

1061. *Solutions of Electrolytes in Liquid Ammonia. Part I. The Transference Numbers of Potassium, Sodium, Lithium, and Ammonium Ions in Nitrate Solutions*

By J. B. GILL

Transference numbers of K^+ , Na^+ , Li^+ , and NH_4^+ ions in nitrate solutions in liquid ammonia have been determined at -45° , -55° , and -65° . Ionic mobilities are in the order $K^+ > Na^+ \approx NH_4^+ > Li^+$, but their differences relative to each other are less than in water. The NH_4^+ ion shows no abnormal mobility properties as does the hydronium ion in water. In ammonia it differs from the NH_4^+ ion in water only in its degree of solvation relative to other ions.

NUMEROUS reports of conductance measurements on solutions of salts in liquid ammonia have appeared in the literature. Very little of this work has been carried out at temperatures other than -33° , the boiling point of liquid ammonia. It is the intention in this Paper and in subsequent work to study the variations of transference numbers and conductances of salts in liquid ammonia over a range of temperatures.

A general lack of transference data in non-aqueous solutions^{1,2} has hitherto made it impossible to obtain individual ion conductances and hence information about ionic sizes and solvation properties. The only data available on solutions of electrolytes in liquid ammonia are those of Franklin and Cady³ which, although excellent at their time, only provide results at -34° , and these are of too low an accuracy for satisfactory extrapolation to limiting values.

The most widely accepted method for the measurement of transference numbers is the moving-boundary method. In order to avoid the very great practical difficulties which would be encountered in setting up a sheared boundary in liquid ammonia solutions, an "autogenic" boundary similar to that described by Franklin and Cady has been adopted in this work, but in which solid mercury, acting as the cell anode, was electrolysed into solution. Nitrates have been chosen as the electrolytes on account of the solubility of mercuric nitrate which acts as the indicator in liquid ammonia.

EXPERIMENTAL

The transference cell, shown in Figure 1 (a), consisted of a precision-bore thin-walled Pyrex glass tube A, 10 cm. long and graduated every 0.5 cm., through the lower end of which was sealed a short piece of tungsten wire B. The tube was graduated with two marks at each position so that each mark covered one quarter of the circumference, leaving clear spaces diametrically opposite each other. The tungsten, covered with a pool of mercury C, which, when frozen, served as anode, was soldered to a copper lead which was led from the cell into the glass tube D. The graduated tube A opened into a wider compartment E which contained, as the cathode compartment, a 3-cm. length of 1-cm. diameter glass tube F. The platinum cathode was mounted on a stout platinum wire which entered through the gas inlet. The ground glass joint G which carried the delivery tube was mounted concentrically with the graduated tube so that the thin delivery tube H, shown in Figure 1 (b), could be placed down to the bottom of the graduated tube to enable delivery and removal of liquid. This delivery tube was constructed from a length of thin-walled 2-mm. bore glass tubing drawn out to fit into the graduated tube as a funnel. A flexible vacuum-tight seal was made by a long rubber balloon O; this enabled the delivery tube to be inserted into and removed from the graduated tube without exposure of the contents of the cell to the atmosphere.

The thermostatted bath was an unsilvered Dewar flask containing liquid propane and a few boiling-chips sealed by a large split cork through which the cell, a spirit thermometer, and the

¹ C. A. Kraus, *Ann. New York Acad. Sci.*, 1949, **51**, 789.

² R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, ch. 7.

³ E. C. Franklin and H. P. Cady, *J. Amer. Chem. Soc.*, 1904, **26**, 499.

gas outlet tube were fitted. Finally, the whole cork surface and fittings were sealed with Picene wax. A rubber band P about 5 cm. wide was fitted over the edges of the cork and the top few cm. of the Dewar flask. With this arrangement a fairly good vacuum could be maintained for a prolonged period. Constant temperatures to better than $\pm 0.1^\circ$ were maintained by boiling the propane under fixed reduced pressures controlled to ± 1 mm. Hg by a manostat. Temperatures were read with the spirit thermometer S which was previously calibrated against a thermocouple which could be read to better than 0.05° .

Standard solutions were prepared in the arrangement shown in Figure 1 (c). The evacuated flask L containing the weighed solid was placed in an acetone–solid carbon dioxide mixture at -55° in an unsilvered Dewar flask. With the tap J closed, ammonia gas entered through the three-way stopcock K by way of the vessel M and condensed until the solution had reached the level of the graduations N in the neck of the flask. The bubbling of gaseous ammonia into the

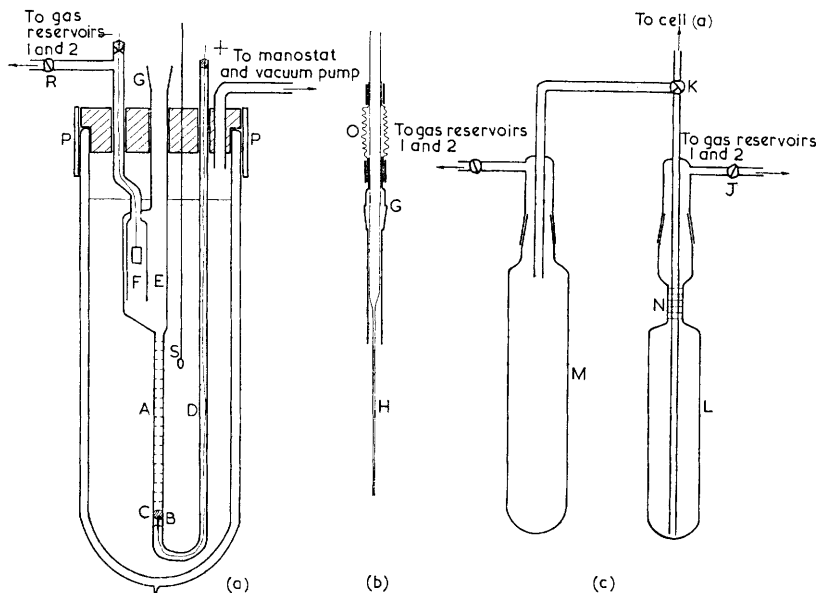


FIGURE 1. (a) Transference cell, (b) thermostatted bath, and (c) standard-flask arrangement

liquid ensured good mixing of the solutions. The flask was calibrated frequently by filling with water at 25° and weighing. A volume correction was applied to correct for the temperature at which the flask was used. No change in volume was observed with usage. When the level of solution had reached the marks N, the temperature in the surrounding Dewar flask was maintained for about 1 hr. at -55° by the periodic addition of small pieces of solid carbon dioxide. Finally, the partial pressure of ammonia in the gas system was adjusted to that of the equilibrium vapour pressure⁴ for the temperature of ammonia in the standard flask L. Taps K and J were now opened, the pressures over the two liquid surfaces equalised, and the volume of solutions read off.

Transfer of liquid from the standard flask L to the transference cell was effected by reducing the pressure by about 1 cm. Hg in the transference cell through gas reservoir 1. The tap K was opened to connect the standard flask to the transference cell, and, with delivery tube H inserted in the graduated tube A, the cell was filled with liquid ammonia solution. Tap K was now turned to connect the transference cell to the disposal flask M, the pressure adjusted to atmospheric in the transference cell through gas reservoir 2, and the pressure in M reduced by about 1 cm. Hg through gas reservoir 1; liquid ammonia solution was thus removed from the cell to the disposal flask M. This operation was repeated 4 or 5 times before each run to ensure

⁴ C. S. Cragoe, C. H. Meyers, and C. S. Taylor, *J. Amer. Chem. Soc.*, 1920, **42**, 206.

thorough washing of the cell and Polythene pipeline. Before each run the delivery tube was lifted above the level of the liquid in the cell, and the ammonia solution which it contained removed to the disposal flask. Taps K and R were then closed. Before starting a run the solution was allowed to stand in the cell for 30—45 min. to attain the temperature of the bath.

The transference cell and the standard flask were connected by 2-mm. bore thin-walled Polythene tubing, which was maintained within a few degrees of the temperature of the solution by enclosing it within a well-lagged rubber tube of $\frac{3}{8}$ in. diameter. Cold nitrogen gas, supplied from a sealed Dewar flask containing a heating coil, was passed through the rubber jacket, and the temperature was controlled by adjustment of the current supply to the heater.

The gas lines connecting the two gas reservoirs, the transference cell, and the standard flask were guarded from the atmosphere by moisture and carbon dioxide traps. The gas reservoirs, about 5-l. capacity, could be isolated independently or interconnected to enable the equalisation of pressures.

A potential difference about 100v d.c. was applied across the cell. This was supplied from a constant-current device similar to that described by Hopkins and Covington⁵ but based on a constant 650v d.c. source provided by a Solartron power pack, type AS 1165. The current was measured potentiometrically through a manganin-wound standard resistance of 10 ohms in series with the cell.

The graduated tube A was calibrated with mercury. Differences in the mercury levels and the adjacent marks were compared against the differences in weights. Calibrations were made over minimum tube distances of 4 cm. (8 marks) with a cathetometer which could be read to ± 0.001 cm.

Preparation of Materials.—All the salts except lithium nitrate were of AnalaR quality and were recrystallised three times and dried in a vacuum over phosphoric oxide for several days. They were then stored in desiccators over phosphoric oxide. Lithium nitrate was recrystallised five times and dried in a vacuum over phosphoric oxide at room temperature for 1 week. Finally, it was dried for 3 weeks at 61° in a vacuum over phosphoric oxide. The water contents of all the salts used were no higher than trace quantities. When in use the salts were stored in a vessel connected through a side-arm to a vessel containing phosphoric oxide. This device had a ground-glass joint which fitted the neck of a weighing bottle narrow enough to fit into the neck of the standard flask L. Contact of the salts with the atmosphere was thus reduced to only a few seconds during each weighing.

The ammonia used was distilled once from a cylinder of pure anhydrous ammonia. Titrations of the water contents of samples by Karl Fischer reagent by a procedure similar to that developed by Hodgson and Glover⁶ showed the moisture content to be less than 0.005%.

Errors.—Current measurements were better than 1 part in 3000, and the cell calibration better than 1 part in 4000. The time at which the boundary passed a mark in the cell could be established to ± 1 sec., and all the times used in the calculation of results were greater than 2000 sec. Temperature coefficients of the transference numbers of K^+ , Na^+ , Li^+ , and NH_4^+ ions are 0.0002, 0.0006, 0.0004, and 0.0005 per °C, respectively. As temperatures were controlled to $\pm 0.1^\circ$, the errors due to any variation in temperature were negligible. The greatest likely source of error was in the evaporation of ammonia during the transference of the solution from the standard flask to the cell. During this process the pressure was reduced by about 1 cm. Hg below atmospheric. If the maximum distillation occurred, then the error due to evaporation would be about 1 part in 1200 at -55° .

In the absence of molar-volume data for the ions, no corrections have been made for volume changes in the solutions during electrolysis; these are likely to be small. The correction due to the specific conductance of the ammonia is negligible. An accuracy of $\pm 0.1\%$ is claimed for the results.

RESULTS

In all cases mercuric ions electrolysed very well into solution from the solid mercury anode, and before the first graduation was reached a clear sharp thin flat boundary had been obtained. Except for ammonium nitrate, the boundaries became difficult to observe at concentrations much below 0.01M.

⁵ D. T. Hopkins and A. K. Covington, *J. Sci. Instr.*, 1957, **34**, 20.

⁶ H. W. Hodgson and J. H. Glover, *Analyst*, 1952, **77**, 74.

Transference numbers were compiled from the equation $t_+ = VcF/1000IT$, where V is the volume swept out in time T , c is the concentration in moles per litre, and F is the Faraday. In each run a series of 30—40 values of V and T were obtained. From these results the standard deviations obtained rarely exceeded 0.0003 in t_+ , and maximum variations in individual results 0.0008 in t_+ .

Concentrations were calculated in molar units, assuming that the ratio of the densities of the solutions were the same as the ratio of the densities of liquid ammonia over the same temperature range. The density data of Cragoe and Harper⁷ were used.

An early series of experiments indicated that there was no variation in t_+ with the potential difference applied, and subsequently runs were designed in which the boundary moved 5 cm. in 2000—3000 sec.

Values obtained in the individual experiments are given in Table I, except that the results for K^+ ion at -45.0° have been extrapolated from a series of results obtained at -48.0° .

TABLE I

| Variation of t_+ with concentration | | | | | | | | | |
|---|----------|-------------------------------------|---------|-------------------------------------|---------|---|----------|---|----------|
| KNO ₃ (-65.0°) | | NaNO ₃ (-65.0°) | | LiNO ₃ (-65.0°) | | NH ₄ NO ₃ (-65.0°) | | KNO ₃ (-55.0°) | |
| t_+ | c | t_+ | c | t_+ | c | t_+ | c | t_+ | c |
| 0.4928 | 0.10736 | 0.3902 | 0.10860 | 0.3443 | 0.10355 | 0.3814 | 0.15645 | 0.4907 | 0.10761 |
| 0.4915 | 0.07285 | 0.3942 | 0.05413 | 0.3544 | 0.05185 | 0.3864 | 0.09430 | 0.4890 | 0.07190 |
| 0.4893 | 0.03647 | 0.3973 | 0.02567 | 0.3630 | 0.02281 | 0.3914 | 0.04659 | 0.4877 | 0.04203 |
| 0.4869 | 0.01129 | 0.3995 | 0.01430 | | | 0.3964 | 0.01796 | 0.4849 | 0.01042 |
| | | 0.4004 | 0.01145 | | | 0.3969 | 0.01581 | | |
| | | | | | | 0.3994 | 0.006420 | | |
| NH ₄ NO ₃ (-55.0°) | | KNO ₃ (-45.0°) | | NaNO ₃ (-45.0°) | | LiNO ₃ (-45.0°) | | NH ₄ NO ₃ (-45.0°) | |
| 0.3918 | 0.15156 | 0.4875 | 0.11413 | 0.4013 | 0.09643 | 0.3524 | 0.10199 | 0.4054 | 0.15916 |
| 0.3954 | 0.09193 | 0.4857 | 0.06762 | 0.4057 | 0.05315 | 0.3670 | 0.03530 | 0.4071 | 0.09331 |
| 0.3997 | 0.04498 | 0.4861 | 0.06092 | 0.4074 | 0.03557 | 0.3692 | 0.02852 | 0.4086 | 0.05212 |
| 0.4037 | 0.01452 | 0.4840 | 0.02839 | 0.4092 | 0.02301 | 0.3725 | 0.01930 | 0.4101 | 0.03136 |
| 0.4051 | 0.008932 | 0.4825 | 0.01210 | 0.4116 | 0.01214 | | | 0.4114 | 0.01445 |
| | | | | | | | | 0.4117 | 0.007896 |

It was originally intended to include the transference numbers of the caesium ion in this work. However, the maximum solubility of caesium nitrate in liquid ammonia at these temperatures was about 0.01M. With such a low solubility the concentration range over which the variation of t_+ can be observed was far too small to allow satisfactory extrapolation of plots of t_+ against $c^{\frac{1}{2}}$ to limiting values.

DISCUSSION

The plots of t_+ against $c^{\frac{1}{2}}$ for all the ions studied are linear, within the limits of experimental error, as seen in Figure 2 (a—d), and the values of the limiting transference numbers, t_+° , shown in Table 2 were obtained by linear extrapolations. From the results in Table 2,

TABLE 2

Limiting cation transference numbers in nitrate solutions in liquid ammonia at various temperatures

| Temp. | K ⁺ | Na ⁺ | Li ⁺ | NH ₄ ⁺ |
|---------------|----------------|-----------------|-----------------|------------------------------|
| -65.0° | 0.4842 | 0.4052 | 0.3794 | 0.4040 |
| -55.0 | 0.4824 | — | — | 0.4092 |
| -45.0 | 0.4805 | 0.4170 | 0.3880 | 0.4140 |

values of the limiting cation conductances relative to the limiting conductance of the nitrate ion can be obtained from the relationship $\Lambda_+^\circ/\Lambda_-^\circ = t_+^\circ/(1 - t_+^\circ)$.

The absolute values of Λ_+° are not obtainable in the absence of conductance data.

⁷ C. S. Cragoe and D. R. Harper, *Sci. Papers, Bur. Stand.*, 1921, **420**, 287.

They are, however, proportional to the values of the ratio $\Lambda_+^\circ/\Lambda_-^\circ$, shown in Table 3, since Λ_-° refers to the nitrate ion in all cases, and it is this ratio which is used in this Paper to compare limiting cation conductances.

TABLE 3
Limiting ion conductances in liquid ammonia $\div \Lambda_{\text{NO}_3^-}^\circ$

| Temp. | K ⁺ | Na ⁺ | Li ⁺ | NH ₄ ⁺ |
|--------|----------------|-----------------|-----------------|------------------------------|
| -65.0° | 0.939 | 0.681 | 0.611 | 0.678 |
| -55.0 | 0.932 | — | — | 0.692 |
| -45.0 | 0.925 | 0.715 | 0.634 | 0.707 |

The limiting conductance of the ammonium ion, regarded as the hydrogen ion in liquid ammonia, is seen to be approximately equal to that of the sodium ion and less than that of

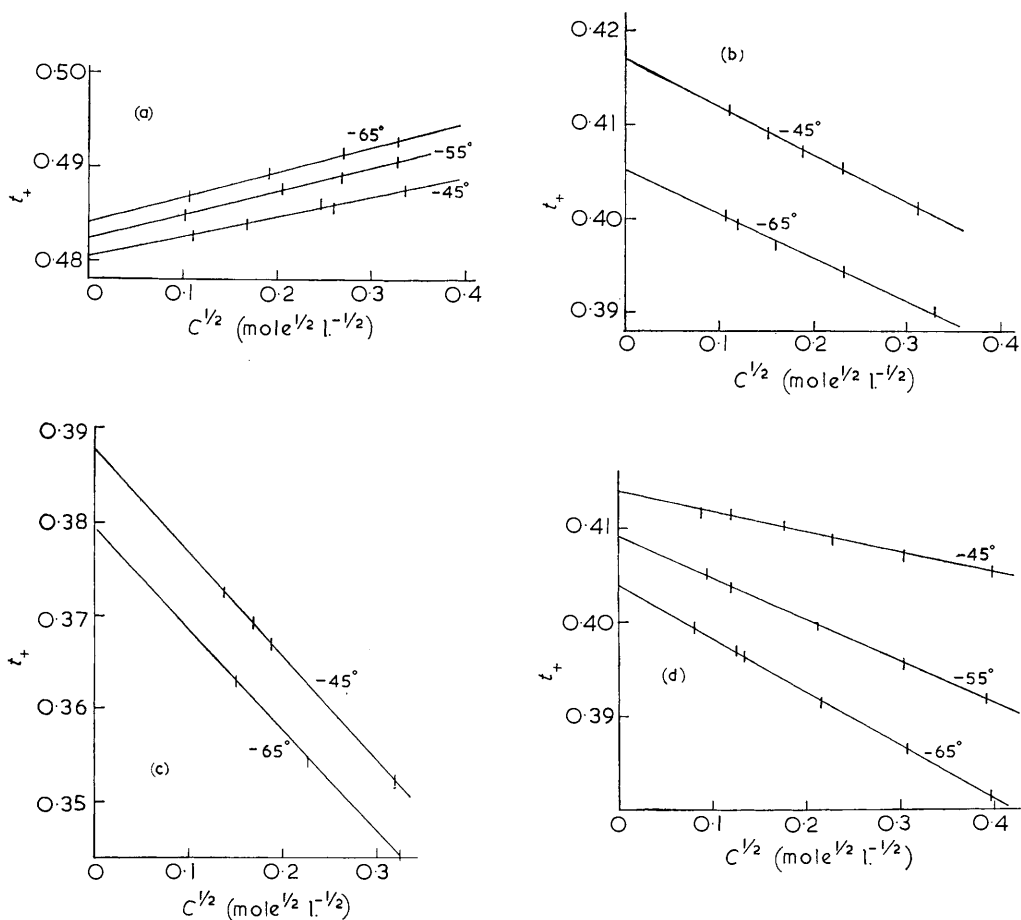


FIGURE 2. Variation of the transference numbers of univalent cations with the square root of concentration at various temperatures in liquid ammonia: (a) K⁺ in KNO₃; (b) Na⁺ in NaNO₃; (c) Li⁺ in LiNO₃; (d) NH₄⁺ in NH₄NO₃

the potassium ion at all temperatures. Thus, the mobility of the hydrogen ion in liquid ammonia is not anomalous as it is in aqueous solutions. Moreover, there is little change with temperature in the ratio $\Lambda_{\text{M}^+}^\circ/\Lambda_{\text{NH}_4^+}^\circ$, where M⁺ is alkali-metal ion. Certainly, there

is no change which can be compared with the change in the ratio $\Lambda_{M^+}^\circ/\Lambda_{H^+}^\circ$ in water over a range of temperature, as can be seen from a comparison in Tables 4 and 5.

In aqueous solutions the high mobility of the hydrogen ion is attributed to the proton-transfer mechanism^{8,9} in which a proton passes, in the direction of the applied field, from a charged hydronium ion to an uncharged arrangement of associated water molecules by the making and breaking of a hydrogen bridge. The properties of molecular association in liquid ammonia are well established, and with considerable hydrogen-bonding an increasing degree of ordering must occur as the temperature decreases, though not to the same extent as in water because of the weaker hydrogen-bonding between the nitrogen atoms and the inability for ammonia to form the three-dimensional arrangements found in water. There appear to be similar structural conditions in ammonia, and the transference of charge by a proton-transfer process seems feasible though to a lesser extent than in water on account of the reduced number of transfer sites available.

If a proton-transfer mechanism contributes appreciably to the mobility of the hydrogen ion in ammonia, it is to be expected that its contribution will increase with decrease in temperature as the degree of molecular association within the solvent increases. The pronounced increase in mobility of the hydrogen ion in water with decreasing temperature relative to the other ions can be seen from Table 5 by the change in the ratios $\Lambda_{K^+}^\circ/\Lambda_{H^+}^\circ$, $\Lambda_{Na^+}^\circ/\Lambda_{H^+}^\circ$, and $\Lambda_{Li^+}^\circ/\Lambda_{H^+}^\circ$. The similar ratios involving the NH_4^+ ion in liquid ammonia show no such trend with change of temperature. In ammonia the ratios $\Lambda_{Na^+}^\circ/\Lambda_{NH_4^+}^\circ$ and $\Lambda_{Li^+}^\circ/\Lambda_{NH_4^+}^\circ$ remain constant with changing temperature whilst $\Lambda_{K^+}^\circ/\Lambda_{NH_4^+}^\circ$ changes only from 1.37 to 1.31 as the temperature changes from -65 to -45° , a small change in the direction opposite to that observed with the $\Lambda_{K^+}^\circ/\Lambda_{H^+}^\circ$ ratio in water.

TABLE 4

Ratios of limiting ion conductances (Λ°) in liquid ammonia

| Temp. | K ⁺ /NH ₄ ⁺ | Na ⁺ /NH ₄ ⁺ | Li ⁺ /NH ₄ ⁺ | K ⁺ /Na ⁺ | K ⁺ /Li ⁺ | Li ⁺ /Na ⁺ |
|---------------|--|---|---|---------------------------------|---------------------------------|----------------------------------|
| -65.0° | 1.38 | 1.00 | 0.90 | 1.38 | 1.54 | 0.90 |
| -55.0 | 1.35 | — | — | — | — | — |
| -45.0 | 1.31 | 1.01 | 0.90 | 1.30 | 1.46 | 0.90 |

TABLE 5

Ratios of limiting ion conductances (Λ°) in aqueous solutions *

| Temp. | K ⁺ /H ⁺ | Na ⁺ /H ⁺ | Li ⁺ /H ⁺ | K ⁺ /Na ⁺ | K ⁺ /Li ⁺ | Li ⁺ /Na ⁺ |
|-----------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| 0° | 0.181 | 0.118 | 0.086 | 1.54 | 2.10 | 0.732 |
| 25 | 0.210 | 0.143 | 0.110 | 1.47 | 1.91 | 0.770 |
| 100 | 0.309 | 0.230 | 0.183 | 1.35 | 1.70 | 0.793 |

* R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, appendix 6.2.

Further evidence for the ammonium ion as a well-defined stable entity in ammonia is given by Jolly¹⁰ who has shown this ion to be 18 kcal./mole more stable than the hydrogen ion in water at 25° . More recently, Kruh and Petz¹¹ obtained a radial distribution function for ammonia molecules within liquid ammonia from X-ray diffraction studies at -74° , which shows each NH_3 molecule to have about seven nearest neighbours at about 4.1 \AA . This indicates a break-up of the slightly distorted cubic close-packed arrangement found in solid ammonia,¹² and with N-N distances of 3.6 \AA only very weak hydrogen bonds are to be expected within the liquid. Furthermore, from the large and almost linear change in density⁷ over the whole of the solvent range, a regular break-up of the close-packed

⁸ J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

⁹ S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, ch. 10.

¹⁰ W. L. Jolly, *J. Phys. Chem.*, 1954, **58**, 250.

¹¹ R. F. Kruh and J. I. Petz, *J. Chem. Phys.*, 1964, **41**, 890.

¹² I. Olavsson and D. H. Templeton, *Acta Cryst.*, 1959, **12**, 832.

arrangement is inferred. In contrast to this, Morgan and Warren¹³ found a radial distribution function in water between 0° and 80° which indicated 4.4–4.8 nearest neighbours at 2.9 Å, and a further set of next nearest neighbours at about 4.5 Å, up to about 30°. An O–O internuclear distance of about 3.5 Å is required for a close-packed arrangement, and it is inferred that the much better defined strongly hydrogen-bonded structure like that of ice exists within the solvent.

It must therefore be concluded that the transport mechanism of the hydrogen ion in liquid ammonia is predominantly that of the normal mobility contribution corresponding to the diffusion of the ion and its associated solvation sphere through the solvent.

The order of ionic mobilities in liquid ammonia is $K^+ > Na^+ \approx NH_4^+ > Li^+$, and in water is $K^+ \approx NH_4^+ > Na^+ > Li^+$. The differences between ionic conductances in liquid ammonia and in water can best be seen by comparing the ratios $(\Lambda_{Na^+} - \Lambda_{Li^+})/\Lambda_{Na^+}$ and $(\Lambda_{K^+} - \Lambda_{Na^+})/\Lambda_{Na^+}$. These are 0.10 and 0.23, and 0.30 and 0.47, at –65° and 25°, respectively, indicating that with reference to the Na^+ ion there are greater differences between the mobilities of K^+ and Li^+ ions in water than in liquid ammonia. Thus, the effective solvated ionic radii have smaller differences relative to each other in liquid ammonia than in water, and there is a smaller change in the degree of solvation in passing through the series.

The ions Li^+ , Na^+ , and NH_4^+ all form fairly stable uni-univalent ammoniated salts in the liquid-ammonia temperature range. This indicates strong co-ordination by ammonia molecules to the cation in all cases except K^+ ion. A well-defined primary solvation sphere around the cation is inferred, but the tendency of ions to arrange the solvent molecules into a secondary solvation sphere is likely to be much less in ammonia with its weaker hydrogen-bonding ability. It is therefore most probable that the ion conductances and ion mobilities observed in liquid ammonia correspond much more nearly to those of a primary solvation sphere than is the case with water.

From Table 4 it is seen that there is constancy over the temperature range studied in the ratios $\Lambda_{Na^+}/\Lambda_{NH_4^+}$, $\Lambda_{Li^+}/\Lambda_{NH_4^+}$, and $\Lambda_{Li^+}/\Lambda_{Na^+}$, but inconstancy in the ratios $\Lambda_{K^+}/\Lambda_{NH_4^+}$, $\Lambda_{K^+}/\Lambda_{Na^+}$, and $\Lambda_{K^+}/\Lambda_{Li^+}$. Only in the cases of the ratios involving the K^+ ion, the largest of the alkali-metal ions studied, and in which the tendency for co-ordination of ammonia molecules into the solvation sphere is least, is there inconstancy in the ion conductance ratios over the temperature range. A greater increase in ion conductance of the K^+ ion with respect to the Na^+ ion occurs as the temperature decreases. This represents either a small increase in the effective solvated ionic radius of the Na^+ ion with respect to the K^+ ion, or a small decrease in the effective ionic radius of the K^+ ion with respect to the Na^+ ion as the temperature decreases. This must be taken to represent a reduced influence by the K^+ ion on the solvent molecules in its solvation spheres compared with the influences exerted by the Li^+ , Na^+ , and NH_4^+ ions.

The great difference found between the NH_4^+ in water and liquid ammonia is its much greater degree of solvation relative to other ions.

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¹³ J. Morgan and B. E. Warren, *J. Chem. Phys.*, 1938, **6**, 666.