·1—0·001*N* (approx.). His data show that potassium iodide is extensively dissociated even in 0·1*N*-solution. The equivalent conductivities found by Centnerszwer were nearly four times as great as those in water. Kahlenberg and Schlundt (*J. Physical Chem.*, 1902, **6**, 447) studied the conductivities of a large number of inorganic and organic substances at 0° but, again, few measurements were made at concentrations less than 0·001*N* and the work is of qualitative interest only. Fredenhagen and Dahmlos (*Z. anorg. Chem.*, 1929, **179**, 77) determined some conductivities in hydrogen cyanide but very few observations were made in the dilute region and no reliance can be placed on them. They concluded that hydrogen cyanide is a poor dissociating medium. Walden (*Z. physikal. Chem.*, 1930, **147**, *A*, 1) refers to the work of Fredenhagen and others, and takes the view that, owing to the possibilities of tautomerism and polymerism, hydrogen cyanide is not a suitable solvent for testing the general validity of the Nernst–Thomson rule. Falkenhagen ("Electrolytes," translated by Bell, 1934, 78) states that "although the dielectric constant of hydrogen cyanide is 95, salts in hydrogen cyanide are bad conductors." On the other hand, many statements occur in the literature in which, on purely theoretical grounds, hydrogen cyanide is considered to be an excellent ionising medium (*e.g.*, Walden, "Elektrochemie nichtwässriger Lösungen," 1924, 49; discussion on a paper by Bredig and Teichmann, *Z. Elektrochem.*, 1925, **8**, 449). This view is taken mainly because of its high dielectric constant and of its apparent similarity to water, in that it has been shown to be an associated liquid with an "association factor" approximately equal to 2 (Bredig and Teichmann, *loc. cit.*; Werner, *Z. physikal. Chem.*, 1929, **4**, *B*, 71).

A systematic study of electrolytes dissolved in hydrogen cyanide has been undertaken in this laboratory. The present communication deals with the equivalent conductivities of a number of uni-univalent salts at 18° over the concentration range 0·002—0·0001*N*.

EXPERIMENTAL.

The Bridge Assembly.—The direct-reading A.C. Wheatstone bridge was built on the lines laid down by Shedlovsky (*J. Amer. Chem. Soc.*, 1930, **52**, 1793) and Jones and Josephs (*ibid.*, 1928, **50**, 1049). The variable non-inductive resistance box (by Tinsley) was of the dial decade type reading up to 11,111·0 ohms and was calibrated at the N.P.L. Resistances higher than the above value were measured by using another calibrated resistance of 10,000 ohms as a shunt across the cell terminals. The current generator was a thermionic valve oscillator of variable frequency, and the detector consisted of a pair of telephones connected through a two-valve radio amplifier to the bridge circuit. A frequency of 1000 cycles per second was used throughout the measurements, and no resistance value less than about 400 ohms was taken into account.

Temperature Control.—High-grade transformer oil was used as the thermostat liquid. A mercury–toluene electrical thermoregulator controlled the heater. Cooling was effected by passing a regulated stream of cold water through a lead pipe immersed in the bath. With efficient stirring a temperature of 18·00° (± 0·01°) was easily maintained. In order to prevent condensation into the cap of the cell, the temperature of the air immediately above the thermostat was kept just above 18° by radiation from an electric lamp.

The Conductivity Cells.—The cells were of the Hartley–Barrett type (J., 1913, **103**, 786) and were constructed of Jena 16^{III} glass. In some of the earlier measurements, cells made of Pyrex glass were used, but no difference in the result was observed. The ground joints were secured by means of strong steel springs between glass hooks fused into the appropriate parts of the cell.

The effect of different electrode surfaces was investigated. It was found that bright platinum electrodes (about 1 cm.^{2} in area and about 1 cm. apart) introduced strong polarisation effects with solutions of potassium chloride in hydrogen cyanide at resistances for which the polarisation with potassium chloride in water was negligible. In detecting the presence of polarisation errors, the change of resistance with increasing frequency was taken as a criterion. Even the use of grey platinised electrodes of similar dimensions and spacing did not avoid appreciable polarisation errors. Finally, black platinised electrodes were found to be suitable. The electrodes (about 1 cm.^{2} in area and about 1·5—2·0 cm. apart) were platinised with the usual " platinum chloride " solution containing a trace of lead acetate. To minimise any possible error due to adsorption, the degree of platinisation was only just sufficient to eliminate polarisation. That adsorption errors were absent may be inferred from the fact that a large increase in the degree of platinisation led to no change in the value of the equivalent conductivity, and further, a sevenfold increase in the actual electrode area was without effect on the results for potassium chloride. No change of resistance with time was encountered in any of the solutions examined, indicating negligible catalytic effect of the platinum.

The electrodes were fixed relatively to each other by means of glass struts between them or by sealing them directly to the electrode lead tubes. A small bottle-shaped cell of the Kohlrausch type was used for testing the conductivity of the solvent during its fractionation.

Cleaning and Drying of the Apparatus.—The glass ware and conductivity cells were soaked in warm chromic–sulphuric acid mixture, washed well with distilled water, steamed, washed again with conductivity water, and finally with redistilled absolute alcohol. Drying was effected by leaving in a hot air- or steam-oven and afterwards cooling in a stream of pure dry air or in a vacuum over phosphoric oxide. Although pure hydrogen cyanide readily darkens when placed in ordinary glass containers, this did not occur when the glass had been treated in the above manner.

Measurement of the Cell Constants.—The cell constants were measured at 18° by the method of Frazer and Hartley (*Proc. Roy. Soc.*, 1925, *A*, **109**, 355) and also by means of the 0·01 *D* solution prepared according to the directions of Jones and Bradshaw (*J. Amer. Chem. Soc.*, 1933, **55**, 1780). In the first of these methods small weights of a relatively concentrated stock solution of potassium chloride were added, successively, to a known weight of pure solvent in the cell. The concentrations employed were such that the cell constant was measured over the same range of resistances as used in the experiments with hydrogen cyanide. The water was obtained from a Hartley still and had a specific conductivity of 1—2 × 10^{-6} mho at 18°. In order to calculate the equivalent conductivity at each concentration, the following equations were used :

$$\Lambda_c = 129{\cdot}91 - 80{\cdot}75\sqrt{C}$$ (Frazer and Hartley, *loc. cit.*).

$$\Lambda_c = 130{\cdot}04 - 61{\cdot}26C^{0{\cdot}452}$$ (Ferguson and Vogel, *Phil. Mag.*, 1925, **50**, 971).

The first equation is applicable only up to a concentration of about 0·002*N*, while the latter can be used for the range 0·0001—0·01*N*. Both equations led to practically the same values for the cell constants.

For the preparation of the 0·01 *D* solution, a suitable amount of potassium chloride was weighed out into a litre flask and the calculated amount of conductivity water added. The values of the constants obtained by both methods agreed well (within 0·1%). The constant of the small bottle cell was determined by intercomparison with another cell of known constant, both cells being filled with a dilute solution of potassium chloride. Eight different cells of the Hartley–Barrett type were used in the course of the work; the cell constants varied between 0·25 and 0·34. The constant of the small cell was 0·01579 at 18°.

Purification of Hydrogen Cyanide.—The starting material for the preparation of the pure anhydrous solvent was the crude liquid manufactured for fumigation purposes. The purification at first consisted in repeated fractional distillation over phosphoric oxide (free from lower oxides), a 3′ column of the point type being used. The distillate was collected in a 2-litre flask, protected from the atmosphere, from which it could be pumped. The large middle fraction was collected each time, and finally a liquid was obtained of b. p. 25·7°/760 mm. and f. p. — 13·35°. Coates, Hinkel, and Angel (J., 1928, 540) found b. p. 25·7°/760 mm., and Coates and Hartshorne (J., 1931, 657) found f. p. — 13·3°. The addition of phosphoric oxide to the pure anhydrous acid, thus obtained, caused no apparent change; the oxide gradually settled out in a powdery form, leaving a perfectly colourless liquid.

The specific conductivity of the distillate so obtained was never much below 5×10^{-7} mho at 18°. Fractionation was carried out with surface evaporation only and no ebullition; a good reflux ratio was maintained, and the rate of distillation was about 1 drop per sec. The residue from the evaporation of about 100 c.c. was minute, but it gave the molybdate test for phosphate. It may be noted that Walden and Birr (*Z. physikal. Chem.*, 1929, **154**, *A*, 273) made similar observations in the case of acetonitrile. However, fractionation of the solvent, as obtained above, without any addition gave a distillate of much lower conductivity. The lowest value recorded was $1{\cdot}6 \times 10^{-7}$ mho. Finally, except for the preliminary purification of the crude liquid, the use of phosphoric oxide was abandoned, and anhydrous magnesium perchlorate was successfully used as a dehydrating agent. Solvent of low specific conductivity was always obtained; in one instance it was as low as $0{\cdot}9 \times 10^{-7}$ mho. Values of the specific conductivity ($\times 10^7$) of hydrogen cyanide reported by other workers (all at 0°) are : 52 (Centnerszwer, *loc. cit.*); 50 (Kahlenberg and Schlundt, *loc. cit.*); 100 (Gomberg and Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1810); 4·5 (Bredig, *Z. angew. Chem.*, 1923, **36**, 456); 6·0 (Fredenhagen and Dahmlos, *loc. cit.*). The solvent was recovered unchanged from the salt solutions by fractionation, and a further fractionation over magnesium perchlorate yielded the pure anhydrous acid ready for new conductivity measurements.

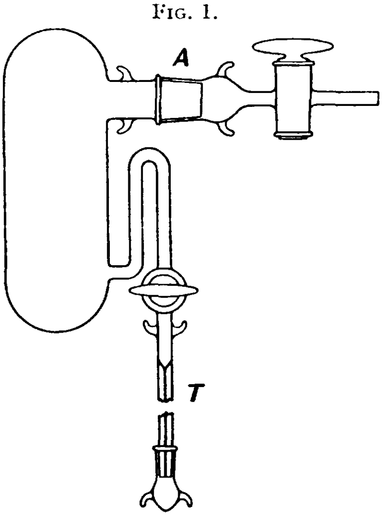
Density and Viscosity.—With a pyknometer of about 50 c.c. capacity, hydrogen cyanide was found to have $d_{4°}^{18°}$ $0{\cdot}6899_8$, in agreement with a value of $0{\cdot}6900_4$ found by Coates and Hartshorne (*loc. cit.*). The densities of approximately 0·02*N*-solutions of lithium and sodium iodides indicated negligible electrostriction, even at this high concentration. The density of all solutions may therefore be taken as equal to that of the pure solvent.

Fredenhagen and Dahmlos (*loc. cit.*) determined the viscosity η of hydrogen cyanide over a wide range of temperature, and interpolation of their η–T plot gave a value of 0·00206 at 18°. Some unpublished work in this laboratory had indicated a much lower value. An accurate determination of this constant was therefore made at 18°. A quartz viscometer similar to that described by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737) was used. The hydrogen cyanide was never allowed to come into contact with the atmosphere. Its time of flow was about 128 secs., and the stop-clock could be read to 0·2 sec. Two independent determinations agreed, giving a value of 0·001986 C.G.S. unit for the viscosity of hydrogen cyanide at 18·00° (± 0·02°), that of water being taken as 0·01056 (I.C.T., 1929, **5**, 10).

Preparation of the Salt Solutions.—The salt solutions were made up according to the weight dilution method (Whetham, *Phil. Trans.*, 1900, **194**, 321) as used in the cell-constant measurements, special precautions being taken to avoid inaccuracy due to the high volatility of hydrogen cyanide.

The stock solutions were made by weighing out a suitable quantity of the salt (0·1—0·3 g.) into a special weight pipette and adding hydrogen cyanide. The weight pipette, of the form shown in Fig. 1, was made of Pyrex glass and had a capacity of about 100 c.c. The taps and joints were finely ground and lubricated with vaselin which had been extracted repeatedly with boiling water and subsequently with hydrogen cyanide. The introduction of deliquescent and hygroscopic salts into the pipettes involved the following procedure. The carefully dried salt was finely powdered in an agate mortar, a suitable weight quickly transferred to a small Pyrex-glass weighing bottle (fitted with a ground-glass cap) and the process of drying repeated. After cooling, the cap was quickly replaced and the whole weighed. The salt was then tipped into the weighed pipette through the tube *A* (in all transferences into the weight pipette and the cell, contact with the air was prevented by means of a stream of pure dry nitrogen). Hydrogen cyanide was pumped over into the pipette from the stock flask by means of a pressure of dry nitrogen. Both the cap of the weighing bottle and that of the pipette were replaced as quickly as possible after each operation, and in each case the whole was weighed. Hydrogen cyanide was also pumped into the tared cell and the whole weighed. After the conductivity of the pure solvent had been measured, the cell was removed from the thermostat and placed in ice-cold transformer oil until the internal pressure was a little less than atmospheric, as shown by a small capillary manometer, attached to the side arm of the cell. An addition of the stock salt solution was then made from the pipette while a slow stream of pure dry nitrogen, saturated with hydrogen cyanide vapour, was passed through the cell. The long capillary tube (*T*) of the pipette was inserted into the cell, and the required quantity of salt solution pumped in. This operation, the incidental removal and subsequent replacement of caps, and the movements of the various stopcocks were made rapidly so as to reduce to a minimum errors due to evaporation and atmospheric contamination. About 4 or 5 additions were made in each run. Not less than about 10 g. of solution were added each time. Experiment showed that the above procedure was successful in avoiding any appreciable loss due to evaporation. The gain in weight of the cell was found to be practically equal (within 0·1%) to the loss in weight of the pipette after 5 additions.

FIG. 1.



For each salt at least two independent runs were carried out, different cells and different samples of the solvent being used, and also samples of the salt obtained by different methods. In the latter case different solvents were used in the recrystallisation, or the samples of salt were obtained by different numbers of recrystallisations from the same solvent. In this way the absolute accuracy of the measurements was ensured.

Calibration.—All weights and thermometers were calibrated against those bearing N.P.L. certificates. All glass apparatus used in the volumetric analysis was calibrated in the usual way.

Purification of the Salts.—All materials used were of the purest quality obtainable.

Lithium Salts.—Lithium carbonate was extracted several times with boiling water to remove traces of other alkali-metal carbonates and then used in the preparation of the chloride, bromide, iodide, and nitrate by neutralisation with the corresponding acids. Lithium chloride was recrystallised from hydrochloric acid in an atmosphere of pure hydrogen chloride. The bromide, iodide, and nitrate were recrystallised from water in the usual way. In all recrystallisations, the crystals were freed from adhering mother-liquor by suction on glass filter discs. Except for the iodide, dehydration was carried out by heating in a vacuum to 110—120° over phosphoric oxide. The crystals of the iodide (slightly tinged with iodine) were allowed to stand in a vacuum over phosphoric oxide for several days. The partially dehydrated compound was then recrystallised from acetone and finally dried by heating in a vacuum over phosphoric oxide, the temperature being raised very gradually to 80°. The samples were greyish, but caused no darkening of the hydrogen cyanide solutions, even on standing for a week. This latter fact is a sure proof of the absence of even a trace of free alkali in the anhydrous product. Lithium perchlorate was recrystallised from water and dehydrated in a vacuum at 140—150° over phosphoric oxide. Lithium thiocyanate was purified by allowing an aqueous solution to crystallise in a vacuum over phosphoric oxide at room temperature. Dehydration was carried out in a vacuum at 80° over phosphoric oxide, and for another sample, in a stream of pure dry nitrogen at 110°.

Sodium salts. The bromide, iodide, nitrate, and perchlorate were recrystallised from water and dried in a vacuum over phosphoric oxide at 100—110°. Another specimen of the bromide was obtained by recrystallisation from hydrobromic acid solution and dried at 130° in an air-oven. Sodium thiocyanate was recrystallised from methyl alcohol and also from methyl alcohol–acetone. It was dried as in the case of the lithium salt. Sodium picrate was obtained by neutralising sodium hydroxide with recrystallised picric acid. The salt was recrystallised from ethyl alcohol and dried in a vacuum over phosphoric oxide at 80°.

Potassium salts. The chloride, bromide, iodide, nitrate, and perchlorate were recrystallised from aqueous solution and dried in a vacuum over phosphoric oxide at 100°. Other samples were dried at 120° in an air-oven. The thiocyanate was recrystallised from ethyl alcohol and dried as in the case of the lithium and sodium salts.

Lithium chloride.

$$\Lambda_c = 345{\cdot}4 - 335\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·66	0·01021	341·9	−0·1
	0·01545	340·5	+0·3
	0·02136	338·4	+0·2
	0·02794	336·2	+0·1
1·86	0·01061	341·8	±0·0
	0·01793	339·4	±0·0
	0·02494	337·0	±0·0
	0·02995	335·0	−0·4
	0·03503	332·9	−0·8
2·93	0·01700	339·7	±0·0
	0·03514	332·3	−1·3
	0·04234	329·4	−1·8
	0·04758	327·1	−2·7

Lithium bromide.

$$\Lambda_c = 346{\cdot}9 - 270\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
1·96	0·01188	343·0	−0·7
	0·02102	341·0	−0·2
	0·02902	339·0	±0·0
	0·03382	337·8	±0·0
	0·03738	337·0	+0·2
	0·04038	336·3	+0·3
2·52	0·006748	344·9	−0·2
2·7	0·01054	344·2	+0·2
1·69	0·01336	343·3	±0·0
	0·02156	341·0	±0·0
	0·02823	339·3	±0·0
	0·03150	338·3	−0·1
	0·03531	337·0	−0·3
	0·03993	335·7	−0·4
	0·04407	334·9	−0·1

Lithium iodide.

$$\Lambda_c = 348{\cdot}0 - 258\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·52	0·01199	344·8	±0·0
	0·01812	343·2	±0·0
	0·02283	342·1	+0·1
	0·02748	341·0	+0·2
	0·03416	339·8	+0·7
2·63	0·01831	342·5	−0·7
	0·02551	341·0	−0·3
3·07	0·02693	341·0	+0·1
	0·03522	338·6	−0·2
	0·04200	337·0	−0·1
	0·04666	335·9	+0·0

Lithium nitrate.

$$\Lambda_c = 336{\cdot}6 - 402\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·16	0·008410	332·5	−0·7
	0·01578	330·0	±0·0
	0·02204	327·9	+0·4
	0·02641	325·8	+0·1
	0·03098	323·8	±0·0
1·91	0·01459	330·2	−0·4
	0·02499	325·8	−0·4
1·7	0·01127	332·4	+0·4
	0·01899	329·6	+0·9
	0·02861	325·1	+0·3
	0·03470	321·9	−0·3
	0·03928	318·8	−2·0

Lithium perchlorate.

$$\Lambda_c = 336{\cdot}9 - 230\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
3·33	0·01251	333·9	−0·1
	0·01923	332·1	−0·3
	0·02395	331·1	−0·3
	0·02820	330·4	±0·0
	0·03266	329·4	±0·0
3·43	0·01404	334·0	+0·3
	0·02014	332·4	+0·2
	0·02787	330·6	+0·1
	0·03327	329·3	±0·0
	0·03881	327·8	−0·2

Lithium thiocyanate.

$$\Lambda_c = 340{\cdot}6 - 400\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·55	0·01422	335·2	—
	0·02208	331·2	—
	0·02883	327·6	—
	0·03526	322·8	—
	0·04036	319·3	—
3·77	0·01334	336·7	—
	0·01954	333·5	—
	0·02511	330·1	
	0·02968	327·2	—
	0·03301	324·8	
1·88	0·007169	338·8	—
	0·01017	337·5	—
	0·01349	336·7	—
	0·01728	334·9	—
	0·02061	333·6	—

Sodium bromide.

$$\Lambda_c = 343{\cdot}8 - 243\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
8·9	0·01969	337·9	−1·2
	0·03210	335·5	−0·5
	0·04156	333·4	−0·3
	0·04890	331·7	−0·2
	0·05441	330·3	−0·2
3·06	0·01251	341·4	−0·4
	0·02216	338·7	+0·2
	0·02671	337·3	±0·0
	0·03401	335·8	+0·2
	0·04005	334·5	+0·4
	0·04571	332·6	−0·1
5·8	0·01171	340·8	−0·2
	0·01918	339·4	+0·2
	0·02267	338·6	+0·3

Sodium iodide.

$$\Lambda_c = 344{\cdot}9 - 238\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
8·35	0·02074	339·4	−0·6
	0·02965	337·7	−0·2
	0·04168	334·7	−0·4
	0·05128	332·5	−0·3
	0·05839	330·9	−0·4
8·45	0·01321	341·3	−0·5
	0·01999	339·8	−0·4
11·4	0·01415	341·8	+0·3
	0·02462	339·2	+0·1
	0·03159	337·7	+0·3
	0·03787	336·3	+0·4
	0·04225	335·2	+0·2
	0·04547	334·3	+0·1
2·28	0·01512	341·3	±0·0

Sodium nitrate.

$$\Lambda_c = 333{\cdot}8 - 250\sqrt{C}.$$

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
4·13	0·02352	327·5	−0·4
	0·03803	323·2	−1·1
	0·05248	318·6	−2·4
9·3	0·02488	327·6	+0·1
	0·03335	325·4	±0·0
	0·04265	322·2	−0·9
	0·04901	319·8	−1·8
2·43	0·008638	330·0	−1·7
	0·01442	329·9	−0·3
	0·01674	329·6	±0·0
3·27	0·02860	326·5	−0·1
	0·04106	322·6	−0·9
	0·05589	317·2	−3·2
2·76	0·01360	330·5	+0·1
	0·02109	328·9	+0·3
	0·02658	327·4	+0·3
	0·03001	326·7	+0·4

Sodium perchlorate.

$\Lambda_c = 335{\cdot}5 - 235\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
1·98	0·01600	331·1	−0·6
	0·02368	329·4	−0·6
	0·02848	328·9	+0·1
	0·03489	327·2	−0·1
1·5	0·02118	330·6	+0·1
	0·03307	327·7	±0·0
	0·03745	326·7	±0·0
	0·04301	325·4	±0·0
1·92	0·01445	332·3	+0·2
	0·02228	330·2	−0·1
	0·02887	329·0	+0·3
	0·03230	327·9	±0·0
	0·03651	326·9	±0·0

Sodium thiocyanate.

$\Lambda_c = 337{\cdot}7 - 230\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
1·97	0·01750	333·4	−0·2
	0·02790	330·9	−0·3
3·36	0·01861	333·4	±0·0
	0·02446	332·4	+0·3
	0·03077	330·9	+0·3
	0·03877	329·1	+0·3
	0·04515	327·2	−0·1
2·56	0·01535	333·9	−0·2
	0·02966	330·6	−0·3
	0·04434	327·4	−0·2
2·12	0·008874	335·3	−0·3
	0·01268	335·2	+0·4

Sodium picrate.

$\Lambda_c = 266{\cdot}9 - 195\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·18	0·01496	264·2	+0·2
	0·02404	262·3	+0·1
	0·03037	261·2	+0·2
	0·03530	260·1	±0·0
4·23	0·01101	264·5	−0·3
	0·01939	263·2	±0·0
	0·02828	261·5	+0·1
	0·03497	260·1	±0·0
	0·03987	258·9	−0·3

Potassium chloride.

$\Lambda_c = 363{\cdot}4 - 280\sqrt{C}$.

5·6	0·02186	356·3	−0·9
	0·04004	351·8	−0·4
	0·05099	349·0	−0·2
	0·05926	346·9	±0·0
6·6	0·01980	357·6	−0·2
	0·03022	354·7	−0·2
	0·03743	352·9	±0·0
	0·04541	351·0	+0·3
	0·05254	349·0	+0·2
3·16	0·02146	357·1	−0·2
	0·03410	354·3	+0·4
3·53	0·01003	360·6	±0·0
	0·01423	359·6	+0·2
3·7	0·01035	360·3	−0·2
	0·01655	358·7	±0·0

Potassium bromide.

$\Lambda_c = 363{\cdot}2 - 248\sqrt{C}$.

5·03	0·01699	358·8	−0·2
	0·03258	355·0	−0·1
	0·04395	352·2	−0·2
	0·05121	350·6	±0·0
	0·05907	348·5	−0·2
10·2	0·01385	359·5	−0·2
	0·02484	357·2	+0·2
	0·03150	355·5	+0·1
	0·04022	353·4	+0·2
	0·04592	352·0	+0·1

Potassium iodide.

$\Lambda_c = 363{\cdot}9 - 235\sqrt{C}$.

5·96	0·01886	359·5	±0·0
	0·03371	356·0	±0·0
	0·04491	353·2	−0·2
	0·05489	351·0	±0·0
	0·05924	349·9	±0·0
9·74	0·01179	360·9	−0·2
	0·02638	357·7	±0·0
	0·03332	356·1	±0·0
	0·03979	354·6	±0·0
	0·04529	353·4	+0·2

Potassium nitrate.

$\Lambda_c = 353{\cdot}9 - 253\sqrt{C}$.

13·0	0·02287	347·0	−1·1
	0·03080	345·7	−0·4
	0·03823	344·2	±0·0
	0·04216	343·4	+0·2
9·35	0·02197	348·1	−0·2
	0·02788	346·8	±0·0
	0·03457	345·0	−0·1
	0·03800	344·8	±0·0
10·3	0·02144	347·9	−0·6
	0·03406	345·4	+0·1
	0·04410	342·6	−0·1
	0·05252	340·3	−0·3
	0·05736	339·1	−0·2
2·9	0·007020	351·7	−0·4
	0·009484	351·6	+0·1
	0·01233	350·9	+0·1
	0·01498	350·3	+0·2

Potassium perchlorate.

$\Lambda_c = 355{\cdot}3 - 275\sqrt{C}$.

3·5	0·01201	352·1	+0·1
	0·01925	350·0	±0·0
	0·02373	349·0	+0·2
3·4	0·02077	349·3	−0·2
	0·02784	347·4	−0·2
	0·03580	345·2	−0·2
	0·04225	343·8	+0·1

Potassium thiocyanate.

$\Lambda_c = 358{\cdot}0 - 243\sqrt{C}$.

3·36	0·01295	354·6	−0·3
	0·01872	353·5	±0·0
	0·02505	352·2	+0·2
	0·03054	351·1	−0·1
	0·03533	349·5	+0·1
2·88	0·02142	352·6	−0·2
	0·03061	350·5	+0·5
	0·03983	348·1	−0·2
	0·04815	346·1	−0·2

Tetraethylammonium picrate.

$\Lambda_c = 282{\cdot}3 - 215\sqrt{C}$.

3·16	0·01372	279·7	+0·4
	0·02122	277·7	±0·0
	0·03283	275·2	±0·0
	0·03801	274·3	+0·2
	0·04421	272·9	+0·1
2·63	0·01470	278·6	−0·5
	0·02179	277·1	−0·4
	0·02669	276·3	−0·2
	0·03325	274·9	−0·2
4·62	0·01080	279·6	−0·4
	0·01858	278·4	+0·1
	0·02436	277·2	+0·2
	0·02685	276·8	+0·3

Rubidium chloride.

$\Lambda_c = 363{\cdot}2 - 195\sqrt{C}$.

2·88	0·01372	360·2	−0·2
	0·02512	357·8	−0·3
	0·03477	356·3	±0·0
	0·04178	354·8	−0·1
1·61	0·01238	360·9	+0·2
	0·02219	358·9	+0·1
	0·03123	357·5	+0·5
	0·04225	355·0	+0·2

Cæsium chloride.

$\Lambda_c = 368{\cdot}2 - 200\sqrt{C}$.

1·41	0·01547	365·0	−0·1
	0·02622	362·8	−0·2
	0·03485	361·1	−0·1
	0·04316	359·7	+0·2
3·09	0·01900	364·7	+0·3
	0·02748	362·8	+0·1
	0·03570	361·1	±0·0
	0·04150	360·0	+0·1
	0·04594	359·0	±0·0

Rubidium chloride was recrystallised from methyl alcohol and precipitated once from aqueous solution by ethyl alcohol. Another sample was obtained from rubidium carbonate and hydrochloric acid and recrystallised in the same way. Drying was effected at 120° in air. Cæsium chloride was recrystallised from methyl alcohol and dried at 120° in air.

Tetraethylammonium picrate was prepared from the hydroxide. An aqueous solution of the latter was prepared from tetraethylammonium iodide. The latter salt was purified by recrystallisation from methyl alcohol–acetone and from ethyl alcohol. An aqueous solution of the purified iodide was shaken for 3 hours at 40—50° with excess of carefully washed silver oxide. The filtrate was neutralised with picric acid, the resulting salt recrystallised several times from conductivity water, and dried in an air-oven at 110° or in a vacuum over phosphoric oxide at 80°. All the specimens prepared had m. p. 260·5° (± 0·5°); Walden (*Z. physikal. Chem.*, 1929, **144**, *A*, 269) found 255·8°.

Analysis of the Salts.—The halides and thiocyanates were analysed gravimetrically by precipitation of the corresponding silver salts, or volumetrically by Volhard's method. No salt was used unless the experimentally found percentage of halide or thiocyanate agreed with the calculated value within 0·1%.

Results.—The tables, pp. 1249—1250, give the equivalent conductivities (Λ_c) and the square root of the concentrations ($\sqrt{C}$) for the salts examined. The concentrations are calculated in g.-equivs. per 1000 c.c. of solution in a vacuum at 18°. In each case, the conductivity of the pure solvent (κ) was subtracted from the observed conductivity of the solution, to obtain the true conductivity of the electrolyte. The value of $\kappa \times 10^7$ for each run is given. The equation relating equivalent conductivity and the square root of the concentration, for each salt, obtained from the best curve drawn through the experimental points, is also given. Deviations (D) of the actual values from these curves are given in the last column.

In the graphical representation of the results (Figs. 2*a*—2*d*) equivalent conductivity is plotted against the square root of the concentration.

DISCUSSION.

Λ_0 *Values.*—These were obtained by extrapolation of the Λ_c–$\sqrt{C}$ plots to zero concentration. The values of Λ_0 (Table I) show that the law of the independent mobility of ions is obeyed.

TABLE I.

	Cl′.	Br′.	I′.	NO_3′.	ClO_4′.	CNS′.	Pic.′.
Li˙	345·4	346·9	348·0	336·7	336·9	341·4	—
Diff.	—	*3·1*	*3·1*	*2·9*	*1·4*	*3·7*	—
Na˙	— *	343·8	344·9	333·8	335·5	337·7	266·9
Diff.	—	*19·4*	*19·0*	*20·1*	*19·8*	*19·7*	—
K˙	363·4	363·2	363·9	353·9	355·3	358·0	—

$\Lambda_{0\,RbCl} = 363{\cdot}2$; $\Lambda_{0CsCl} = 368{\cdot}2$; $\Lambda_{0NEt_4Pic.} = 282{\cdot}3$.

* Sodium chloride could not be included owing to its low solubility.

Walden's Rule and Ionic Mobilities.—If the motion of any ion obeys Stokes's law, then for any given salt the product of Λ_0 and the viscosity of the solvent (η) should be constant, independent of solvent and temperature. The recent measurements of Walden and others have shown that there is only a rough parallelism between conductivity and viscosity. Except for certain salts containing large organic ions, the product $\Lambda_0\eta$ varies from solvent to solvent and is not independent of temperature. For these large ions Stokes's law must be applicable. A survey of the data for tetraethylammonium picrate in a number of non-aqueous solvents at different temperatures shows that $\Lambda_0\eta$ is reasonably constant and is close to a mean value of 0·563 (Walden and Birr, *Z. physikal. Chem.*, 1931, **153**, *A*, 1). Ekwall (*ibid.*, 1933, **163**, *A*, 442) found that for aqueous solutions of this salt at three different temperatures, the mean value of $\Lambda_0\eta$ is 0·560. In hydrogen cyanide at 18°, this salt gives $\Lambda_0\eta = 0{\cdot}561$ and thus yet another solvent is added to those in which Stokes's law is apparently obeyed by these large organic ions.

As yet, no transport-number measurements have been made in hydrogen cyanide, so that direct calculation of the ionic mobilities is not possible. However, by the application of the law of the independent mobility of ions and Stokes's law, fairly accurate values of the mobilities can be found from the relation $l_{0(\text{Pic.})}\eta = 0{\cdot}267$, where $l_{0(\text{Pic.})}$ = mobility of the

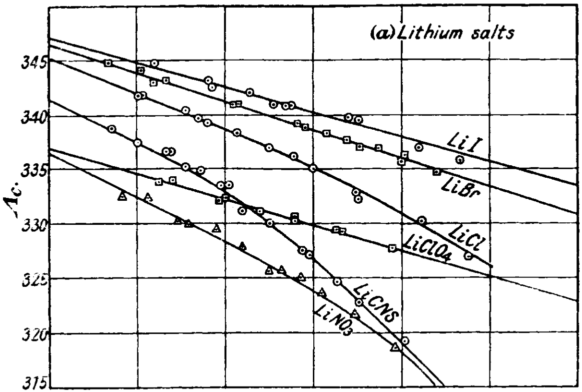


FIG. 2*a*.

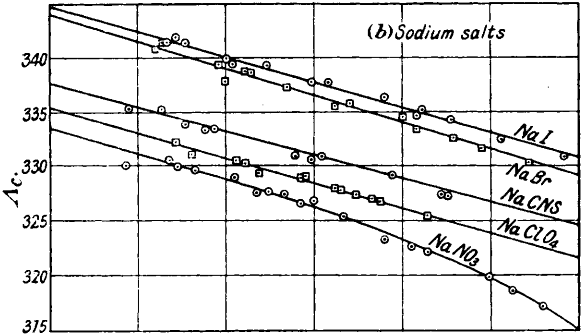


FIG. 2*b*.

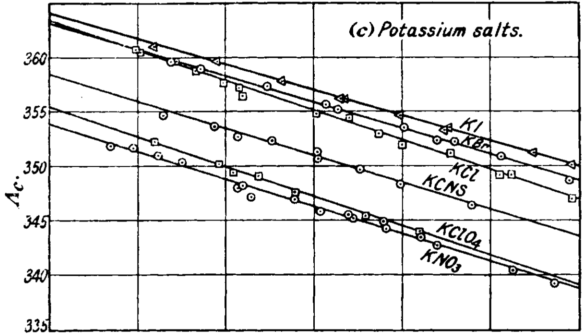


FIG. 2*c*.

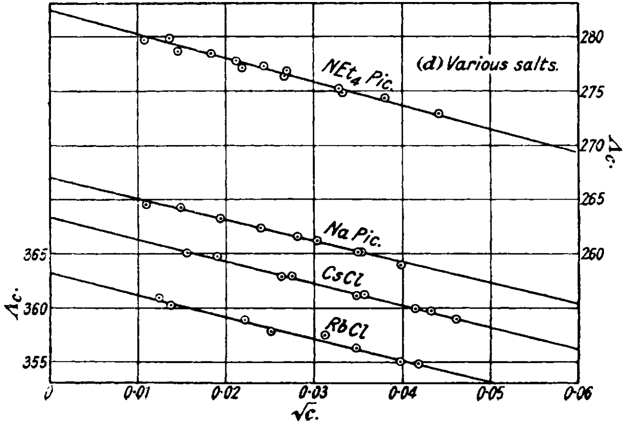


FIG. 2*d*.

picrate ion. Experimental evidence of the validity of this relation for a large number of solvents has been obtained by Walden and his co-workers (*Z. physikal. Chem.*, 1923, **106**, *A*, 89; **107**, *A*, 220; 1929, **140**, *A*, 119; 1931, **153**, *A*, 1). Table II gives the values of the ionic mobilities in hydrogen cyanide based on the calculated value of 134·5 for the picrate ion. For comparison, the values in water at 18° are given in parentheses.

TABLE II.

$Li^{\cdot}$	135·5 (33)	$Rb^{\cdot}$	153·2 (67)	Cl'	210·0 (65)	NO_3'	201·4 (62)
$Na^{\cdot}$	132·4 (43)	$Cs^{\cdot}$	158·2 (68)	Br'	211·4 (67)	ClO_4'	203·4 (56)
$K^{\cdot}$	151·4 (64)	$NEt_4^{\cdot}$	144·5 (28)	I'	212·5 (67)	CNS'	205·3 (57)

The mobilities are very high compared with those in other solvents, as would be expected from the low viscosity of hydrogen cyanide (about one-fifth of that of water).

The order of increasing mobilities for the alkali-metal ions is different from that in any solvent yet investigated. It is $Na^{\cdot} < Li^{\cdot} < K^{\cdot} < Rb^{\cdot} < Cs^{\cdot}$. The lithium ion is slightly faster than the sodium ion. In all other solvents the order is $Li^{\cdot} < Na^{\cdot} < K^{\cdot} < Rb^{\cdot} < Cs^{\cdot}$. Considering the ionic radii, the mobilities would be expected to increase in the inverse order. The usual explanation is that the relative solvation of the ions is in accordance with Fajans's theory (Fajans and Joos, *Z. Physik*, 1924, **23**, 1), and the size of the solvated complex, which is inversely proportional to the mobility, decreases in the order Li > Na > K > Rb > Cs. For hydrogen cyanide, therefore, it appears that the increase in solvation as we go from sodium to lithium is not large enough to compensate for the decrease in ionic radius. The solvated complex containing the sodium ion will be larger than that containing the lithium ion and hence will have the lower mobility. Evidence that, in spite of its higher dipole moment, hydrogen cyanide does not solvate these inorganic ions so readily as does water, has also been adduced from the examination of solid–liquid equilibria for inorganic salts in hydrogen cyanide in this laboratory (unpublished). The number of solid solvates found is small.

Except for the picrate ion the anion mobilities are very little different from each other. As in aqueous solution and in contrast to the general order in non-aqueous solutions, the mobilities of the polyatomic anions are less than those of the monatomic anions, as would be expected from the greater size of the former.

Practically all the accurate conductivity measurements in non-aqueous solvents have been carried out at 25°, so that no direct comparison of the ionic mobilities in hydrogen cyanide with those in other solvents will be made. Instead, the values of $l_0\eta$ for each ion will be compared. In Table III comparison is made with the other nitrilic solvents, acetonitrile (Walden and Birr, *Z. physikal. Chem.*, 1929, **144**, *A*, 269), benzonitrile (Martin, J., 1928, 3270), ethyl cyanoacetate and *o*-toluonitrile (Philip and Rangaramanujam, J., 1932, 1512). Table III shows that the constancy of the $l_0\eta$ value for a given ion is best for ions of large atomic volume; further, cations give a greater degree of constancy than anions. In Table IV, $l_0\eta$ values for various ions in hydrogen cyanide, water (Davies, "Conductivity of Solutions," 1933, 205), methyl alcohol (Frazer and Hartley, *loc. cit.*), and pyridine (Walden, Audrieth, and Birr, *Z. physikal. Chem.*, 1932, **160**, *A*, 337) are compared.

TABLE III.

	$Li^{\cdot}$.	$Na^{\cdot}$.	$K^{\cdot}$.	$NEt_4^{\cdot}$.	Cl'.	Br'.	I'.	NO_3'.	ClO_4'.
HCN	0·28	0·27	0·31	0·294	0·41	0·41	0·42	0·40	0·40
$CH_3{\cdot}CN$	0·21	0·24	0·30	0·296	0·31	0·33	0·35	0·36	0·36
$C_6H_5{\cdot}CN$	0·22	0·23	0·28	0·308	—	0·23	0·36	—	—
$CH_2(CN){\cdot}CO_2Et$	0·15	0·24	0·28	0·294	—	0·33	0·35	—	—
o-$C_6H_4Me{\cdot}CN$	0·12	0·24	0·28	0·288	—	0·32	0·36	—	—

TABLE IV.

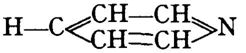
	$Li^{\cdot}$.	Na .	$K^{\cdot}$.	$Rb^{\cdot}$.	$Cs^{\cdot}$.	$NEt_4^{\cdot}$.	Cl'.	Br'.	I'.	ClO_4'.
H_2O (18°)	0·35	0·46	0·68	0·71	0·72	0·298	0·69	0·71	0·71	0·59
$CH_3{\cdot}OH$	0·22	0·26	0·30	0·31	0·34	0·296	0·29	0·30	0·33	0·39
HCN (18°)	0·28	0·27	0·31	0·31	0·32	0·294	0·41	0·41	0·42	0·40
C_5H_5N	0·16	0·21	0·24	—	—	0·34	0·41	0·43	0·42	0·42

As for other non-aqueous solvents, the $l_0\eta$ values for hydrogen cyanide are roughly half those in water. The agreement between the values for hydrogen cyanide and methyl alcohol is good, except for the lithium and halogen ions, while the values for the anions in pyridine are in good agreement with those for hydrogen cyanide.

Regarding the effect of the solvent on the mobility of an ion there are two main views. The solvation theory considers each ion to be associated with a definite number of solvent molecules and Stokes's law may be applied to the solvated complex. The molecular volume of the solvent is an important factor in determining the effective size of the ion. A greater constancy of $l_0\eta$ is to be expected for cations of large atomic volume, since these will be relatively unsolvated in all solvents. Table III shows this clearly in the case of nitriles. Regarding the agreement of the $l_0\eta$ values in methyl alcohol and hydrogen cyanide, it is noteworthy that their molecular volumes are nearly the same.

Born (*Z. Physik*, 1920, **1**, 221; see also Schmick, *ibid.*, 1924, **24**, 56) takes the view that the resistance to the motion of an ion is due, in part, to the bulk viscosity of the solvent, and in part to a dipole interaction between the ions and the solvent molecules. Deviations from Stokes's law for the small inorganic ions are assumed to be due to this electrical interaction, the effect of which is greater the smaller the ion. For sufficiently large ions, the effect will be relatively small and $l_0\eta$ for a given ion will be constant, independent of solvent and temperature. Tables III and IV support this view. In the nitrilic solvents it is for the cations that $l_0\eta$ gives the greater degree of constancy. Here the —C≡N group is oriented towards the cation and it may be expected that any electrical interactions would be fairly similar for the different solvents. The —C≡N group is oriented away from the anions and the replacement of an alkyl or aryl group by a hydrogen atom might well be expected to alter the electrical interaction in the neighbourhood of the ion, to an apppreciable extent. The agreement of the $l_0\eta$ values in hydrogen cyanide and pyridine may be due to the somewhat similar structures (I) and (II). In each case the group oriented towards the anions is H—C≡ and the interaction between anions and solvent molecules may thus be similar in each solvent. At first sight it might appear that the cation mobilities should exhibit a similar constancy in both solvents. However, there is a difference in the electrical nature of the nitrogen atoms in the two molecules, and it is these which are in close proximity to the cations. In hydrogen cyanide, the lone pair of electrons on the nitrogen atom is subject to an attraction towards the centre of the molecule (*Ann. Reports*, 1928, **25**, 139), while in pyridine the " aromatic sextet " (*ibid.*, p. 120) is complete without calling on the lone pair.

(I.) H—C≡N


(II.)

The Debye–Hückel–Onsager Equation.—The majority of the salts obey the Kohlrausch empirical equation, $\Lambda_c = \Lambda_0 - x\sqrt{C}$ over the whole concentration range studied. According to the Debye–Hückel–Onsager theory, for uni-univalent salts

$$x = \left[\frac{5{\cdot}776 \times 10^5}{(\varepsilon T)^{\frac{3}{2}}}\Lambda_0 + \frac{58{\cdot}0}{(\varepsilon T)^{\frac{1}{2}}\eta}\right]\sqrt{2}$$

where ε and η are the dielectric constant and viscosity of the solvent, respectively, at the temperature T. For hydrogen cyanide at 18°, $\varepsilon = 119$ (Fredenhagen and Dahmlos, *loc. cit.*) and $\eta = 0{\cdot}001986$, hence

$$\Lambda_c = \Lambda_0 - (0{\cdot}127\ \Lambda_0 + 222)\sqrt{C}$$

Table V gives the percentage deviation $100\ (x_{\text{exp.}} - x_{\text{theo.}})/x_{\text{theo.}}$ for each salt.

TABLE V.

	Li.	Na.	K.
Chloride	+26		+ 4
Bromide	+ 2	− 8	− 7
Iodide	− 3	−10	−12
Nitrate	+52	− 5	− 5
Perchlorate	−13	−11	+ 3
Thiocyanate	+52	−13	− 9

Sodium picrate	−23
Tetraethylammonium picrate	−17
Rubidium chloride	−27
Cæsium chloride	−31

Except for a few cases (which will be considered later) there is good agreement between theory and experiment. The Debye–Milner electrostatic picture of ionic solution is thus applicable to electrolyte solutions in hydrogen cyanide, which, contrary to the opinion of Fredenhagen, is a powerful dissociating medium for the salts investigated. That hydrogen cyanide obeys the Nernst–Thomson rule may be seen clearly by comparing (Table VI) the conductivity ratios for tetraethylammonium picrate with those in other solvents (cf. Walden, *Z. physikal. Chem.*, 1930, **147**, *A*, 27).

TABLE VI.

Solvent.	ϵ (20°).	Λ_v/Λ_0. v = 1000 l.	Λ_v/Λ_0. v = 10,000 l.	Solvent.	ϵ (20°).	Λ_v/Λ_0. v = 1000 l.	Λ_v/Λ_0. v = 10,000 l.
HCN (18°) ...	116	0·985	0·993	$C_2H_5{\cdot}OH$ ...	25	0·852	0·952
H_2O (18°) ...	81	0·965	0·992	$COMe_2$	21	0·835	0·946
$CH_3{\cdot}OH$	35	0·933	0·978	COMeEt ...	18	0·812	0·943
$CH_3{\cdot}CN$	36	0·928	0·978				

The Λ_c–$\sqrt{C}$ plots for the chloride, nitrate, and thiocyanate of lithium and for sodium nitrate are concave to the concentration axis in the more concentrated regions, but follow a linear relation at the dilute ends of the curves. It is seen that the three lithium salts give values of $x_{\text{exp.}}$ appreciably greater than predicted, although that for sodium nitrate is in good agreement with theory. These deviations may be explained in terms of ionic association. The association tendency of nitrates has been observed in other solvents.

The order of increasing tendency for association with a given anion is seen to be ($Cs^{\cdot}$, $Rb^{\cdot}$, $K^{\cdot}$) $<$ $Na^{\cdot}$ $<$ $Li^{\cdot}$. Electrolytic solvents have been classified roughly as levelling or differentiating (*Ann. Reports*, 1930, **27**, 326). In the former (mainly hydroxylic substances, the molecules of which possess donor and acceptor properties) the association tendency is relatively small, since the ions are stably solvated and their specific chemical affinities suppressed. For a given anion, the association increases as the size of the solvated cation (as deduced from the mobilities) decreases (Bjerrum, *Kgl. Danske Videnskabs. Selsk. Math.-phys. Med.*, 1926, **7**, No. 9), *i.e.*, in the order Li $<$ Na $<$ K $<$ Rb $<$ Cs. In the differentiating solvents, *e.g.*, nitromethane, acetonitrile, the order of increasing ion association is reversed, although the size of the solvated ions is in the same order as in the levelling solvents. This is ascribed to the weaker solvation of both ions, and more particularly that of the anion. The solvent molecule possesses only donor properties and the anions are relatively unsolvated. The association tendency is that expected of the unsolvated ion (Bjerrum, *loc. cit.*), the small lithium ion now showing the greatest association tendency. As already stated, the order of decreasing effective radii, as deduced from the mobilities in hydrogen cyanide, is $Na^{\cdot} > Li^{\cdot} > K^{\cdot} > Rb^{\cdot} > Cs^{\cdot}$. Thus in passing from sodium to lithium we should expect an increase in association tendency whether the bare ion or the solvated complex is considered. However, passing to potassium, it is seen that although there is a decrease in the radius of the solvated ion (as shown by the great mobility), the association tendency decreases. As in the differentiating solvents, the co-ordinating power of the relatively unsolvated anion for the cation, also not strongly solvated, overcomes that of the solvent molecule, and ion-pair formation takes place according to Bjerrum's views. The relative tendencies of the anions to promote ionic association are exhibited clearly only in the case of the lithium salts, and the order is (ClO_4', I′, Picrate′) $<$ Br′ $<$ Cl′ $<$ NO_3' $<$ CNS′. The picrate ion has been included on the basis of measurements carried out with sodium picrate. A general survey of the conductivity measurements in a large number of solvents (*Ann. Reports*, 1930, **27**, 326) has given a very similar order: (ClO_4', I′, Picrate) $<$ (Br′, NO_3') $<$ (Cl′, CNS′).

A notable feature of the results for hydrogen cyanide is the predominance of negative deviations from the theoretical slope. Rubidium and cæsium chlorides show remarkably large negative deviations. Other salts with large ions have been found to exhibit this feature in hydrogen cyanide. They will be dealt with in a later communication. Negative deviations from the theoretical slopes have been found to some extent in water, methyl alcohol, acetonitrile, etc. (Ekwall, *loc. cit.*; *Ann. Reports, loc. cit.*). Whatever their origin, such deviations will be most evident (in dilute solution) in solvents of high dielectric constant, since, when the latter is small, they will be obscured by the positive deviations due to ionic association.

Dissociation Constants.—Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 476; 1935, **57**, 488) have devised an exact method of solving the conductivity equations of incompletely dissociated binary electrolytes and obtaining the true degree of dissociation α, the value of Λ_0, and the dissociation constant K. By applying their method to the case of lithium chloride, nitrate, and thiocyanate in hydrogen cyanide, the following values have been found :

	$\alpha_{0\cdot001N}$.	Λ_0.	K.
Lithium chloride	0·991	345·5	0·11
Lithium nitrate	0·987	336·0	0·07
Lithium thiocyanate	0·979	341·4	0·043

SUMMARY.

(1) Accurate measurements of the conductivities of some uni-univalent salts in pure anhydrous hydrogen cyanide have been made at 18° over the concentration range 0·0001—0·002N.

(2) The density and viscosity of the solvent at 18° have been determined.

(3) The Λ_0 values are in agreement with the law of the independent mobility of ions.

(4) The product $\Lambda_0\eta$ for tetraethylammonium picrate in hydrogen cyanide agrees with the mean value of the product for a large variety of solvents, in accordance with Walden's rule. On the basis of this rule, the ionic mobilities in hydrogen cyanide have been calculated.

(5) Most of the salts obey the Kohlrausch rule $\Lambda_c = \Lambda_0 - x\sqrt{C}$ over the whole concentration range investigated, and the values of x are in good agreement with those calculated by means of the Debye–Hückel–Onsager equation. Large positive deviations from the theory, due to incomplete dissociation, have been found in the case of certain lithium and sodium salts.

(6) Dissociation constants for lithium chloride, nitrate, and thiocyanate have been calculated.

(7) Negative deviations also occur, the origin of which is at present unknown.

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