The hydrogen atom transfer mechanism implied above is particularly attractive in that it furnishes a ready explanation of the role of hydrogen in the reaction and does not involve extensive rearrangement of the hydration shells of the reactants. Similar arguments have been advanced for many of the aqueous reactions of the actinides, and evidence for or against hydrogen atom transfer has been sought by determining the kinetic isotope effect produced by the substitution of deuterium.[16] However, interpretation of the results is generally ambiguous due to unknown effects of D_2O on solvation.[21]

For the present case the gross kinetic isotope effect at 25° is indicated from Table I to be $k_H/k_D = 1.61 \pm 0.05$. This value must be corrected for the deuterium effect on the prior hydrolysis equilibrium (equation 7). Using the hydrolysis quotient results previously determined,[15] we obtain the net corrected value $k_{8H}/k_{8D} = 1.4 \pm 0.1$. Although these results are consistent with the concept of a hydrogen atom transfer mechanism, heavy water effects of comparable magnitude have been observed in reactions that do not explicitly involve hydrogen or water,[21,22] hence the observations cannot be cited as unambiguous evidence for the proposed mechanism. Alternatively we may postulate a direct electron transfer mechanism with the product UOH^{+4} reacting rapidly to give UO_2^{+2} after the dismutation of the activated complex.

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(21) A. E. Ogard and H. Taube, THIS JOURNAL, **80**, 1084 (1958).

(22) S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF ALABAMA, UNIVERSITY, ALABAMA]

The Equivalent Conductance of the Hexafluorocomplexes of Group IV (Si, Ge, Sn, Ti, Zr, Hf)[1]

BY ROBERT H. SCHMITT,[2a,b] E. L. GROVE AND R. D. BROWN

RECEIVED DECEMBER 30, 1959

The limiting equivalent conductance values have been determined for the hexafluorocomplex ions of six elements in Group IV. The potassium, rubidium and cesium salts for each of the fluorocomplexes were prepared and used in determining the value. The plot Λ *vs.* $C^{1/2}$ yielded the curve of the typical weak electrolyte. However, when these values were corrected for the hydronium ion contribution, the plots yielded a straight line corresponding to the equation $\Lambda = \Lambda_0 - bC^{1/2}$.

The limiting equivalent conductance values for the hexafluorocomplex ions of silicon, germanium, tin, titanium, zirconium and hafnium were determined in aqueous solution. The potassium, rubidium and cesium salts of each of the above hexafluorocomplexes were prepared and purified, and their corrected equivalent conductance values were determined. The use of three salts for each of the hexafluorocomplexes served as a means of checking the quality of the procedure and the limiting equivalent conductance value determined.

Experimental

Apparatus and Method.—The basic equipment consisted of the Leeds and Northrup Jones conductance bridge, Hewett-Packard Audio Oscillator Model 200AB, the Kay Lab Twin-T rejection filter No. 503A placed between the bridge and detector and a Dumont 401 oscilloscope and ear phones as detectors. The conductance cells were of the design recommended by Jones and Bollinger.[3]

The constant temperature bath, in which paraffin oil was used as the liquid, was controlled with a Labline #3202 differential thermoregulator. Due to the properties of the paraffin oil, large temperature gradients were found in the bath when the usual knife-blade or resistance-coil heating elements were used. An infrared heating lamp placed above the bath produced very even heating. A kerosene-oil mixture at 14 ± 1° from an external refrigeration unit was circulated through the cooling coils of the bath. The temperature of this bath, as measured with a Leeds and Northrup platinum resistance thermometer and a Mueller bridge assembly, both with National Bureau of Standards Certificates, was held at 25.00 ± 0.005° for several months.

The Leeds and Northrup *p*H Indicator Assembly was used for all *p*H measurements. After the *p*H of a given solution had been determined, it was closely bracketed with standard solutions as *p*H 4.20 and 4.40.

Materials.—Most of the hexafluorocomplex salts were prepared by adding the alkali halide to the hexafluorocomplex acid and precipitating the resulting hexafluorocomplex salt, filtering, washing and recrystallizing the salt several times. These compounds were prepared in platinum and/or polyethylene containers. De-ionized water was used in all steps. The prepared salts were examined spectrographically for impurities.

Hexafluorosilicates.—The cesium hexafluorosilicate was prepared by double decomposition of previously prepared cesium hexafluorostannate. The latter salt is about four times as soluble as the former.

Hexafluorogermanates.—Potassium hexafluorogermanate was prepared according to the method given by Brauer.[4] The rubidium and cesium salts were prepared in a similar manner except that rubidium fluoride was used instead of the chloride.

Hexafluorostannates.—The potassium hexafluorostannate was prepared by the method described by Marignac.[5] The rubidium and cesium salts were prepared by using alpha-stannic oxide. Calcium carbonate was added to concentrated stannic chloride solution until further addition produced no effervescence. The gelatinous white precipitate, alpha-stannic oxide, was thoroughly washed, then partially dissolved in 48% hydrochloric acid. After about 12 hr. the clear supernatant liquid, containing the hexafluorostannic acid, was siphoned off, concentrated and filtered. The fluorostannic acid was carefully added to solutions of rubidium chloride and cesium chloride till no further precipitation took place.

Hexafluorotitanate.—Very pure titanium dioxide, prepared according to Brauer,[6] was dissolved in excess hydrofluoric acid, and then the concentrated solution of alkali halide was

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(2) (a) 14 Rue De La Paix, Schiltigheim, France. (b) Abstracted from the dissertation presented by Robert H. Schmitt in partial fulfillment of the requirements for the doctorate degree.

(3) G. Jones and G. M. Bollinger, THIS JOURNAL, **53**, 411 (1931).

(4) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 544.

(5) J. C. Marignac, *Ann. Minnes.*, **15**, 221 (1859).

(6) G. Brauer, *ibid.*, p. 857.

added to the fluorotitanic acid. Rubidium fluoride was used in place of rubidium chloride.

Hexafluorozirconate.—The zirconium oxide was not purified, since the chief impurity, hafnium, is easily removed by recrystallizations of the hexafluorozirconate salt. Rubidium fluoride was again used in place of rubidium chloride.

Hexafluorohafniates.—Recrystallization of these salts is very important, since this is the only method to remove any zirconium that may be present.

Potassium Chloride.—Reagent grade potassium chloride was repurified[7] for the conductivity cell constant determinations. A spectrographic examination indicated that no other alkali or alkaline earth elements were present. The potassium chloride solutions, made up according to the Jones and Bradshaw[8] definition of demal solution, were kept in sealed polyethylene bottles so that the cell constant could be checked often with identical solutions; 0.1 and 0.01*D* concentrations were used. Experimental determinations indicated that the resistance of the potassium chloride solution, near 25°, became constant 30 minutes after having been placed in the constant temperature bath, whereas the variation in resistance for the fluorocomplex solution was at a minimum after 30 to 35 minutes; this variation would introduce less than 0.01% error. Thus readings for both the potassium chloride and the fluorocomplex solutions were taken at 30 and at 35 minutes. To insure that any reaction and/or absorption of the complex ion had not changed the cell constant, this constant was determined before and after each conductivity determination of a hexafluorocomplex solution.

Results and Discussion

The uncorrected and corrected equivalent conductances of the several concentrations of the potassium, rubidium and cesium salts of the hexafluorocomplexes are shown in Table I. The column *h* represents the degree of hydrolysis of the hexafluorocomplex ion.

The plot for the uncorrected equivalent conductances *vs.* $C^{1/2}$, where *C* is concentration in equivalents per liter, yields the curve of a typical weak electrolyte, Fig. 1. However, cryoscopic determinations carried out with 0.01, 0.02 and 0.03 molar hexafluorocomplex compounds in aqueous solution indicated that three ions were formed for each molecule of salt present. In addition, the *p*H values of the solutions were found to be relatively constant for the concentration ranges from 10^{-1} to 10^{-4} equivalent per liter.

From the above observations the following equilibria were postulated, where the symbol M represents an element of Group IV. For the potassium salt the dissociation is represented as

$$K_2MF_6 \rightleftarrows 2K^+ + MF_6^{-2} \qquad (1)$$

Then, due to the competition of hydroxyl ions with the fluoride ions as substituents in the coordination sphere of the hexafluorocomplexes

$$MF_6^{-2} + 2n\ HOH \rightleftarrows MF_{6-n}(OH)_n^{-2} + nF^- + nH_3O^+ \qquad (2)$$

The value of *n* is small. The values for *h*, Table I, indicate that the reaction represented by equation 2 does not go to completion even to the extent of the replacement of one fluoride ion with the hydroxyl ion. If *n* becomes large, as upon the addition of OH^- from a strong base, the complex becomes insoluble and precipitates as a hydrate. Then

$$H_3O^+ + F^- \rightleftarrows HF + H_2O \qquad (3)$$

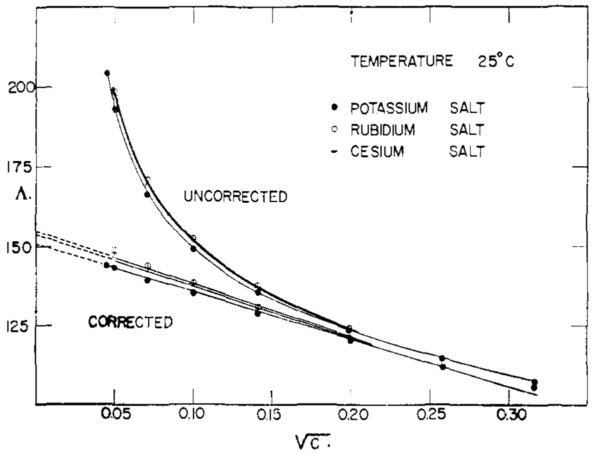

Fig. 1.—Equivalent conductance of the hexafluorotitanates.

The *p*H values for the range of concentrations of the different solutions remained relatively constant, Table I. As the solutions are diluted, the decrease in total concentration is compensated for by a shift in equilibrium, to the extent that the *p*H values remain constant.

Since the *p*H remains approximately constant, as the concentration of the hexafluorocomplex is decreased the contribution of the fast moving hydronium ion becomes a major factor in the conductance of the solution. This results in a sharp increase in the equivalent conductance at the low concentrations. To obtain the conductance due to the salt, the original conductance values are corrected for the hydronium ion contribution. This correction, as adopted from Owen and Gurry[9] is summarized:

Since the hydronium ion concentration can be approximated from *p*H measurements, and if Δk represents the change in specific conductance for the hydronium ion, then

$$\lambda H_3O^+ \times C_{H_3O^+} = 1000\ \Delta k$$

Since in dilute solutions $H_3O^+ = 350$

$$\Delta\Lambda = \text{correction} = C_{H_3O^+} \times 350/C_{salt}$$

therefore Λ salt $= \Lambda - \Delta\Lambda$

Since the reaction to the right of equilibrium 2 is small, it is assumed that the fluoride ion and the hydroxypentafluoro"M" ion formed will compensate for the loss of the hexafluoro"M" ion. The corrected data for each salt fall on a straight line corresponding to the equation $\Lambda = \Lambda_0 - bC^{1/2}$.

Taking the limiting equivalent conductance values for potassium, rubidium and cesium to be 73.5, 77.8 and 77.3, respectively,[10] and applying the Kohlrausch law of independent migration of ions, the values of the limiting equivalent conductances determined for the fluorocomplex ions are found to be as listed in Table II.

The errors are introduced mainly by the correction term calculated from the *p*H measurement. It is estimated that the *p*H readings are accurate within ±0.02 *p*H unit. The corrected values calculated from the *p*H data vary within the limits

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[7] R. D. Brown, W. B. Bunger, W. L. Marshall and C. H. Secoy, THIS JOURNAL, **76**, 1532 (1954).

[8] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[9] B. B. Owen and R. W. Gurry, *ibid.*, **60**, 3074 (1938).

[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 231.

TABLE I

CONDUCTANCE DATA AT 25°

Complex ion	C[a]	Potassium				Rubidium				Cesium			
		Λ	pH	Λ[b]	h	Λ	pH	Λ[b]	h	Λ	pH	Λ[b]	h
SiF_6^{-2}	0.0400									121.2	3.30	116.8	0.044
	.0200									138.7	3.29	129.8	.091
	.0100	156.3	3.29	138.3	0.18	160.4	3.29	142.5	0.18	159.7	3.29	141.8	.18
	.0081					169.5	3.29	146.9	.22				
	.0050	184.5	3.28	147.7	.37	188.9	3.28	152.2	.37	188.2	3.28	151.5	.37
	.0036	201.1	3.28	150.2	.52								
	.0025	229.1	3.28	155.7	.75	234.4	3.28	161.0	.75	233.0	3.28	159.6	.75
GeF_6^{-2}	.0400	116.6	3.27	111.9	.043								
	.0300					128.4	3.27	122.0	.064	128.1	3.27	121.7	.064
	.0200	140.5	3.25	130.7	.10	142.4	3.25	132.6	.10	142.0	3.25	132.2	.10
	.0140	151.3	3.24	136.9	.15	153.7	3.24	139.4	.15	153.1	3.24	138.6	.15
	.0098	164.1	3.23	143.0	.23	167.9	3.23	146.8	.23	167.0	3.23	146.0	.23
	.0049	199.7	3.22	156.6	.47	203.4	3.22	160.4	.47	202.5	3.22	159.5	.47
	.00245	257.6	3.21	169.8	.97	261.5	3.21	173.4	.97	280.3	3.21	172.3	.97
SnF_6^{-2}	.1111	105.8	3.23	104.0	.020					105.9	3.23	104.1	.020
	.0666	114.0	3.25	111.0	.031					114.8	3.25	111.8	.031
	.0400	122.1	3.30	117.7	.044	125.2	3.30	120.8	.044	123.6	3.30	119.2	.044
	.0200	133.4	3.32	125.0	.082	137.3	3.32	128.9	.082	136.4	3.32	128.0	.082
	.0100	145.3	3.32	128.6	.16	149.7	3.32	133.0	.16	148.8	3.32	132.1	.16
	.0050	161.2	3.33	128.5	.32	165.4	3.33	132.7	.32	165.0	3.33	132.3	.32
	.0025	202.8	3.33	137.3	.64	208.1	3.33	142.6	.64	206.9	3.33	141.4	.64
TiF_6^{-2}	.1000	107.4	3.42	105.7	.012								
	.0666	114.7	3.42	112.2	.018								
	.0400	123.6	3.43	120.3	.029	124.3	3.43	121.0	.024	124.0	3.43	120.7	.029
	.0200	135.6	3.42	129.0	.060	137.7	3.42	131.1	.060	137.1	3.42	130.5	.060
	.0100	149.0	3.41	135.4	.12	152.3	3.41	138.7	.12	151.8	3.41	138.2	.12
	.0050	166.3	3.42	139.6	.24	170.9	3.42	144.2	.24	170.1	3.42	143.4	.24
	.0025	193.0	3.45	143.3	.45	198.7	3.45	149.0	.45	197.9	3.45	148.2	.45
	.0020	204.6	3.46	143.9	.53								
ZrF_6^{-2}	.0800	113.0	4.42	112.8	.0010	113.0	4.42	112.8	.0010	112.9	4.42	112.7	.0010
	.0400	121.2	4.42	120.9	.0020	122.7	4.42	122.4	.0020	122.3	4.42	122.0	.0020
	.0200	128.4	4.48	127.8	.0035	130.7	4.48	130.6	.0035	130.3	4.48	129.7	.0035
	.0140	131.5	4.50	130.7	.0047	134.3	4.50	133.5	.0047	133.8	4.50	133.0	.0047
	.0098	134.0	4.52	132.9	.0064	137.5	4.52	136.4	.0064	136.9	4.52	135.8	.0064
	.0049	138.5	4.53	136.4	.013	142.8	4.53	140.7	.013	142.1	4.53	140.0	.013
	.00245	143.0	4.53	138.8	.025	147.7	4.53	143.5	.025	146.9	4.53	142.7	.025
HfF_6^{-2}	.0800	113.4	4.42	113.2	.0010	114.6	4.42	114.4	.0010	114.6	4.42	114.4	.0010
	.0400	122.5	4.42	122.2	.0020	124.9	4.42	124.5	.0020	124.4	4.42	124.1	.0020
	.0200	130.5	4.48	129.9	.0035	133.2	4.48	132.6	.0035	132.9	4.48	132.3	.0035
	.0100	136.5	4.52	135.4	.0063	139.9	4.52	138.8	.0063	139.4	4.52	138.3	.0063
	.0050	140.8	4.53	138.7	.012	145.0	4.53	142.9	.012	144.3	4.53	142.2	.012
	.0025	144.5	4.53	140.3	.025	149.3	4.53	145.1	.025	148.5	4.53	144.3	.025

[a] *C*, concentration in equivalents per liter. [b] Λ, corrected equivalent conductance.

TABLE II

LIMITING EQUIVALENT CONDUCTANCE FOR THE HEXAFLUOROCOMPLEX IONS

SiF_6^{-2}	91 + 1.5%	TiF_6^{-2}	77 + 1.0%
GeF_6^{-2}	100 + 1.5%	ZrF_6^{-2}	72 + 0.2%
SnF_6^{-2}	69 + 1.0%	HfF_6^{-2}	75 + 0.2%

shown in Table II. The correction and the correction error were less for the hexafluorozirconates and hexafluorohafniates since the reaction for these ions in equilibrium 2 is less than for the other hexafluorocomplex ions.

The degree of hydrolysis, or *h*, is the approximate molar concentration of fluoride ion from the hexafluorocomplex divided by the molar concentration of this salt. This approximate concentration of fluoride ion is the sum of the concentration of the fluoride ion in solution (equal to the hydronium ion concentration) and the concentration of the unionized hydrofluoric acid. The values for *h*, Table I, were found to be less than 1 for the relatively strong hexafluorosilicic and hexafluorogermanic acids. The values for *h* for the hexafluorozirconates and hexafluorohafniates were found to be very small. Thus, the hexafluorosilicate and hexafluorogermanic ions behave as relatively strong Lewis acids while the hexafluorozirconate and hexafluorohafniate ions act as relatively weak Lewis acids.

The solubility of some of these salts could not be found in the literature, and for others, if more than one solubility was listed, there was usually wide disagreement. To determine the solubilities, two saturated solutions for each salt were prepared at 40°, and with constant stirring these solutions were brought to equilibrium at 25°. Known volumes were evaporated to dryness at 70°, weighed and then kept over P_2O_5 for several days and reweighed. In addition two saturated solutions for each salt were prepared below 20° and brought to equilibrium at 25° and then treated as above. All solutions were handled in polyethylene ware. Spectrographic analyses of these salts showed no or only minor traces of impurities. The solubilities are listed in Table III.

TABLE III

SOLUBILITIES OF THE HEXAFLUOROCOMPLEXES AT 25°

Compound	Solution, mole/l.
K_2SiF_6	0.00572
Rb_2SiF_6	.00690
Ce_2SiF_6	.0234
K_2GeF_6	.0221
Rb_2GeF_6	.0167
Ce_2GeF_6	.0471
K_2SnF_6	.128
Rb_2SnF_6	.0615
Ce_2SnF_6	.0792
K_2TiF_6	.0595
Rb_2TiF_5	.0248
Cs_2TiF_6	.0551
K_2ZrF_6	.0812
Rb_2ZrF_6	.0848
Cs_2ZrF_6	.112
K_2HfF_6	.128
Rb_2HfF_6	.186
Cs_2HfF_6	.174

Acknowledgment.—The spectrographic analysis of the salts prepared for this research was performed by Mr. Ellis Creitz of the United States Bureau of Mines.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA]

The Conductance of Tetra-*n*-butylammonium Picrate in Benzene–*o*-dichlorobenzene Solvent Mixtures at 25°

BY W. R. GILKERSON AND R. E. STAMM

RECEIVED MARCH 7, 1960

The conductance of tetra-*n*-butylammonium picrate as a function of concentration has been determined in 75, 50, 25, 10 and 0 mole % *o*-dichlorobenzene and benzene solvent mixtures at 25°. The ion pair dissociation constant *K* and limiting equivalent conductance have been obtained. The latter does not follow Walden's rule. From the slope of a log *K versus* reciprocal dielectric constant plot, a distance of closest approach, *a*, of 6.64 Å. was obtained.

The exact dependence of the ion pair dissociation constant *K* for the process in solution upon di-

$$AB \rightleftharpoons A^+ + B^-$$

electric constant, temperature, nature of the solvent and nature of the salt has been the subject of considerable recent discussion.[1–5] In order to pinpoint the various factors which affect the pairing process a wide variety of systems must be studied. Fuoss and co-workers (see ref. 5) are investigating salts in polar–nonpolar solvent mixtures in the dielectric range 20 to 78.5. Stern and co-workers are studying salts in pure solvents in the low dielectric range of 10 to 5 (ref. 3). We report here an examination of the pairing of tetra-*n*-butylammonium picrate in benzene-*o*-dichlorobenzene (*o*-DCB) mixtures as solvent. This system ranges in dielectric constant from 2.275 to 10.0 (see Table I). The salt chosen is soluble enough over the entire range of solvent composition. Since the dipole moment of *o*-DCB is 2.5 debyes,[6] while benzene has no moment, we might expect preferential solvation by the former if dipole–ion interaction is the predominant feature of this effect. Further, the salt chosen has been examined in pure *o*-DCB by several workers.[3,7,8] The values of the dissociation constant *K* and the limiting equivalent conductance Λ_0 are in good agreement at 25°.

Experimental

Solvents.—Benzene (Merck reagent grade) was recrystallized, passed through a 35 × 2 cm. column packed with Alcoa activated alumina, grade F-20, refluxed over sodium ribbon for 30 minutes and distilled on a three foot packed column, b.p. 80.1°. The middle cut was again passed through an alumina column prior to use. The specific conductance of the pure benzene was 4×10^{-13} ohms^{-1} cm.$^{-1}$.

o-DCB (Eastman red label) was passed through the alumina column and distilled at 10 mm., b.p. 62°. The middle cut was passed through the alumina column prior to use. The specific conductance of the *o*-DCB was 1.3×10^{-9} ohms^{-1} cm.$^{-1}$. Solvent mixtures were made up by weight.

Salt.—The tetra-*n*-butylammonium picrate was prepared as described previously (ref. 4). Solutions were prepared in a nitrogen-filled drybox.

Cells.—Two of these were of the Kraus type, having cell constants of 0.03000 and 0.01800 as determined by intercomparison with a 0.01D KCl solution.[9] The third cell was originally designed[10] as a capacitance cell but has been used here to determine the conductance of the most dilute benzene solutions. The air capacity of the cell was determined to be 24.57 pf., using benzene as a standard. The cell constant, for conductance purposes, was found to be 0.00474 by comparison with one of the other cells.

Conductance Measurements.—Two bridges were used. For the lower resistances, the Leeds and Northrup bridge

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[1] J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

[2] R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

[3] P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

[4] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[5] H. Sadek and R. M. Fuoss, THIS JOURNAL, **81**, 4511 (1959).

[6] E. C. Hurdis and C. P. Smyth, *ibid.*, **64**, 2212 (1942).

[7] F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **39**, 917 (1953).

[8] H. L. Curry and W. R. Gilkerson, THIS JOURNAL, **79**, 4021 (1957).

[9] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[10] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).