44. *Solutions in Sulphuric Acid. Part X.* Transport-number Measurements.*

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The apparent transport numbers of the lithium, sodium, potassium, silver, barium, and strontium ions in solutions of their hydrogen sulphates in sulphuric acid have been measured. The very small values obtained in every case have been interpreted as providing further evidence that the conductivity of these solutions is due very largely to the hydrogen sulphate ion which conducts almost entirely by a chain mechanism similar to that which had been proposed to explain the abnormal mobilities of the hydrogen and hydroxyl ions in water. The nature of the chain conduction process in sulphuric acid is discussed and compared with what is known concerning chain conduction in other solvents. The transport numbers of the cations investigated are compared and discussed, and their variation with concentration is also briefly discussed. Finally, the temperature variation of the transport number of the potassium ion is briefly discussed.

THE earliest experiments on ionic transport in sulphuric acid were carried out by Hantzsch (*Ber.*, 1925, **58**, 941). He attempted to prove the presence of the nitracidium cation ($H_2NO_3^+$) in water–sulphuric acid–nitric acid mixtures by migration experiments. The electrode reactions at the cathode, however, resulted in considerable reduction of both acids which rendered the measurements very inaccurate, and Hantzsch was unable to detect any transport of nitric acid. Hammett and Lowenheim (*J. Amer. Chem. Soc.*, 1934, **56**, 2620) later demonstrated that there is a very small but real transport of barium and strontium ions in solution of their hydrogen sulphates. They measured the transport numbers of these ions and detected some variation with concentration. Angus and Leckie (*Trans. Faraday Soc.*, 1935, **31**, 958) electrolysed nitrosonium hydrogen sulphate in 18—19% oleum and showed that a migration of the nitrosonium ion occurred. Quite recently the difficulties encountered by Hantzsch in attempting to demonstrate the migration of nitric acid were overcome by Bennett, Brand, and Williams (*J.*, 1946, 975) by working in oleum solutions. They showed that in oleum containing 4—18% of sulphur trioxide the main subject of cathodic reduction was the oleum and found a definite transport of nitric acid towards the cathode. Other work has shown that this cationic form of nitric acid is the nitronium ion (see, *e.g.*, Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277). The reason that it is considerably easier to demonstrate the transport of cations in oleum than in sulphuric acid is that in oleum basic solutes, such as nitric acid, exist in the form of hydrogen disulphates rather than as hydrogen sulphates, and the hydrogen disulphate ion ($HS_2O_7^-$) has a very much smaller mobility than the hydrogen sulphate ion.

In the present work Hammett and Lowenheim's measurements on the transport numbers of the barium and strontium ions in solutions of their hydrogen sulphates have been repeated, and in addition, the transport numbers of the lithium, sodium, potassium, and silver ions in solutions of their hydrogen sulphates have been determined at 25°. The variation of the transport number of the potassium ion with temperature has also been investigated.

EXPERIMENTAL

Apparatus.—All measurements were made by Hittorf's method in a cell similar to that used by Hammett and Lowenheim (*loc. cit.*). It contained three compartments (each about 50 c.c.), connected to each other by narrow bent tubes to minimise diffusion from one compartment to another (see Figure). Two taps, *A*, were joined to the connecting tubes so that the solutions in the three compartments could be readily separated by application of a small air-pressure. Platinum electrodes, *B*, were placed in each of the outer compartments. The outlet tubes, *C*, were protected with phosphoric oxide guard-tubes. The current used, 20—25 milliampères, was small enough to prevent any appreciable heating of the solution and consequent errors due to convection. The quantity of electricity was measured by a copper coulometer which had

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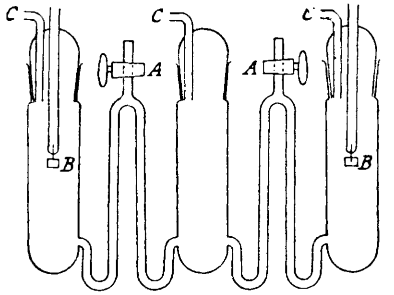
* Part IX, preceding paper.

been checked against a silver coulometer constructed according to Rosa and Vinal's method (*Bur. Stand. Bull.*, **1936**, **13**, 479). The cell was immersed in a thermostat at 25°. At the end of each experiment, the solutions in the three compartments were separated, removed, and weighed. After thorough mixing, samples were taken and analysed.

Methods of Analysis.—Barium and strontium were determined by diluting a weighed portion of the solution with a large excess of water in the case of barium and a 1 : 1 water–alcohol mixture in that of strontium, and filtering, washing, drying, and weighing in the usual manner. Silver determinations were carried out by diluting a weighed portion of the solution with a large excess of water, and precipitating silver chloride by slow addition of an excess of hydrochloric acid. The precipitate was then treated by standard procedures. Analysis for sodium, potassium, and lithium was carried out by slowly driving the sulphuric acid off a weighed portion of solution by prolonged heating in a platinum crucible. The resulting solid was then heated to constant weight at 600°.

Materials.—Sulphuric acid was prepared from a weak oleum by adding small quantities of water until a minimum conductivity of 0·0103 ohm^{-1} was obtained. The initial weak oleum was prepared by distilling sulphur trioxide from 60% oleum into 98% "AnalaR" sulphuric acid. Sodium, potassium, lithium, and silver sulphates were all "AnalaR" materials dried at 150° and stored in a vacuum-desiccator. Barium sulphate was prepared by slow addition of a slight excess of sulphuric acid to a barium chloride solution. The precipitated barium sulphate was filtered off, washed, and ignited in a muffle furnace at 500°. Strontium sulphate was prepared similarly.



Transport-number apparatus.

Results.—Table 1 contains the results of the measurements of the transport numbers of the silver, potassium, lithium, sodium, barium, and strontium ions in solution of their hydrogen sulphates at 25° and at various concentrations.

TABLE 1. *Apparent transport numbers.*

Solute	m	Q, coulombs	Equiv. gained by cathode compartment ($\times 10^4$)	Equiv. lost by anode compartment ($\times 10^4$)	t_c	t_a	t
$AgHSO_4$	0·2490	3329	9·62	8·46	0·028	0·024	0·026
	0·3056	4899	11·28	11·22	0·022	0·022	0·022
$KHSO_4$	0·6244	6166	19·18	19·42	0·030	0·030	0·030
	1·2262	6818	17·65	17·40	0·025	0·025	0·025
$NaHSO_4$	0·7918	7780	18·10	16·26	0·022	0·020	0·021
$LiHSO_4$	0·5562	5745	9·28	6·92	0·015	0·012	0·013
$Ba(HSO_4)_2$	0·1738	5175	4·94	4·80	0·009	0·009	0·009
	0·1969	5718	5·62	5·39	0·009	0·009	0·009
	0·2073	5632	5·38	3·94	0·009	0·007	0·008
	0·2292	9598	10·18	9·21	0·010	0·009	0·010
	0·2418	5644	4·41	4·39	0·008	0·007	0·008
	0·3062	7702	6·46	6·07	0·008	0·008	0·008
	0·5391	8314	4·21	3·87	0·005	0·005	0·005
	0·7981	9345	4·26	3·78	0·004	0·004	0·004
$Sr(HSO_4)_2$	0·2111	5764	4·55	4·11	0·008	0·007	0·007
	0·2788	7818	6·30	5·46	0·008	0·007	0·007
	0·5819	7620	4·06	3·34	0·005	0·004	0·005
	0·8247	9340	3·12	3·32	0·003	0·003	0·003

The values given in this table are apparent or Hittorf transport numbers and no attempt has been made to determine true transport numbers by using a reference non-electrolyte as did Hammett and Lowenheim (*loc. cit.*). It is exceedingly difficult to find a suitable reference non-electrolyte, for even trichloroacetic acid, used by Hammett and Lowenheim, is probably slightly ionised (see Part XII), and in any case there is considerable doubt as to the reliability of this method of determining true transport numbers since it is not possible to be certain that the reference substance does not preferentially " solvate " the electrolyte and thus get transferred with it (cf. Longsworth, *J. Amer. Chem. Soc.*, 1947, **69**, 1258).

The variation of the transport number of the potassium ion with temperature over the range 25—61° was also investigated, and the results (Table 2) show that there is probably a very slight increase in the transport number with increasing temperature.

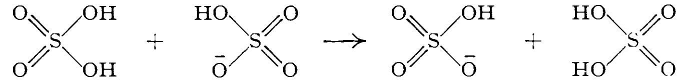
TABLE 2. *Apparent transport numbers of potassium hydrogen sulphate at different temperatures.*

Temp.	m	Q, coulombs	Equiv. gained by cathode compartment ($\times 10^4$)	Equiv. lost by anode compartment ($\times 10^4$)	t_c	t_a	t
25·0°	0·6244	7900	19·18	19·42	0·030	0·030	0·030
36·8	0·6536	7531	18·68	19·31	0·032	0·033	0·032
45·1	0·6388	8936	25·84	24·68	0·032	0·030	0·031
55·0	0·7098	7579	30·24	19·77	0·034	0·033	0·033
61·0	0·6556	7496	22·98	18·39	0·039	0·031	0·035

DISCUSSION

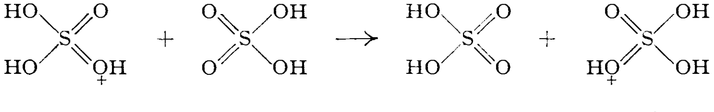
Abnormal Conduction in Sulphuric Acid.—The small differences between the transport numbers of different ions and the small variations with concentration being temporarily ignored, our results confirm those of Hammett and Lowenheim (*loc. cit.*) concerning the barium and strontium ions and show further that the transport numbers of the lithium, sodium, potassium, and silver ions in solutions of their hydrogen sulphates are also very small. As Hammett and Lowenheim (*loc. cit.*) pointed out, it is quite impossible to account for the extraordinarily small transport numbers of these cations by assuming that they are partly present in the form of negatively charged complex ions, as in the case of cadmium iodide in water, *e.g.*, $2KHSO_4 = K^+ + K(HSO_4)_2^-$. Such a hypothesis is contradicted by the cryoscopic evidence that all these substances ionise in a simple manner (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; and Part I, *J.*, 1950, 2473), *e.g.*, $KHSO_4 = K^+ + HSO_4^-$. Moreover, the very small cation transport numbers cannot be attributed to there being other ionic species present in the solution resulting from the self-dissociation of the sulphuric acid. It is shown later that the relatively large conductivity of the pure solvent is almost entirely due to the ions resulting from the autoprotolysis, and this is almost completely repressed in the solutions we have investigated.

It appears therefore that the hydrogen sulphate ion has a mobility 50—100 times greater than that of the cations investigated. As was first suggested by Hammett and Lowenheim (*loc. cit.*), the only reasonable way to account for this abnormal mobility of the hydrogen sulphate ion is to assume that it conducts by a type of Grotthus chain mechanism, analogous to that generally accepted to explain the abnormal mobilities of the hydrogen and hydroxide ions in water. One step in this process which is repeated along a long chain of sulphuric acid molecules may be represented diagrammatically as follows:



Thus by a succession of proton transfers the charge of a hydrogen sulphate ion is transferred through the solution without the actual movement of any ion. It is often stated that, in order for the same molecules to take part in a similar process, they must rotate into new positions, and therefore the process of abnormal conduction consists of a combination of proton transfer and molecular rotation. This is a substantially correct but nevertheless misleading description of the process. Because of the very large excess of solvent molecules, any given solvent molecule will only occasionally take part in a conducting chain, and there will in general be ample time for it to rotate into its original position so that molecular rotation could never be the rate-determining stage of chain conduction as it sometimes appears to be. Much more important is the fact that, because of the thermal motion of the molecules, any given molecule will, in general, not be in exactly the right position to receive a proton from, or pass a proton on to, a neighbouring molecule, and hence each molecule must undergo a certain amount of rotation when it takes part in a conducting chain. The fact that, having done so, it is left in a position in which it cannot repeat the process without rotating to a new position is largely irrelevant, since whether or not it has already taken part in a conducting chain a certain amount of rotation will be necessary.

By analogy with water, for which it is known that both the hydrogen and hydroxyl ions have abnormal mobilities, it might be expected that the hydrogen ion in sulphuric acid ($H_3SO_4^+$) would also have an abnormal mobility. That it does indeed have an abnormal mobility, which must be very nearly equal to that of the hydrogen sulphate ion, follows from the fact that the minimum in the specific conductivity–concentration curve for the system SO_3–H_2O occurs to within the limits of experimental error exactly at the composition H_2SO_4 (Part IX, *loc. cit.*). As a result of its self-ionisation, sulphuric acid contains small concentrations of hydrogen, hydrogen sulphate, hydroxonium, and hydrogen disulphate ions (Part IV, *J.*, 1950, 2516). The transport number of the hydroxonium ion has not been measured, but since it is known that at low concentrations water is at least 90% ionised (Part II, *J.*, 1950, 2493) and since it has been shown (Part IX, *loc. cit.*) that its conductivity is almost identical with that of potassium hydrogen sulphate, it follows that the hydroxonium ion must have a very small mobility like the potassium ion. The hydrogen disulphate ion has also been shown by conductivity measurements to have a very small mobility (forthcoming paper). Hence neither of these ions contributes very much to the conductivity of sulphuric acid, which must be due mainly to the hydrogen sulphate ion and probably also the hydrogen ion ($H_3SO_4^+$). If it is assumed that, like other ions except the hydrogen sulphate ion, the hydrogen ion has a very small mobility, then it may be seen that when sulphur trioxide is added to sulphuric acid, producing hydrogen ions and hydrogen disulphate ions, and the self-ionisation is correspondingly repressed, the conductivity would initially fall, as highly conducting hydrogen sulphate ions are replaced by poorly conducting hydrogen disulphate ions. Eventually, of course, because of the increasing concentration of ions in the solution, the conductivity would pass through a minimum, and then increase. The minimum would, however, occur on the sulphur trioxide side of the composition of sulphuric acid. On the other hand, if it is assumed that the hydrogen ion has a considerably larger mobility than even the hydrogen sulphate ion, a similar argument shows that the conductivity minimum would be on the aqueous side of the composition of sulphuric acid. In fact, the very small conductivity due to the hydroxonium and hydrogen disulphate ions being discounted, the minimum will occur at the composition H_2SO_4 only if the mobility of the hydrogen ion is equal to that of the hydrogen sulphate ion. The abnormal mobility of the hydrogen ion must be due to a similar mechanism, involving proton transfer and molecular rotation, to that which is responsible for the abnormal mobility of the hydrogen sulphate ion. A single step of this process may be represented diagrammatically in the following manner :



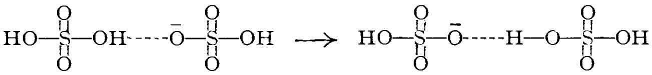
Whether the proton transfer or the molecular rotation is the rate-determining process in the abnormal conduction of the hydrogen and hydroxyl ions in water has been the subject of controversy (Eyring and Stearn, *J. Chem. Phys.*, 1937, **5**, 113; Wannier, *Ann. Physik*, 1935, **24**, 545), and there does not seem to be sufficient evidence to warrant a definite conclusion. Our conclusion that the mobilities of the hydrogen and hydrogen sulphate ions are equal or very nearly so provides some evidence, however, that in sulphuric acid molecular rotation is rate-determining. The first stage in the process of abnormal conduction is different for the two ions; for the hydrogen ion it is the transfer of a proton from a hydrogen to a sulphuric acid molecule, while for a hydrogen sulphate ion it is the transfer of a proton from a sulphuric acid molecule to a hydrogen sulphate ion, and it is unlikely that the rates of these two processes would be exactly the same. The second stage involving the rotation of sulphuric acid molecules is, however, common to both and must occur at the same rate in both cases. That molecular rotation should be the rate-determining step of abnormal conduction in sulphuric acid, even if it is not in water, can be very plausibly attributed to the high viscosity of sulphuric acid.

Comparison of Abnormal Conductivities in Different Solvents.—It is of interest to compare the abnormal mobilities of the hydrogen and hydrogen sulphate ions in sulphuric acid with the mobilities of analogous ions in other solvents. At first sight the mobilities of the hydrogen and hydrogen sulphate ions in sulphuric acid appear to be exceptionally abnormal, being 50—100 times greater than the mobilities of other ions. This is due, however, primarily to the high viscosity of sulphuric acid, which causes the mobilities of ions that conduct by the ordinary diffusion mechanism to be exceptionally small and not to any special facility of the chain conduction mechanism in sulphuric acid (cf. Hammett and Lowenheim, *loc. cit.*; and Part XII, *loc. cit.*).

In water the hydrogen and hydroxyl ions have mobilities some 4—5 times that of other ions, the hydrogen ion having a greater mobility than the hydroxyl ion. In methyl and ethyl alcohols the hydrogen ions, $CH_3\cdot\overset{+}{O}H_2$ and $C_2H_5\cdot\overset{+}{O}H_2$ respectively, have small abnormal mobilities, while the methoxide and ethoxide ions have normal mobilities. In ammonia both the ammonium (hydrogen) ion and the amide ion have normal mobilities, and in acetic acid and formic acid both the acetate and the formate ion respectively have normal mobilities. No abnormal mobility has been detected in hydrogen fluoride or hydrogen cyanide (Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw Hill, New York, 1941). In nitric acid the nitrate ion appears to have a normal mobility (unpublished experiments by D. J. Millen and W. H. Lee).

It has been suggested (Glasstone, Laidler, and Eyring, *op. cit.*) that abnormal mobilities are related to the autoprotolysis constant of the solvent and only occur in solvents having a large value of this. As sulphuric acid has a very large autoprotolysis constant (Part IV, *loc. cit.*), the very abnormal mobilities of the hydrogen and hydrogen sulphate ions in this solvent would appear to provide support for this suggestion. It does not, however, account for the normal mobilities of the acetate and formate ions in acetic and formic acids respectively, both of which have larger autoprotolysis constants than water.

All those liquids in which abnormal mobilities due to chain conduction have been found are associated by hydrogen bonding, and it seems reasonable to suppose that in the proton-transfer stage of the process the proton moves along a hydrogen bond, *e.g.*,



$$HO-\overset{O}{\underset{O}{S}}-OH\cdots\cdots\bar{O}-\overset{O}{\underset{O}{S}}-OH \longrightarrow HO-\overset{O}{\underset{O}{S}}-\bar{O}\cdots\cdots H-O-\overset{O}{\underset{O}{S}}-OH$$

and that the stronger the hydrogen bonding the easier the proton transfer becomes. It is noteworthy that the only solvents in which it is known that abnormal mobilities are considerably greater than the normal mobilities and in which the hydrogen ion and the corresponding anion *both* have abnormal mobilities are water and sulphuric acid. In water there is extensive association in three dimensions due to strong hydrogen bonds, and it seems very reasonable to assume that a similar extensive association occurs in sulphuric acid, whilst in all the other solvents that have been investigated, association is into linear polymers or dimers only, and in addition, in some cases, the hydrogen bonding is relatively weak and the degree of association therefore correspondingly small. This suggests that the nature and extent of the association in the liquid are of importance in determining the degree of abnormal mobility of the characteristic ions of the solvent. This is perhaps not an unreasonable conclusion, as it may be seen that the propagation of a conducting chain will be relatively easy in a liquid associated into large three-dimensional polymers since the majority of the molecules along the path of the chain, the average direction of which is, of course, determined by the applied field, will be in the correct position, or almost the correct position to continue the chain. Thus the average time of rotation of the molecules in the chain will be relatively small, and if rotation is the rate-determining stage, the mobility will be correspondingly great. The mobility will obviously depend on the degree of association, as the smaller is the degree of association, the more molecules will have a random orientation rather than one fixed by the structure of the liquid, and so the longer will be the average time required for a molecule to rotate into a suitable position to carry on the chain, and hence the smaller will be the mobility. In a liquid associated into linear polymers, however, a chain will only be able to travel easily along such a polymer and since these will have a random orientation it will not in general be able to travel easily in the direction of the applied field. Either it will have to take a very circuitous path or it will have continually to jump from one group of associated molecules to another, each jump requiring a considerable amount of molecular rotation. In either case the mobility will obviously be much reduced. In a liquid associated into dimers, as acetic acid probably is, a considerable molecular rotation will be needed, at least every other time a proton is transferred, and the average time of rotation will be relatively large and the mobility correspondingly small.

Hence we may conclude that, where hydrogen bonding is strong, proton transfer fast, and molecular rotation is the rate-determining stage of chain conduction, the chain-conduction mobility will depend on the nature and extent of the association due to hydrogen bonds in the liquid. On the other hand, where the hydrogen bonding is relatively weak, proton transfer may be slower than molecular rotation and the extent and nature of the association will not then be of importance. In such a case, moreover, the whole process may be so slow that abnormal conduction is not observed.

Comparison of the Transport Numbers of Various Cations in Solutions of their Hydrogen Sulphates.—The results for the barium ion given in Table 1 are in fair agreement with those of Hammett and Lowenheim over the concentration range investigated, and our results for strontium are in good agreement with their single determination. A detailed comparison of the transport numbers of different cations is not possible at present as they have not all been investigated sufficiently thoroughly over a wide enough concentration range. The results given in Table 1 for the barium, strontium, and potassium ions show that there is a small but fairly definite decrease in the transport number with increasing concentration over the range 0·2—1·6 molal, and a similar decrease was found by Hammett and Lowenheim (*loc. cit.*) for the barium ion over approximately the same concentration range. We have not investigated the low concentration range in which Hammett and Lowenheim found an increase in the transport number of the barium ion with increasing concentration. This may, however, be quite real, and can be attributed to the presence in the solution at these low concentrations of the hydrogen ion from the autoprotolysis of the solvent, which, having as large a mobility as the hydrogen sulphate ion, would carry quite a large fraction of the current towards the cathode and hence cause a decrease in the transport number of the barium ion. It seems probable that there is a fairly general decrease in the transport numbers of alkali and alkaline-earth metal cations over the concentration range we have investigated. This can be attributed partly at least to the increasing viscosity of solutions of these cations with increasing concentration (Part XI, *J.*, 1953, 215) which reduces the normal mobility of the cations more than it does the abnormal mobility of the hydrogen sulphate ion (Part XII, *loc. cit.*).

Because of the variation of transport number with concentration, an exact comparison of the transport numbers of the cations we have investigated is not possible from the results given in Table 1. However, it seems very probable from these results that at a given concentration the transport numbers would decrease in the order

$$K^+ > Ag^+ > Na^+ > Li^+ > Ba^{++} > Sr^{++}$$

For the univalent cations this is the same order as is found in dilute solutions of various of their salts in water. It is generally accepted that in aqueous solutions this variation is due to an increase in solvation with increasing charge density on passing from the potassium ion to the lithium ion. This suggests that there might be a similar increase in solvation in this series in sulphuric acid. Other evidence that the extent of solvation does increase in the series $K^+ < Ag^+ < Na^+ < Li^+ < Ba^{++} < Sr^{++}$ is presented in Part XI.

Temperature Variation of the Transport Numbers of the Potassium Ion.—In Table 2 are presented the results of the determination of the transport number of the potassium ion in solutions of its hydrogen sulphate at very similar concentrations and at five different temperatures over the range 25—61°. There appears to be a very slight increase in the transport number with increasing temperature but this is scarcely larger than the probable experimental error. This suggests that, although the normal mobility of the cation increases with increasing temperature because of the decreasing viscosity of the solution, this must be almost exactly compensated by an increase in the abnormal mobility of the hydrogen sulphate ion because the rate of molecular rotation increases with increasing temperature.

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[*Received, June* 16*th*, 1952.]