[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Electrometric Titrations of Zirconium and Hafnium Solutions[1]

BY EDWIN M. LARSEN AND ADRIAN M. GAMMILL

Previous quantitative investigations of the changes in *p*H during the addition of bases to solutions of zirconium salts appear to be limited to single studies of zirconium in chloride and sulfate solutions.[2,3,4]

Since the concentration effects on the *p*H of precipitation have not been reported for zirconium solutions, and since no data are available for hafnium solutions, it was deemed advisable to undertake an investigation of the solutions of these elements with the more common anions in order to establish differences in the behavior of these two elements.

Experimental

Materials Used.—The low hafnium-zirconium was prepared by phosphate fractionation[5] and the low zirconium-hafnium was obtained as a commercial preparation. Further purification involved the removal of silicon dioxide with hydrofluoric acid, and recrystallization of the oxychloride 8-hydrates. Spectrographic analyses[6] showed an impurity of 0.4% hafnium in the zirconium and 0.75% zirconium in the hafnium preparation.

Inasmuch as it is difficult, if not impossible, to prepare the normal oxysalts of the sulfate, nitrate and perchlorate, solutions of these were prepared by precipitating the hydroxides or hydrous oxides from the oxychloride solutions, and then digesting the washed precipitate in sufficient 8 *N* hot acid so that upon dilution the cation concentration would be approximately 0.038 *M* and the anion concentration 0.152 *N*. The chloride solutions were prepared by dissolving the oxychloride in sufficient dilute hydrochloric acid to yield a solution with the same cation to anion ratio as above. All the stock solutions thus contained 2 moles of acid in excess (except for the sulfate solutions which contained only 1 mole of acid in excess) of that necessary to give a solution which would conform in composition to a solution of the oxysalt. This was done to give a stock solution of greater stability, and so that the precipitation point could be approached more slowly.

Standardization was effected by gravimetric determination of zirconium and hafnium as the oxides, and by total acidity determinations for the anions. The standard base (0.1010 *N*) was prepared by diluting a concentrated carbonate-free solution of sodium hydroxide with carbon dioxide-free water, and standardizing against potassium hydrogen phthalate.

Experimental Procedure.—The effect of dilution for each salt was determined by titrations over an eight-fold dilution range at approximately the following initial cation concentrations: 0.038, 0.019, 0.0095 and 0.0047 *M*. The effect of the anion concentration was observed by adding sufficient acid to increase the anion–cation ratio from 4 to 6 and to 9 at the 0.0095 *M* cation concentration.

The titrations of 50-ml. samples were carried out in 250-ml. beakers placed in a thermostat controlled at 25 ± 0.05°. The change in *p*H during the titration was followed with a Beckman model G *p*H meter, the glass electrode of which was repeatedly calibrated against a *p*H 4.0 buffer. In addition buffers at *p*H 1.4, 6.0 and 8 were used to check the linearity of the *p*H scale. Approximately five-minute intervals were allowed for the attainment of equilibrium between the addition of increments of sodium hydroxide with the size of the increment dependent on the portion of the titration curve being titrated, it being 0.5 ml. or less near the points of precipitation and coagulation. The mixture was stirred by bubbling nitrogen through the solution.

The points of precipitation and coagulation were determined with the aid of a beam of light conducted down a lucite rod to the base of the beaker opposite the observer. Since a variety of terms have been used to describe significant points in similar work, definitions of the reproducible points noted in this work are as follows. The *p*H of precipitation was that *p*H at which a permanent turbidity was just visible to the naked eye as viewed opposite the beam of light. The *p*H of coagulation was that *p*H at which the precipitate coagulated and the supernatant liquid was clear as viewed opposite a beam of light. It was found that the reproducibility of these points was of the order of ±0.05 *p*H unit for the solutions of highest concentration and approximately ±0.07 *p*H unit at the lowest concentrations.

Results and Discussion

Chloride, Nitrate and Perchlorate Solutions.—Representative titration curves for zirconium and hafnium solutions of the three anions at initial metal ion concentrations of approximately 0.038 *M* and with an anion–cation ratio of 4 are given in Fig. 1. These curves start from the point where the composition of the solution is equivalent to MOX_2. The curves for all the runs are practically superimposable except for differences in the initial *p*H, and the *p*H's of precipitation and coagulation. The latter two points are designated by doubly and singly barbed arrows, respectively. The titration curve does not deviate greatly from a strong acid–strong base curve, differing by the presence of a buffering region between the points of precipitation and coagulation. No inflection is

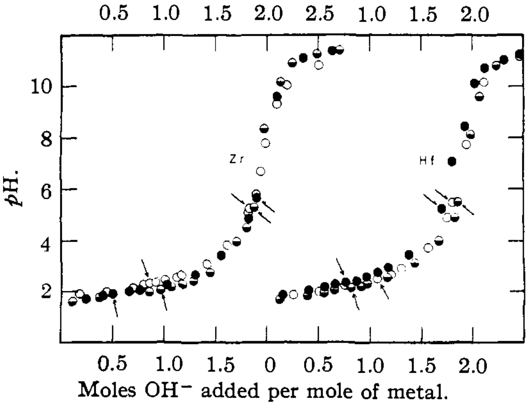

Fig. 1.—The relationship between the *p*H of the solution and the ratio of the moles of hydroxyl ion added per mole of zirconium or hafnium in perchlorate ◒, chloride ●, and nitrate ○ solutions.

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[1] Based on research carried out under Task Order 4 of Contract N7onr-28504 between the Office of Naval Research and the University of Wisconsin.

[2] Hildebrand, THIS JOURNAL, **35**, 847 (1913).

[3] Britton, *J. Chem. Soc.*, **127**, 2120 (1925).

[4] Kurbatov and Kurbatov, *J. Chem. Phys.*, **13**, 208 (1945).

[5] Larsen, Fernelius and Quill, *Ind. Eng. Chem.*, **15**, 512 (1943).

[6] C. Feldman, Oak Ridge National Laboratories.

observed at the point of precipitation, nor is there any evidence of redissolving of the precipitate at higher pH's. The curve rises steeply as the ratio of moles of hydroxyl ion added to the moles of metal ion in MOX_2 approaches the theoretical value of 2.

The points of coagulation are all below the theoretical value of 2, but usually are within a milliliter or less of the theoretical quantity of 0.1 N sodium hydroxide used in the titrations. The appearance of the coagulation point before the theoretical value has been interpreted as signifying[3,7] the formation of basic salts with the hydroxyl ion deficiency being made up by the anion present in the solution. One could assume as well, however, that the extensively hydrolyzed species already present, reacted further with water to form the neutral metal hydroxide or hydrated oxide and the hydronium ion, the latter ion then being titrated to the end-point.

The pH's of precipitation and the ratios of moles of hydroxyl ion added to the metal ion concentration, the R values, are given in Table I as a function of the metal ion concentration at precipitation. The anion–cation ratio for these systems was approximately 4. The metal ion concentration is expressed as $M(OH)_x^{4-x}$ although the molar concentration probably is only a fraction of this value owing to polymeric ion formation.

TABLE I

EFFECT OF DILUTION ON THE PRECIPITATION OF ZIRCONIUM AND HAFNIUM HYDROXIDES

Anion	Metal ion concn., moles/l. at pptn. $\times 10^3$ Zr	Hf	Salt concn., moles/l. at pptn. $\times 10^2$	pH pptn.	R pptn.	R coagulation
ClO_4^-	18.0		5.3	2.05	0.87	1.87
	12.2		3.6	2.16	.82	1.89
	7.5		2.2	2.31	.77	1.89
	4.2		1.2	2.47	.81	1.91
		18.6	5.2	2.13	.80	1.96
		12.6	3.5	2.23	.75	1.87
		7.6	2.1	2.38	.75	1.86
		4.3	1.2	2.60	.87	1.91
Cl^-	20.0		4.8	1.88	.50	1.88
	13.4		3.0	1.97	.34	1.83
	7.9		1.7	2.14	.23	1.94
	4.3		0.9	2.29	.23	1.93
		19.1	5.1	2.34	.73	1.70
		12.7	3.5	2.43	.81	1.75
		7.7	2.1	2.49	.76	1.82
		4.3	1.2	2.73	.88	1.86
NO_3^-	17.2		5.7	2.34	.85	1.83
	12.2		3.8	2.36	.69	1.73
	7.6		2.1	2.39	.36	1.86
	4.3		1.2	2.40	.24	1.80
		17.8	8.3	2.47	1.07	1.80
		12.1	3.5	2.48	0.96	1.80
		7.4	2.1	2.57	0.86	1.86
		4.1	1.2	2.87	1.01	1.90

Several significant trends can be observed in these data. In all cases the hafnium solutions have a higher pH of precipitation than the zirconium solutions. This is consistent with the general principle that the basicity of an ion in solution follows in the same order as the crystal ion sizes. Since Zr^{+4} is slightly smaller than Hf^{+4} one would, on this basis, expect the zirconium to have a lower pH of precipitation value; and since the difference is only 0.01 Å., one would not expect to observe large differences in the pH's of precipitation. It is interesting to note therefore that the differences in the pH of precipitation in perchlorate solutions are very small, while in nitrate and chloride solutions the differences are much larger. The behavior in the perchlorate solutions would be in agreement with the present idea[8] that little or no anion–cation complexing occurs in perchlorate solutions. The relatively large differences in the pH's of precipitation for zirconium and hafnium in nitrate and chloride solutions can be considered to be a reflection of differences in the degree of cation–anion interaction.

The differences in the behavior of the chloride and nitrate solutions are even more striking when the R values at the precipitation point are considered. In a titration of a salt which yields an insoluble precipitate one would expect the R value to be constant at all metal ion concentrations if the composition of the precipitate were the same, and if the cation–anion ratio were constant, except for the salt effect on the solubility of the compound. In the dilution runs the ionic strengths[9] of the solutions varied from 0.1 to 0.02 over the range of concentrations studied. One would expect the solubility to decrease with decreasing salt concentration. Therefore the precipitate should appear at progressively lower R values. A slight trend in this direction is noted in the perchlorate solutions of zirconium and hafnium, and in the hafnium nitrate and chloride solutions. It was also observed that the R values generally rose in the last dilution, an effect similar to that observed in the precipitation studies on the rare earths by Trombe.[10] In the zirconium chloride and nitrate solutions, however, the decrease in R values is more likely due to changes in the composition of the precipitate, with zirconium having a greater tendency to form insoluble basic salts than hafnium.

The effect of increase in anion concentration on the R value is shown in Table II. The increased anion concentration results in a higher R value of precipitation although the magnitude of the effect is not the same in all cases. For all the hafnium solutions and the zirconium perchlorate solutions, the over-all effect is approximately the same. The zirconium nitrate and chloride solutions showed a more pronounced effect due to the in-

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[7] Ruer, *Z. anorg. Chem.*, **42**, 87 (1904).

[8] Connick and McVey, THIS JOURNAL, **71**, 3182 (1949).

[9] Ionic strength calculated on the assumption that $M(OH)_2^{++}$ was the ionic species.

[10] Trombe, *Compt. rend.*, **216**, 888 (1943).

TABLE II

EFFECT OF INCREASED ANION–CATION RATIO ON THE PRECIPITATION OF ZIRCONIUM AND HAFNIUM HYDROXIDES

Anion	Metal ion concn., moles/l. at pptn. × 10^3 Zr	Hf	Anion-cation ratio	Salt concn. at pptn. × 10^2	*p*H pptn.	*R* pptn.	
ClO_4^-	7.5		4.0	2.2	2.31	0.87	0.34
	6.6		5.6	3.0	2.56	1.03	
	4.7		11.9	5.1	2.77	1.21	
		7.6	4.0	2.2	2.37	0.87	0.34
		5.5	6.0	3.3	2.66	1.08	
		5.2	9.7	4.6	2.84	1.21	
Cl^-	7.9		3.9	1.7	2.14	0.23	0.59
	6.2		6.9	3.5	2.54	0.85	
	5.3		9.7	4.4	2.68	0.82	
		7.5	4.0	2.2	2.49	0.75	0.35
		6.6	6.1	3.2	2.70	0.98	
		5.4	9.2	4.4	2.88	1.10	
NO_3^-	7.7		4.4	2.1	2.39	0.36	0.77
	6.5		6.0	3.1	2.51	0.83	
	5.1		9.8	4.6	2.81	1.13	
		7.4	4.0	2.1	2.57	0.86	0.40
		5.9	7.1	3.8	3.02	1.28	
		5.1	9.7	4.6	3.27	1.26	

crease in anion concentration, thus emphasizing the differences between zirconium and hafnium already shown in the dilution runs. This phenomenon probably is the result of several contributing factors which cannot be resolved by the present data. It cannot be simply due to anion–cation complexing, for this would require that the perchlorate ion behave in the same fashion as the nitrate and chloride. Nor does it seem to be solely a salt effect since the anion concentration was increased by the addition of the appropriate acid, whereupon the actual salt concentration at precipitation for these runs did not differ greatly because of the dilution during the titration. In fact the variation in salt concentration in these runs is much less than in the dilution runs at constant anion–cation ratio, under which condition the *R* values were reasonably constant.

There is some question whether or not such systems can be treated as equilibrium systems. Britton,[11] however, states that it is possible to arrive at solubility products from data such as these which are in good agreement with those obtained by other methods. It has been customary in cases such as these to calculate solubility products[12,13] on the assumption that the first appearance of a precipitate gives the *p*H at which the solubility product of the precipitated compound is first exceeded.

If an equilibrium is established and if the points of precipitation are of significance then the logarithm of the hydroxyl ion concentration should be a linear function of the logarithm of the metal ion concentration over the precipitation range. This is expressed

$$M(OH)_4 \longleftrightarrow M(OH)_x^{4-x} + (4-x)(OH^-) \quad (1)$$

$$K_{sp} = [M(OH)_x^{4-x}][OH]^{4-x} \quad (2)$$

$$\log K_{sp} = \log M(OH)_x^{4-x} + (4-x)\log OH^- \quad (3)$$

It is seen from these equations that if one plots logarithm $M(OH)_x^{4-x}$ against the logarithm of the hydroxyl ion, the value of the charge on the metal ion can be calculated from the slope of the line $x - 4$.

To evaluate the solubility products only the data from the perchlorate solutions were used, since in this system, as evidenced by the previous data, complex ion formation and basic salt formation probably were at a minimum. The data for these plots were obtained as follows: For a given titration the metal ion concentration remaining in solution at any point in the precipitation range was found by correcting for the amount precipitated, on the assumption that the precipitation started at the *p*H of precipitation and ended at the *p*H of coagulation. The hydroxyl ion concentration was obtained from *p*H measurements, using 14 for pK_w at 25°. The ionic strength of a given solution remained essentially constant over this range. These data for a set of dilution runs are plotted in Fig. 2. Equation (3) has been found to be valid over three-fourths of the precipitation range, deviating appreciably from linear-

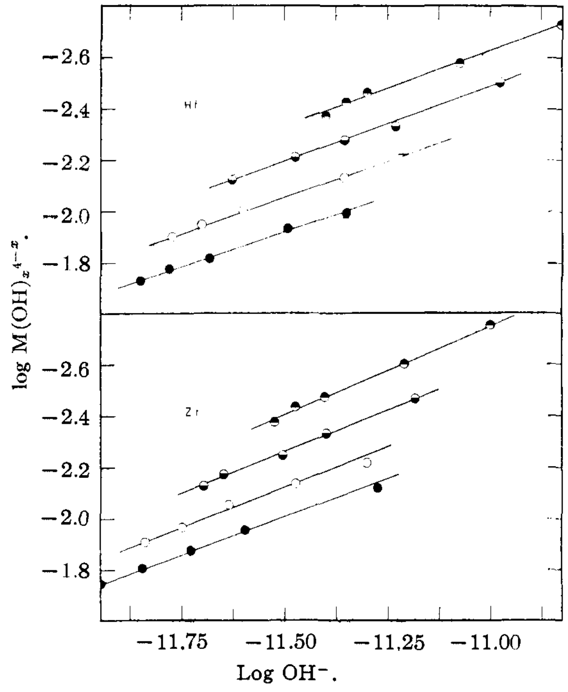

Fig. 2.—The relationship between the hydroxyl ion concentration and the zirconium or hafnium ion concentrations in perchlorate solutions, over three-fourths of the precipitation range at different ionic strengths: $\sqrt{\mu}$ = 0.13 ◓, 0.17 ◒, 0.22 O and 0.27 ●,

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[11] Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, N. Y., 1929, p. 256.

[12] (a) Evans and Pryor, *J. Chem. Soc.*, **S1**, 157 (1949); (b) Moeller, THIS JOURNAL, **63**, 2625 (1941).

[13] Moeller and Kremers, *J. Phys. Chem.*, **48**, 395 (1944).

ity as the coagulation point is approached. The slope of the linear portion of the curve is −0.6. The average number of hydroxyls on the metal ion species has been calculated to be 3.4 and the charge on the ion +0.6. This has been interpreted to mean that a polymeric species exists in solution over three-fourths of the precipitation range with the average formula $(M(OH)_{3.4}^{+0.6})_n$. Solubility products calculated for a set of dilution runs at the *p*H of precipitation from these data are given in Table III. It can be seen that the solubility product decreases with decreasing ionic strength of the solution as would be expected. The ionic strengths of the solutions were calculated on the basis of the $M(OH)_{3.4}^{+0.6}$ ion. Calculations based on multiples of this ion would change the value slightly.

TABLE III

SOLUBILITY PRODUCTS OF ZIRCONIUM AND HAFNIUM HYDROXIDES IN PERCHLORATE SOLUTIONS

Metal ion concn., moles/l. × 10³		OH ion concn., moles/l. × 10¹²	*pK*	$\sqrt{\mu}$
Zr	Hf			
18.0		1.12	8.92	0.27
12.2		1.46	9.01	.22
7.5		2.04	9.13	.17
4.2		2.95	9.29	.13
	18.6	1.35	8.85	.27
	12.6	1.70	8.96	.22
	7.6	2.40	9.09	.17
	4.3	3.98	9.21	.13

Solubility products calculated on the basis of the $M(OH)_2^{++}$ ion in solution for the same systems give 3×10^{-26} for zirconium and 4×10^{-26} for hafnium. This compares favorably to the 1×10^{-26} value for zirconium hydroxide calculated by Latimer[14] from Britton's data.[3] Latimer also estimated the value for hafnium to be 1×10^{-25}.

Sulfate Solutions.—The present study indicates a marked difference in the behavior of the sulfate solutions of zirconium and hafnium as contrasted to the behavior of the nitrate, chloride and perchlorate solutions. Sulfate solutions of the composition $MOSO_4$ were not stable as evidenced by the fact that precipitation always occurred before the excess acid present had been neutralized. Even in the presence of excess acid it was difficult to prepare solutions for dilution runs because of the tendency toward spontaneous precipitation. For this reason it was necessary to prepare the solutions and make the titrations as soon as possible.

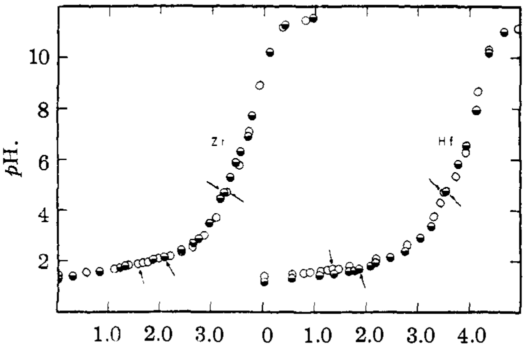

Fig. 3.—The relationship between the *p*H of the solution and the moles of hydroxyl ion added per mole of zirconium or hafnium ions in sulfate solution at the following initial metal ion concentrations: ● 0.037, ○ 0.0185.

Plotted in Fig. 3 as *p*H *vs.* the mole ratio of added hydroxyl ion (total) to the metal ion concentration are the data for two of the dilution runs in which the sulfate to metal ion concentration was approximately 2. The points of precipitation and coagulation are shown by the doubly and singly barbed arrows, respectively. The precipitate which first appeared was very granular and dense in nature compared to the flocculent precipitates obtained in the previous cases. As the initial metal ion concentration was reduced the precipitate appeared at lower hydroxyl ion to metal ion ratios, indicating the probable change in the composition of an insoluble basic salt. The curves show many little irregularities with a definite break occurring near the coagulation point. The coagulation point is much below the theoretical value of 4. Because of the slow production of insoluble hydrolysis products these data are difficult to interpret. The only conclusion one can safely draw is that at equivalent metal ion concentrations, and anion–cation ratios, the hafnium precipitates at a lower *p*H than the zirconium. Table IV contains a summary of the more important data obtained in these experiments.

TABLE IV

THE EFFECT OF DILUTION AND OF THE ANION CONCENTRATION ON THE *p*H OF PRECIPITATION FOR THE SULFATE SOLUTIONS

Metal ion concn. at pptn.		*p*H pptn.	Anion–cation ratio
Zr	Hf		
0.0211		2.16	
.0145		1.83	1.93
.0089		1.83	
	0.0231	1.67	
	.0153	1.70	2.06
.0155		2.17	
.0121		1.85	2.89
.0083		1.61	
	.0217	1.72	
	.0151	1.62	2.14
.0145		2.15	
.0115		2.16	3.3
.0075		2.00	
.0046		1.91	
	.0133	2.08	
	.0098	2.09	3.66
	.0066	1.84	

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[14] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 253-254.

Acknowledgment.—The authors acknowledge that the research on the chemistry of zirconium and hafnium has been supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

1. The *p*H of precipitation of hafnium hydroxide is always higher than for zirconium hydroxide for the perchlorate, nitrate and chloride solutions at equivalent concentrations.

2. The difference in the *p*H of precipitation for zirconium and hafnium from perchlorate solutions is very small, but the difference is quite marked in the nitrate and chloride solutions. The zirconium precipitates at progressively lower ratios of hydroxyl ion added to the metal ion concentration as the metal ion concentration is reduced, whereas the hafnium precipitates at nearly constant ratios.

3. Increased anion concentration increases the *p*H of precipitation in all cases.

4. For the sulfate solutions, the hafnium precipitates at lower *p*H's than the zirconium. The precipitates were probably basic sulfates.

5. For the perchlorate solutions, over three-fourths of the precipitation range, the logarithm of the hydroxyl ion concentration is a linear function of the metal ion concentration. From the slope of -0.6, the average formula of the ion in solution is shown to be $(M(OH)^{+0.6}_{3.4})_n$.

6. Solubility products for zirconium and hafnium hydroxides are calculated.

MADISON, WIS. RECEIVED FEBRUARY 7, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Interaction of Aluminum Bromide with Alkyl Halides and Benzene[1]

BY ROSS E. VAN DYKE

I. Introduction

It is generally assumed that in alkyl halide solutions of the aluminum halides the aluminum coordinates the halogen from the alkyl halide and forms the AlX_4^- ion. Support for this theory appears to be based upon the case of the double salts formed by the aluminum halides and alkali metal halides in which the AlX_4^- ion appears to be a stable configuration.[2] The principal experimental evidence presented in support of this theory is due to Wertyporoch,[3] who electrolyzed solutions of aluminum bromide in ethyl bromide and reports for some solutions a higher concentration of aluminum in the vicinity of the anode than was observed at the cathode. On the basis of these experiments many investigators have accepted the interaction between ethyl bromide and aluminum bromide as presented in Eq. 1.

$$C_2H_5Br + AlBr_3 \rightleftarrows C_2H_5^+ + AlBr_4^- \qquad (1)$$

The molar conductance of aluminum bromide in methyl bromide is of the order of 2×10^{-2}, while the dielectric constant of the solvent is about 10 at 0°.[4] These results indicate that the ionic concentration of these solutions is small and that the extent of interaction between solute and solvent is very small compared with that observed in the case of more basic solvents such as pyridine.[4] In order to gain additional information as to the nature and extent of interaction between alkyl bromides and aluminum bromide, several phase studies and electrolysis experiments have been carried out. These results as well as the results of some studies with benzene as solvent are reported here.

II. Experimental

1. Materials.—Anhydrous aluminum bromide was prepared and purified as described by Jacober and Kraus.[4] The capillaries attached to the filled ampules were sealed off with no contamination of the salt.

Ethyl bromide (ether free, Eastman Kodak Co. product) was pretreated with aluminum bromide. The alkyl halide was then scrubbed in the vapor phase at 40° with dilute alkali solution and condensed on anhydrous calcium chloride. Final drying was accomplished with finely divided activated aluminum oxide in a stainless steel cylinder. Methyl bromide (Matheson product) was purified in a similar manner.

Benzene (C. P., J. T. Baker product) was further purified as described by Batson and Kraus.[5] The product was subjected to several fractional crystallizations and was finally distilled from sodium as needed.

2. Apparatus and Method.—The vapor pressure–composition studies were carried out as described previously.[6] Vapor pressures were read with a cathetometer and closed-end manometer. Temperature control in these experiments was maintained with a precision of ±0.1°.

Solutions for electrolysis were prepared by condensing the alkyl halide onto weighed aluminum bromide ampules in a large evacuated flask. The ampules were easily cracked with careful shaking. The flask was equipped with an outlet stopcock for sampling and another for transfer to the migration apparatus (Fig. 1). With the solution flask sealed to the migration cell at A, the solution was transferred to the evacuated cell with the aid of dry nitrogen pressure when necessary. Upon conclusion of electrolysis, samples of approximately equal size were withdrawn simultaneously from the two legs of the H tube into the evacuated sample flasks D and E. These flasks were then sealed off just below stopcocks B and C. The narrow necks of the sample flakes were graduated in 0.1-ml. divisions from which the total volume of sample could be

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[1] The contents of this paper have been presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1949.

[2] Kendall, Crittenden and Miller, THIS JOURNAL, **45**, 963 (1923).

[3] Wertyporoch, *Ber.*, **64B**, 1369 (1931).

[4] Jacober and Kraus, THIS JOURNAL, **71**, 2405 (1949).

[5] Batson and Kraus, *ibid.*, **56**, 2017 (1934).

[6] Van Dyke and Crawford, *ibid.*, **72**, 2829 (1950).