The Electrical Conductivity of Aqueous Solutions of Potassium Hexafluorophosphate and Sodium Monofluorophosphate[1]

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The salts of monofluorophosphoric acid have properties which are similar to those of sulphuric acid. Some monofluorophosphates are isomorphous with the corresponding sulphates. Alum-like double salts are known. The hexafluorophosphates are similar to the perchlorates in many of their properties (6).

Aqueous solutions of sodium monofluorophosphate are stable in neutral or alkaline solutions but are not stable in acid solutions or in solutions containing cations which form insoluble fluorides. Aqueous solutions of potassium hexafluorophosphate are very stable (6).

We have measured the electrical conductivity of aqueous solutions of potassium hexafluorophosphate and sodium monofluorophosphate with the object of determining the mode of ionization of these salts and whether these salts are strong or weak electrolytes.

EXPERIMENTAL

The conductance bridge was constructed following the design of Luder (4). Additional shielding of some of the components was found to improve the ease of obtaining a sharp null point. The control knob of the trimming condenser in parallel with the conductance cell was mounted on a six inch long lucite shaft, which allowed adjustments to be made without the effect in the capacitance of the operator's hand. A ground was provided for the operator.

The Luder bridge is a direct reading bridge since the ratio arms are equal (10,000 ohms). The decade resistances were assembled from decade units manufactured by the General Radio Company in two shielded boxes. The assembled resistances were calibrated to within ±0.05 ohms using a high quality D. C. Wheatstone bridge. Resistance as large as 211,111 ohms could be directly measured with the bridge. The smallest decade had steps of 0.1 ohm.

A Hewlett-Packard model 200A audio oscillator operating at 1000 cycles was coupled to the bridge by means of a General Radio type 578-B isolation transformer. A switch was installed between the transformer and the bridge so that the power to the bridge could be turned off between measurements. If the bridge is powered between runs there is a tendency for the cell to heat up and polarize.

The null point was detected using a tuned 1000 cycle audio amplifier constructed after the design of Luder (4) and a pair of earphones.

The absolute sensitivity of the bridge varied with the magnitude of the resistance being measured. The limit of usefulness of the 0.1 ohm decade was 10,000 ohms. The overall sensitivity of the bridge was approximately 5 parts in 100,000 from 2000 to 100,000 ohms.

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[1] Taken in part from the M. S. Thesis of David G. Rands. (1953)

Two conductivity cells were used in this research. Cell No. 1 was of the Washburn type, made of pyrex glass (Cenco No. 70015B) with a cell constant of 0.7554 cm^{-1} at 25°C. Cell No. 2 was also of the Washburn type made of pyrex glass but had a cell constant of 0.07212 cm^{-1} at 25°C. The electrodes in both cells were plated with platinum black and well aged in distilled water prior to use.

The cell constant of cell No. 1 was determined using a 0.01N solution of potassium chloride whose specific conductance was assumed to be 1.4114×10^{-3} ohm^{-1} cm^{-1} at 25°C. Conductivity water was used to make this solution. Cell No. 2 was intercompared with cell No. 1 using a 0.001N potassium chloride solution.

The cells were placed in a constant temperature bath and allowed to reach the bath temperature prior to measurement. Fifteen to twenty minutes was required for the cell to reach the bath temperature. The bath temperature was automatically maintained at 25 ± 0.02°C by the use of a conventional electronic regulator system. Kerosene was used as the bath liquid. The bath was cooled using a copper coil through which ice cold water was allowed to slowly flow.

The cell was rinsed three times with the solution prior to making the preliminary measurement. The cell was then emptied and refilled with the solution and a second measurement made. This procedure was repeated until successive values did not differ from each other by more than the expected error. Usually three or four fillings of the cell were required before satisfactory readings were obtained.

We conservatively estimate that the resistance values are accurate to within 0.05%. The principal error was caused by variations in the bath temperature. The temperature of a kerosene bath is more difficult to control than the temperature of a water bath.

The potassium hexafluorophosphate KPF_6 used in this research was donated by Dr. W. E. White of the Ozark-Mahoning Company. Dr. White had a sample of potassium hexafluorophosphate especially purified for our use. The solubility temperature relation for potassium hexafluorophosphate is such that recrystallization from water is feasible. KPF_6 may be analyzed using a nitron method (3) which is quantitative for the PF_6^- ion. Our analysis indicated that the sample was $99.6 \pm 0.2\%$ KPF_6. The *p*H of aqueous solutions of the sample was between 4 and 5 which may indicate a very small amount of potassium fluoride as impurity.

The sodium monofluorophosphate, Na_2PO_3F, was also donated by Dr. White. Dr. White had a sample specifically prepared for our use. Stoichiometric quantities of reagent grade sodium fluoride and sodium hexametaphosphate were fused together in a tightly closed platinum bottle. The fused mixture was poured on a plate and allowed to cool in a dessicator. Mr. Estill, of the Ozark-Mahoning Company, made an analysis of a sample of the sodium monofluorophosphate. He found 13.04% total fluorine (compared to 13.20% for Na_2PO_3F). Estill also analyzed for $PO_3F^=$ ion and found the sample to be 97.3% Na_2PO_3F. The methods available for fluorine and monofluorophosphate analysis are not completely satisfactory. There is reason to believe that the monofluorophosphate analysis method yields low results. In any case the Na_2PO_3F sample used in this research contained no more than 99% Na_2PO_3F. Sodium monofluorophate may not be purified by recrystallization from aqueous solutions. Extensive searches for a suitable solvent for recrystallization of this salt have not been successful. The purification method reported by Hill and Audrieth (2) was tested on an ordinary sample of sodium monofluorophate. Repeated application of the method of Hill and Audrieth failed to yield a sample of constant conductance.

TABLE I

Conductance of Sodium Monofluorophosphate

SOLUTION NO.	NORMALITY $\times 10^3$	K OBS $\times 10^3$ OHMS^{-1}	K SOLV $\times 10^6$ OHMS^{-1}	EQUIVALENT CONDUCTANCE OHMS^{-1}	Λ_0' OHMS^{-1}
1	26.13	2.399	1.14	91.77	119.8
2	6.464	0.6558	1.28	101.3	115.0
3	1.915	0.2049	1.28	106.3	113.8
4	0.7901	0.08692	1.28	108.4	113.2
1A	62.62	5.271	1.82	84.14	128.8
2A	18.17	1.720	1.82	94.55	117.8
3A	5.891	0.5997	1.10	101.6	114.7
4A	1.877	0.2015	1.10	106.8	114.2
1B	78.20	6.429	0.904	82.19	132.6
2B	28.72	2.617	1.16	91.08	120.6
3B	7.442	0.7497	1.16	100.6	115.3
4B	1.594	0.1724	1.16	107.3	114.1
1C	106.6	8.469	1.08	79.43	139.5
2C	25.32	2.342	1.11	92.45	120.1
3C	4.339	0.4509	1.11	103.7	114.9
4C	0.7958	0.08775	1.04	109.0	113.8
1D	301.7	20.64	1.09	68.40	181.7
2D	118.9	9.280	1.09	78.04	142.6
3D	63.38	5.327	1.09	84.03	129.0
4D	35.27	3.155	1.09	89.42	122.3
5D	12.37	3.199	1.19	96.84	115.9

TABLE II

Conductance of Potassium Hexafluorophosphate

SOLUTION NO.	NORMALITY x 10^3	K OBS x 10^3 OHMS^{-1}	K SOLV x 10^6 OHMS^{-1}	EQUIVALENT CONDUCTANCE OHMS^{-1}	Λ_0[†] OHMS^{-1}
1	11.78	1.437	1.35	121.9	131.7
2	3.819	0.4822	1.35	125.9	131.5
3	0.9660	0.1244	1.14	127.6	130.4
4	0.1264	0.01751*	1.14	129.5	130.5
1A	15.33	1.839	1.14	119.9	131.0
2A	3.063	0.3865	1.14	125.8	130.8
1B	6.472	0.8017	1.20	123.7	130.9
2B	2.249	0.2843	1.20	125.9	130.1
3B	1.025	0.1316	1.19	127.2	130.1
4B	0.4164	0.05474	1.19	128.6	130.4

* This solution measured in No. 2 Washburn Cell. $K_2 = 0.07212\ cm^{-1}$.

Conductivity water was prepared by redistilling distilled water to which alkaline permanganate had been added in an all glass (Pyrex) still. The still was run for several weeks before reasonable conductivity water was obtained. To avoid contamination of the condensate the still was equipped with a trap between the flask and the condenser. The neck of the 5 liter distillation flask was wound with a helix of nichrome wire which allowed the neck to be kept above the condensing temperature of the water vapor. This heating of the flask neck reduces the tendency of soluble impurities being carried over by a liquid film.

The date obtained in this research for the conductivity of sodium monofluorophosphate and potassium hexafluorophosphate are given in Tables I and II respectively.

ANALYSIS OF DATA

According to the modern theory of electrolytic conductance due to Debye and Onsager the equivalent conductance of a dilute solution of a strong electrolyte is a linear function of the square root of the concentration. This limiting law may be written (5):

$$\Lambda = \Lambda_o - (A + B\,\Lambda_o)\sqrt{C} \qquad (1)$$

where $\Lambda = 1000K/C$, Λ_o the limiting equivalent conductance of the substance, C the concentration in equivalents per liter, A a numerical constant which is a function of the temperature, viscosity and dielectric constant of the solvent and B is another numerical constant which is a function of the temperature and dielectric constant of the solvent. Both A and B also depend upon the valence type of the electrolyte and the relative mobilities

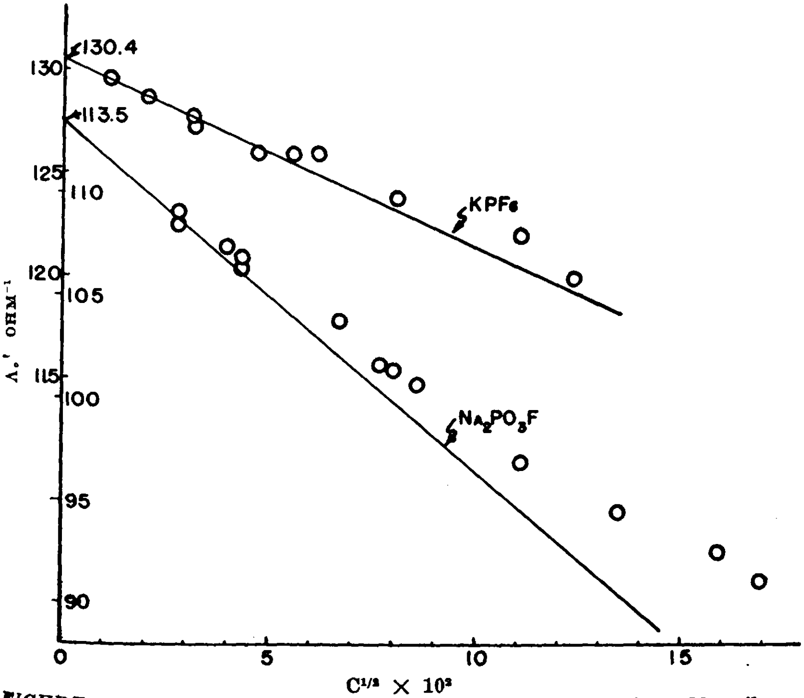

FIGURE 1. *Conductivities of Aqueous Solutions of Sodium Monofluorophosphate and Potassium Hexafluorophosphate at 25°C.*

of the anion and cation. For any 1-1 electrolyte in water at 25°C A and B have the values 60.19 and 0.2289 respectively. If sodium monofluorophosphate is assumed to be a 2-1 electrolyte with a limiting conductance of 113.5 ohm^{-1} then A and B are 110.6 and 0.5265 respectively.

A plot of the equivalent conductance of the two salts studied in this research against the square root of the normality is shown in Figure 1. The straight lines drawn on this figure are the loci predicted by the Onsager-Debye equation (1). It is seen that the experimental points lie above the theoretical line. This type of deviation from theory has been found to be characteristic of strong electrolytes.

To compute the best value of the limiting conductance, Λ_o, we have used the method of Shedlovsky. Equation 1, when solved for Λ_o gives the equation:

$$\Lambda_o' = \frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} \qquad (2)$$

where Λ_o' is written in place of Λ_o. It is found that Λ_o' is not a constant but a function of the concentration. For 1-1 and many 2-1 electrolytes Λ_o' is found to be a linear function of the concentration. Therefore, a plot of Λ_o' vs C will give a straight line which may be extrapolated to zero concentration to find Λ_o. Graphs of Λ_o' *vs* C for the salts studied in this research are shown in Figure 2. From these graphs the limiting conductances of sodium monofluorophosphate and potassium hexafluorophosphate are found to be 113.5±0.5 and 130.4±0.5 ohm^{-1} respectively. The uncertainties attached to these values have been estimated taking the purity of the compounds into account.

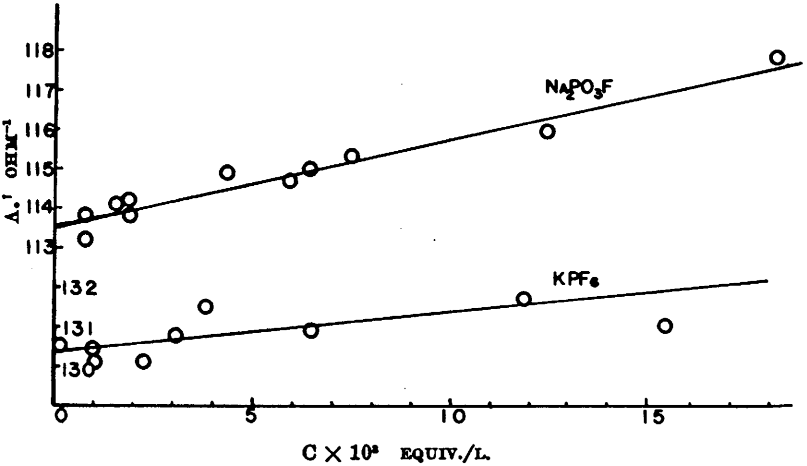

FIGURE 2. Shedlovsky Plots of Apparent Limiting Conductivities for Na_2PO_3F and KPF_6.

From the values given by Harned and Owen (1) for the limiting ionic conductances of the sodium and potassium ions, 50.15 and 73.50 ohm^{-1} respectively one may compute the limiting conductance of the $PO_3F^{=}$ ion to be 63.3±0.5 ohm^{-1} while the PF_6^- ion has a value of 56.9±0.5 ohm^{-1}. These values are for 25°C.

SUMMARY

The conductivities of dilute aqueous solutions of sodium monofluorophosphate and potassium hexafluorophosphate have been measured at 25°C. Both of these salts are found to be strong electrolytes and to ionize in the manner expected from their formula, i.e. KPF_6 is a 1-1 electrolyte while Na_2PO_3F is a 2-1 electrolyte. The limiting equivalent conductances are found to be 113.5±0.5 ohm^{-1} for sodium monofluorophosphate and 130.4±0.5 ohm^{-1} for potassium hexafluorophosphate.

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