ductivities for seven consecutive fractions at 0° are 41.9×10^{-6}, 5.10×10^{-6}, 3.07×10^{-6}, 2.68×10^{-6}, 2.68×10^{-6}, 2.86×10^{-6}, 4.32×10^{-6} ohm^{-1} cm.$^{-1}$, the middle fractions being of highest purity. A slow increase of conductivity occurred upon standing, apparently due to ingress of traces of moisture.

In using hydrofluoric acid for experimental measurements the following have been noted. Any contact of the low conductance acid with metal increases the conductance; distillation is preferable to liquid transfer even in closed systems. Transfers in dry boxes have resulted in increased conductance. This statement is not true if one starts with acid of 10^{-4} ohm^{-1} cm.$^{-1}$ specific conductance. To date we have not been able to handle 10^{-6} without ending up with 10^{-5} or even 10^{-4} ohm^{-1} cm.$^{-1}$ acid. We continue to investigate this problem.

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CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Ionic Mobilities in Anhydrous Hydrofluoric Acid[1]

BY MARTIN KILPATRICK AND T. J. LEWIS[2]

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Conductance and transference number measurements in anhydrous hydrofluoric acid are described, and a table of ionic mobilities drawn up. The mechanism of electrical conductance in this solvent is discussed.

The calculation for the autoprotolysis constant of anhydrous hydrofluoric acid involved the assumption that the mobility of the solvated proton in this solvent is the same as that of the potassium ion.[3] This assumption is open to criticism in view of the high mobility of the proton in water, sulfuric acid, methanol and ethanol which is generally attributed to the ease with which a proton will jump from an ion to a solvent molecule. A knowledge of ionic mobilities in hydrofluoric acid will enable a more accurate value of its autoprotolysis constant to be calculated, and may clarify the conditions required for chain conduction to occur in protonic solvents. Previous workers have measured the equivalent conductances of inorganic fluorides in this solvent at −15 and 20°[4,5] but there has been no previous determination of the transference numbers which are needed to calculate the mobilities of the individual ions.

The corrosive nature of this acid forbids the use of apparatus made of glass or base metal, but the availability of the plastics Teflon and Fluorothene, has presented new possibilities.[6] The harder and more transparent Fluorothene (trifluoromonochloroethylene polymer) has been the material most used in this work.

Experimental

The Conductance Cells.—Cell A (Fig. 1) was built entirely of Fluorothene plastic. A tube of length 10 cm. and internal diameter 1 cm. was closed at both ends by caps which screwed down tightly to form vacuum tight seals. The electrodes passing through these caps were held in place by Fluorothene plugs which left no air gap around the platinum wire. The electrode plates were bright platinum disks of diameter 5 mm. Each of the two openings in the roof of the cell led through stopcocks to auxiliary chambers. A is a filling chamber. Stopcock C may be removed and solids introduced into A by means of a weight buret. B is an overflow chamber. A thin Fluorothene tube connecting A and B allowed circulation of the acid and ensured the thorough mixing of the solutions. Acid was introduced by evacuating the cell, attaching it through stopcock C to the fractionating column, and collecting at 0°. The cell constant, measured with 0.1 *m* potassium chloride solution, was 8.077 cm.$^{-1}$.

Cell B (Fig. 2) was designed and constructed by Kilpatrick and Luborsky. It consisted of a rimmed platinum cup, over which a Fluorothene plate was tightly screwed in place. An outer case of magnesium protected the platinum cup. The Fluorothene cap contained two openings. One was an inlet tube for solutes and acid, and was made of platinum. Through the other opening passed a short platinum wire. By distilling in HF until electrical contact was made with this wire, a constant liquid level in the cell was assured. The HF inlet tube and the platinum cup were used as the two electrodes. The cell constant was 0.271 cm.$^{-1}$. The experimental procedure was as follows. The solute was first added to the cell. In the case of antimony pentafluoride this was performed by introducing the viscous liquid through the platinum tube by means of a glass syringe. Acid was then distilled into the cell until contact was made with the platinum wire. The volume of the solution was known from a previous calibration. Successive dilutions were made by siphoning out part of the solution through the platinum tube until contact between it and the solution was broken. Pure HF was then distilled in until contact was restored with the platinum wire.

Cell C was designed by G. Balog and M. E. Runner primarily for use with the pure acid.[6] When solutes were to be added to the acid an auxiliary filling chamber was attached through a stopcock and $^1/_8$-inch Fluorothene tubing. The procedure for adding antimony pentafluoride was as follows. Satisfactory ampoules were made by sealing off lengths of $^1/_8$-inch Fluorothene tubing with hot pincers. These ampoules were then marked, and when ready for use were snipped open and dropped into the filling chamber. At the end of the experiment the ampoule fragments were recovered, and the difference in their weight and that of the original ampoule gave the weight of SbF_5 which had been added to the solution.

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[2] Post-doctoral Research Fellow under the American Chemical Society Petroleum Research Fund.

[3] M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **76**, 5865 (1954).

[4] K. Fredenhagen and G. Cadenbach, *Z. physik. Chem.*, **A146**, 245 (1930).

[5] M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953).

[6] M. E. Runner and G. Balog, *Anal. Chem.*, **28**, 1180 (1956); M. E. Runner, G. Balog and M. Kilpatrick, THIS JOURNAL, **78**, 5183 (1956).

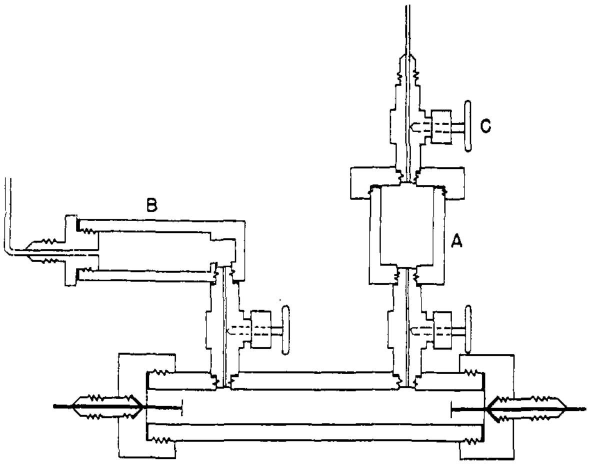

Fig. 1.—The conductance cell A.

The Transference Cell.—Cell D (Fig. 3) is a modified Hittorf three-compartment cell, constructed entirely from Fluorothene. A and C are the anode and cathode compartments, respectively, and B is the central compartment in which the composition of the solution should remain unchanged during the passage of the direct current. Stopcocks D and E allow the contents of each compartment to be thoroughly mixed without diffusion from one to another. Each compartment was fitted with a screw cap containing two openings. Through one opening passed an electrode wire, while the other was an outlet for the hydrogen and fluorine formed during the electrolysis. These waste gases passed along polythene tubes to bottles containing sulfuric acid. Other electrodes passed through the base of each compartment so that there were two electrodes in each, and each was a small conductance cell in itself. One electrode in each of the end compartments could be used for the passage of both direct and alternating current.

The HF solutions were analyzed by the measurement of their specific conductances. If, from separate experiments, values are obtained for the specific conductances of the fluorides which were used, then these values can be later used as standards, and the composition of a solution obtained from its conductance–composition graph. This type of analysis, besides being experimentally convenient, has an extra advantage. There will always be a certain amount of ionized water present in the solution which will carry some of the current. Less error is introduced by a method of analysis which measures the total concentration change of all ions in the solution, than by some form of gravimetric analysis which measures the concentration of metallic ions alone. Any water which infiltrates into the system during the course of the experiment will invalidate the analyses, but a small constant amount of water in the acid should not interfere, since the mobility of the H_3O^+ ion is unlikely to differ greatly from those of the alkali metal ions. A method of analysis similar to this has been used to measure the transference numbers of the nitronium and nitrate ions in anhydrous nitric acid.[7]

Other Apparatus.—The experiments at 0° were carried out in an oil thermostat, controlled to ±0.01°.

Resistance measurements were made on a Leeds and Northrup a.c. bridge. No frequency effect was observed through the range 500 to 2000 cycles/sec.

Materials.—Anhydrous hydrofluoric acid was prepared in a system designed and constructed by Balog and Runner, described elsewhere.[6]

The alkali fluorides were of reagent grade, and were dried and used without further purification.

Antimony Pentafluoride.—Harshaw technical grade SbF_5 was given a preliminary distillation from a platinum still fitted with aluminum head. This simple distillation converted the crude yellow-colored liquid into essentially two separate clear fractions, the first (about $^1/_3$ of the total volume) of which was quite mobile in comparison to the second and developed a white precipitate on standing. No attempt was made to identify this fraction or the precipitate. The second fraction was purified further by fractionation through a 20-cm. column packed with glass helices. The column was wound with a nichrome heating element for auxiliary heating, and the still head was provided with a system of stopcocks which allowed the distillation to be carried out in an inert atmosphere of nitrogen.

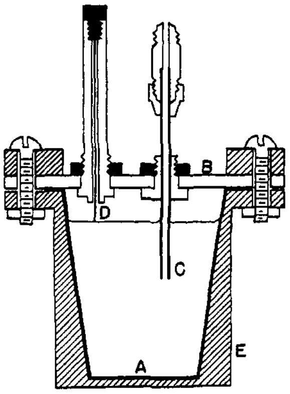

Fig. 2.—The conductance cell B.

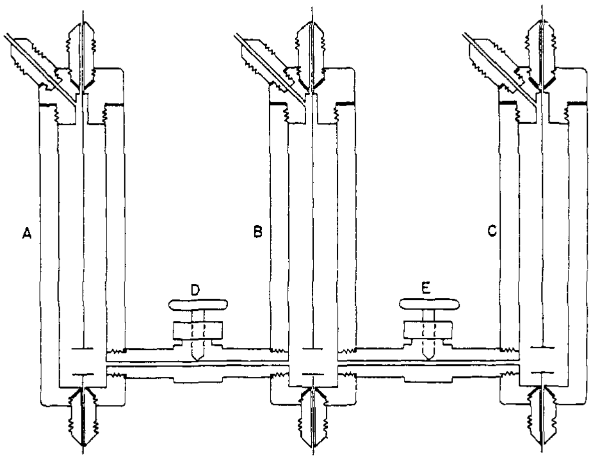

Fig. 3.—The transference cell.

The SbF_5 collected had a boiling range of 140–142° at a pressure of 751.2 mm. (lit. 142.7° at 760 mm.). The product solidified after prolonged cooling at −5° to a white solid which melted in the range 6.5–7.5° (lit. 7.0°). The melting point was determined by immersing the SbF_5 in a Dewar flask containing water initially at 0°, slowly raising the temperature of the water until melting of the SbF_5 was noted, then recording the reading of a thermometer immersed in the SbF_5. The solid–liquid mixture was mixed as much as possible during this period, but this effort was not very effective due to the very viscous nature of SbF_5.

The SbF_5 was then sealed into glass ampoules, being transferred to the ampoules by vacuum distillation.

Sodium fluoantimonate was prepared by mixing equimolar proportions of antimony pentafluoride and sodium fluoride in a Fluorothene vessel. HF was then distilled in until a clear solution was obtained. This was evaporated down until crystals formed, after which the supernatant liquid was removed through a siphon tube. This procedure was repeated until white crystals were obtained. These were dried in a vacuum desiccator.

Results

The experimental results are given in the following tables.

Discussion

All solutes studied appear to obey the Kohlrausch square root law, though in all cases the slope of the conductance–composition line is rather

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[7] W. H. Lee, Ph.D. Thesis, University of London, 1953.

TABLE I

THE EQUIVALENT CONDUCTANCES OF THE SOLUTIONS AT 0°

Molality	Equiv. conductance	Molality	Equiv. conductance
a. Sodium fluoride[a]		c. Antimony pentafluoride	
0.0144	376		
.0225	341	0.0041	236
.0305	315	.0041	239
.0332	219	.0072	230
.0353	326	.0073 [c]	245
.0378	315	.0127	212
.0446	314	.0128	225
.0597	298	.0224	201
.0665	298	.0242	199
.0888	276	.0355	200
.1100	265	.0460 [b]	170
.1348	246	.0609	168
.3177	205	.0694	161
b. Potassium fluoride[b]		d. Sodium fluoantimonate[c]	
0.00363	366	0.0035	278
.00451	360	.0065	257
.0124	364	.0070	254
.0167	332	.0085	258
.0179	353	.0121	277
.0243	332	.0126	234
.0256	332	.0144	247
		.0183	224
		.0215	210
		.0229	207
		.0403	193

[a] Measurements with cell A. [b] Measurements with cell C. [c] Measurements with cell B.

TABLE II

TRANSFERENCE NUMBERS WITH SODIUM FLUORIDE AT 0°

NaF, *m*	Coulombs passed	Equiv. transferred	t_{Na^+}
0.268	15.2	5.16×10^{-5}	0.32
.289	25.4	7.60×10^{-5}	.29
.334	25.8	7.74×10^{-5}	.29
.360	46.1	11.0×10^{-5}	.23
.600	78.0	26.0×10^{-5}	.32

TABLE III

TRANSFERENCE NUMBERS WITH POTASSIUM FLUORIDE AT 0°

KF, *m*	Coulombs	Equiv. transferred	t_{K^+}
0.0172	12.1	3.57×10^{-5}	0.29
.0233	6.1	1.75×10^{-5}	.28
.0258	7.3	2.66×10^{-5}	.35
.234	9.1	2.54×10^{-5}	.27
.237	27.3	9.07×10^{-5}	.32

TABLE IV

VARIATION WITH TEMPERATURE OF THE CONDUCTANCE OF KF SOLUTIONS

KF, *m*	Specific conductance $\times 10^3$, ohm^{-1} cm.$^{-1}$	Temp., °C.
0.00451	1.75	0
	1.26	−23
	0.70	−63
.0124	4.57	0
	3.71	−23
	2.23	−63
.0167	5.68	0
	4.19	−23
	2.44	−63
.0179	6.38	0
	5.23	−23
	2.43	−63
.0243	8.07	0
	6.23	−23
	3.78	−63

greater than that predicted by the Onsager limiting law. The Onsager slopes have been computed from the viscosity data of Simons and Dresdner[8] and the dielectric data of Fredenhagen and Dahmlos.[9]

Within our experimental accuracy, the conductance curves of sodium and potassium fluoride are indistinguishable. The square root law is followed to high concentrations, and the extrapolated equivalent conductance at infinite dilution is 391 with an experimental slope of 400 (theory 364).

From the shape of their conductance curves, antimony pentafluoride and sodium fluoantimonate are both shown to be strong electrolytes. Antimony pentafluoride ionizes according to the equation

$$SbF_5 + 2HF \longrightarrow H_2{}^+F + SbF_6{}^- \qquad (1)$$

The acidic nature of SbF_5 in anhydrous hydrofluoric acid has been reported previously.[10] Limiting equivalent conductances were again obtained by extrapolation. It was found that $(\Lambda_0)_{SbF_5} = 275$, and $(\Lambda_0)_{NaSbF_6} = 313$.

Except for those in Table IV, all specific conductances listed have been obtained by subtracting the specific conductance of the pure solvent from that of the solution. In the experiments with SbF_5 and $NaSbF_6$ the specific conductance of the initial acid was between 5×10^{-5} and $10 \times {}^{-5}\Omega^{-1}$, while less pure acid, varying between 1×10^{-4} and 10×10^{-4} was used in the alkali fluoride experiments. Pure acid is essential when studying SbF_5, since any fluoride ions initially present will combine with hydrogen ions liberated by the SbF_5 to reform HF.

The equivalent conductances obtained at −23 and −63° are too few and too scattered for a direct extrapolation to infinite dilution. However, if the assumption is made that the Onsager equation is obeyed, a value of the equivalent conductance at infinite dilution for each experimental point can be calculated from the equation $\Lambda_0 = \Lambda + A\sqrt{c}$. Since the constant A involves Λ_0 a method of successive approximations was used.

The transference numbers listed in Tables II and III clearly show that the bulk of the current is carried by the fluoride ion. Combining these transference numbers with the limiting equivalent conductances, a short table of ionic mobilities may be compiled.

The low mobility of the hydrogen ion clearly eliminates any possibility of a chain mechanism of conduction. But the mobility of the fluoride ion

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(8) J. H. Simons and R. D. Dresdner, THIS JOURNAL, **66**, 1070 (1944).

(9) K. Fredenhagen and J. Dahmlos, *Z. anorg. allgem. Chem.*, **178**, 272 (1928).

(10) L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, New York, N. Y., 1953.

TABLE V

IONIC MOBILITIES AT INFINITE DILUTION

Ion	Mobility		
	+20°	0°	−15°
Na^+	150	117	99
K^+	150	117	99
H^+	102	79	67
SbF_6^-	251	196	167
F^-	350	273	231
BF_4^{-a}	234	183	140

[a] From the investigation of Kilpatrick and Luborsky.[5]

is considerably higher than that of any other ion studied, and it may be that this ion is undergoing some abnormal process. This is the reverse of the situation occurring in ethanol and methanol, where the hydrogen ion is chain conducting, but the corresponding alcoholate ions have normal mobilities.

The literature contains few data relating the mobility of the hydrogen ion to the mobilities of the alkali metal ions in solvents other than water and the lower alcohols. Figures for liquid ammonia are available, however, and the following limiting equivalent conductances have been reported, at −40°, ammonium chloride 275, sodium chloride 290, ammonium perchlorate 272 and potassium chloride 307.[11] Here, in a solvent which does not support chain conducting, the mobility of the NH_4^+ ion, effectively a solvated proton, is rather less than the mobilities of the Na^+ and K^+ ions.

The factors which facilitate chain conducting are not known with any certainty. Some authors have emphasized the importance of the height of the potential barrier through which a proton must pass in its transfer from ion to solvent molecule.[12] These authors also discussed the proportionality of the abnormal conduction and the solvent autoprotolysis. Others have pointed out the necessity for the ion to have a dipolar structure.[13] Finally, the importance of three-dimensional hydrogen bonding in the solvent has been considered.[14]

From the above considerations one would not expect conditions to be as favorable for chain conducting in hydrofluoric acid as they are in water and sulfuric acid. HF is only linearly associated,[15] whilst the two other solvents mentioned are hydrogen bonded in three dimensions. Also, the low viscosity of HF will result in ions having a high Stokes' mobility, and any chain conducting may be completely masked. But of the ions H_2F^+ and HF_2^-, one would expect only the former to have a dipolar structure, and hence an abnormal mobility.

There is a mechanistic difference between the proton transfers in which the two ions, OH^- and $F{-}H{-}F^-$, take part. Consider the two cases

$$\text{H-O}^{\ominus} + \text{H-O-H} \longrightarrow \text{H-O-H} + {}^{\ominus}\text{O-H} \qquad (2)$$

$$\text{F-H-F}^{\ominus} + \text{H-F} \longrightarrow \text{F-H} + \text{F}^{\ominus}\text{-H-F} \qquad (3)$$

In the case of the hydroxyl ion, a solvent molecule splits up, and the hydrogen ion formed then attaches itself to a hydroxyl group. But in the case of the fluoride ion it is the ion which breaks up, and the fluorine formed attaches itself to an H–F molecule.

This picture is probably over simplified. The exact structure of the solvated fluoride ion is not known, but we have made rough calculations which suggest that a more highly solvated form than HF_2^-, probably $H_3F_4^-$, is the most stable form. These calculations were made both by the summation of the spectroscopic potential function and by the adoption of a simple electrostatic model. But the difference in energy between $H_3F_4^-$, $H_2F_3^-$ and $H_4F_5^-$ is small and HF molecules must be continually attaching themselves and breaking away from the fluoride ion group. This could immediately set up a situation to enhance the transfer of a charge. The solvated ion takes on an extra HF molecule into its chain with only a small increase in potential energy. An H–F group then splits away from the other end of the chain

$$\text{F-H-F-H-F-H-F}^{\ominus} + \text{H-F} \longrightarrow \text{F-H} + \text{F-H-F-H-F-H-F}^{\ominus} \qquad (4)$$

and the fluoride ion does not have to rotate before being in a position to repeat the process.

Acknowledgment.—The authors are indebted to Mr. G. Balog for pure specimens of antimony pentafluoride.

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