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 $(\mathrm{M(OH)}^{+0.6}_{3.4})_n$.

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.

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

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).

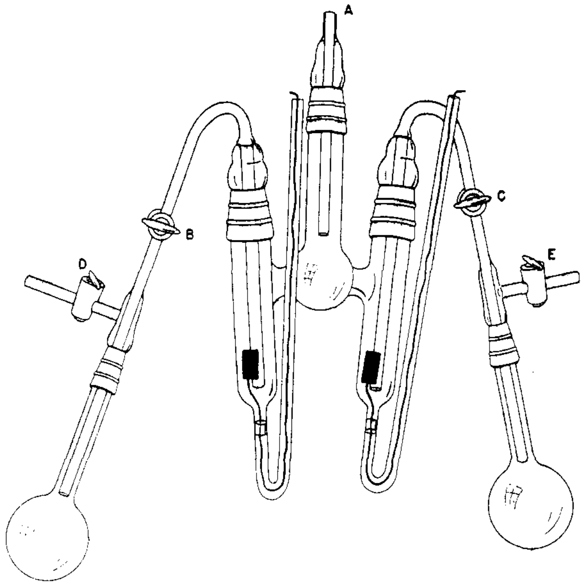

Fig. 1.—Electrolysis apparatus.

determined. The migration cell had a volume of approximately 150 ml. and was equipped with bright platinum electrodes which were attached as described previously.[7] The electrolyses were carried out at −78° by means of a 400 volt d. c. filtered power supply with the current varying between 1 and 5 milliamp. depending upon the concentration. Dow-Corning silicone and du Pont FCD-441 perfluorogrease were used as stopcock lubricants.

Analyses.—Aluminum was determined by the 8-hydroxyquinoline procedure. The metal deposited at the cathode was separated by filtration, washed with dry ethyl bromide and dissolved in dilute acid for analysis.

Molecular Weights.—The molecular weight of aluminum bromide in benzene was determined by the Beckmann method using a magnetic stirrer. Solvent freezing points were reproducible on the Beckmann thermometer with a precision of ±0.001°.

III. Results

The vapor pressure–composition data for alkyl halide and benzene solutions of aluminum bromide are presented in Tables I and II. Several series of data are presented graphically for each system in Figs. 2, 3 and 4. Numerical values of one series for each system are presented in the tables.

Table I

A. $AlBr_3$–C_2H_5Br System at 25°		B. $AlBr_3$–CH_3Br System at −58.3°	
P, cm.	Mole ratio C_2H_5Br/$AlBr_3$	P, cm	Mole ratio CH_3Br/$AlBr_3$
41.50	7.555	3.64	7.570
37.34	4.880	3.36	5.382
29.59	2.695	3.06	3.835
21.35	1.800	1.86	1.931
16.36	1.405	1.43	1.480
5.85	0.484	1.42	1.241
5.21	.159	1.38	0.873
0.00	.000	1.38	.662
		1.37	.414
		0.00	.00

Table II

$AlBr_3$–C_6H_6 System at 15°

P, cm	Mole ratio C_6H_6/$AlBr_3$
5.34	8.140
5.18	4.755
5.17	3.598
5.09	1.788
5.13	1.008
2.14	0.585
2.60	0.418
0.00	0.000

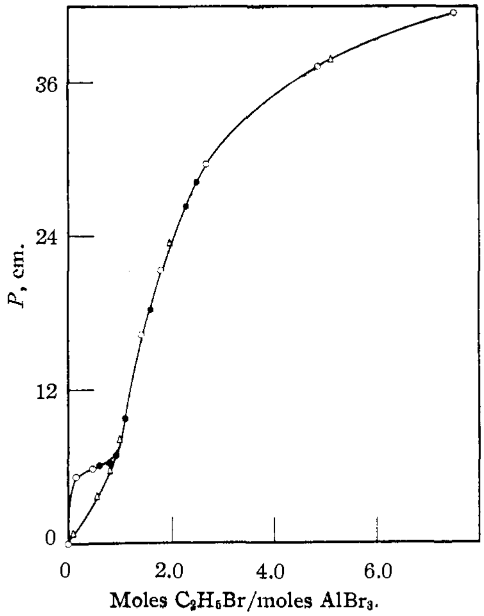

Fig. 2.—Vapor pressure–composition diagram for ethyl bromide solutions at 25°.

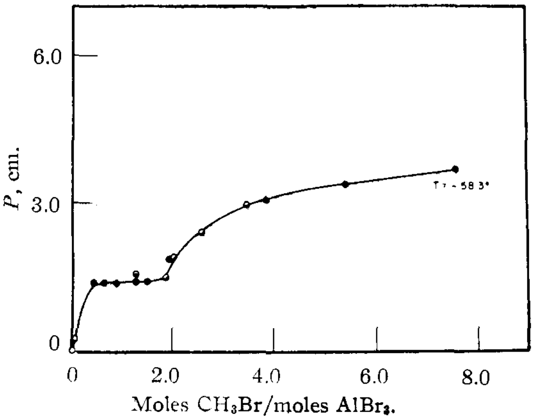

Fig. 3.—Vapor pressure–composition diagram for methyl bromide solutions.

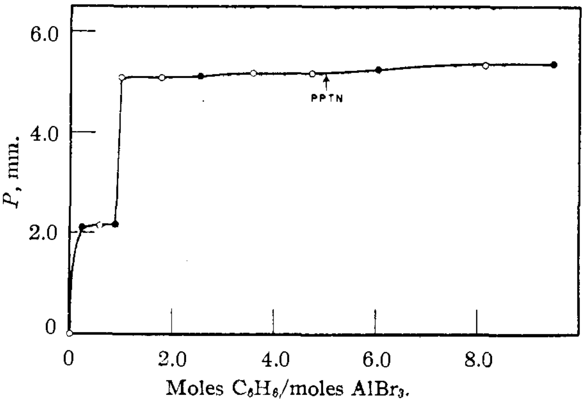

Fig. 4.—Vapor pressure–composition diagram for benzene solutions at 15°.

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(7) Hnizda and Kraus, This Journal, **71**, 1565 (1949).

IV. Discussion

Alkyl Halide Solutions.—According to Fig. 2 the vapor pressure of ethyl bromide solutions of aluminum bromide decreases sharply with increasing concentration. At a point approximating a molar ratio near unity a break appears in the curve which coincides with the observed deposition of a solid phase. The absence of a second break in the curve indicates that the solid phase must be aluminum bromide. Solutions of aluminum bromide in ethyl bromide are extremely sensitive to impurities. For example, as shown in Fig. 2 for a solution contaminated by apiezon stopcock lubricant (data represented by triangles) the vapor pressure curve does not exhibit a pronounced break in coincidence with the separation of a solid phase at a molar ratio of approximately 1.0. This indicates that the hydrocarbon impurity disrupts the equilibrium between phases with probable cracking of the ethyl bromide to some extent.

Apparent molecular weight values for aluminum bromide in ethyl bromide were calculated from vapor pressure data at 25°, assuming the validity of Raoult's law. These values are presented in Table III.

TABLE III

Apparent mol. wt.	Molal concn.
267.0	0.4075
257	1.211
206	1.879
167	3.400

These values indicate that aluminum bromide is monomeric in ethyl bromide solution. The decrease in apparent molecular weight at very high concentrations may be due in part to the fact that the assumption of Raoult is not valid in this range. The apparent absence of a definite complex of aluminum bromide in ethyl bromide indicates that the monomeric salt must be stabilized by a solvation energy somewhat in excess of the association energy of the dimeric salt.

The results for methyl bromide solutions as shown graphically in Fig. 3 are in substantial agreement with those for ethyl bromide solutions. Morris[8] has determined the vapor pressure curve for methyl bromide solutions of aluminum bromide at 0°. At this temperature the curve exhibits but one break at a molar ratio of approximately 1.2. According to Fig. 3 for methyl bromide solutions at $-58.3°$ a plateau appears at a molar ratio approximating two which coincides with the deposition of a solid phase. The appearance of only one such break in the vapor pressure curve indicates that the solid phase must be aluminum bromide. According to these results it appears that the temperature coefficient of solubility of aluminum bromide in methyl bromide is exceedingly small.

Methyl or ethyl bromide solutions of aluminum bromides are colorless when prepared with due precautions as to moisture or hydrocarbon stopcock lubricants. In the course of these studies it was observed that methyl bromide solutions were less sensitive to such contamination than were the ethyl bromide solutions. The electrolyses were, therefore, carried out at $-78°$ with methyl bromide as solvent. The results of two electrolysis experiments are summarized in Table IV.

TABLE IV

ELECTROLYSIS OF ALUMINUM BROMIDE IN METHYL BROMIDE AT $-78°$

Solution used, ml.	127.0	132.0
Orig. soln., mmoles. $AlBr_3$/ml.	0.915	0.602
Anode soln., mmoles. $AlBr_3$/ml.	0.913	0.601
Cathode soln., mmoles $AlBr_3$/ml.	0.869	0.561
Equiv. of electricity, faradays	0.00624	0.00790
Calcd. Al, mmoles.	2.08	2.63
Recov. Al, mmoles.	1.15	1.55

The principal electrode reactions involve deposition of metallic aluminum at the cathode and liberation of bromine at the anode. It was not possible to make a quantitative recovery of these products due to the very finely divided state of the aluminum deposit and the diffusion of bromine to some extent through the solution. These results indicate that aluminum bromide dissociates to form Br^- and probably $AlBr_2^+$ ions. At the cathode, disproportionation of the $AlBr_2^+$ ion occurs with deposition of aluminum. According to Table IV about 55–60% of the calculated quantity of aluminum was recovered (assuming no secondary reactions). If one assumes a secondary reaction involving migration of $AlBr_4^-$ to the anode with or without liberation of bromine, the aluminum concentration should increase in the neighborhood of this electrode. As may be seen from the third column in Table IV this is clearly not the case. On the other hand a comparison of data in columns 2, 3 and 4 suggests that the anion is the predominant carrier of the current in these solutions which is in accord with the proposal that the principal ionic species are Br^- and $AlBr_2^+$.

It is of interest to note that in electrolyzing solutions which were contaminated by apiezon grease no appreciable deposits of aluminum or bromine were observed. These solutions were brownish-yellow in color and had a higher specific conductance than did the uncontaminated solutions. The aluminum concentration did not change appreciably at either electrode and such changes as did take place were not reproducible either in magnitude or direction. This phase of the problem will require further investigation.

Benzene Solutions.—Plotnikov[9] reports indications of compound formation between benzene and aluminum bromide from melting point–composition phase studies. However, the com-

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(8) C. L. Morris, Thesis, Brown University, June, 1941.

(9) Plotnikov and Gratsianskii, *Bull. Acad. Sci., U. R. S. S. Classe Sci. Chem.*, 101–104 (1947).

position reported does not coincide with that of a definite molecular complex. According to Fig. 4 benzene forms a complex containing one mole of benzene per mole of aluminum bromide which has a decomposition pressure of approximately 2.0 cm. at 15°. The system is homogeneous for molar ratios of $C_6H_6/AlBr_3$ of approximately 5.0 and above. For molar ratios less than 5.0 the complex precipitates at 15°. Ulich[10] has reported molecular weight values for aluminum bromide in benzene ranging from 511 to 463 in the molal concentration range of from 0.3 to 0.040. In contrast to these values, this Laboratory, using the freezing point method, has obtained reproducible values of 534.0 for concentrations as low as 0.0820 molal. This determination is extremely sensitive to traces of moisture, which fact may well account for the results of Ulich. These results would indicate, therefore, that the complex $Al_2Br_6{\cdot}2C_6H_6$ does not dissociate appreciably in this concentration range.

Acknowledgment.—The author wishes to express his indebtedness to Mr. Harry E. Crawford for valuable assistance rendered in connection with some of these experiments.

V. Summary

1. Addition compounds of methyl or ethyl bromide with aluminum bromide are not indicated from vapor pressure–composition diagrams. In benzene a complex is formed having a composition corresponding to 1 mole of C_6H_6 per $AlBr_3$.

2. Aluminum bromide is monomeric in ethyl bromide and dimeric in benzene indicating that the addition compound is $Al_2Br_6{\cdot}2C_6H_6$.

3. Electrolysis of alkyl halide solutions of aluminum bromide indicates that this salt behaves as a normal 1–3 electrolyte in these solutions.

BALTIMORE, MD. RECEIVED FEBRUARY 10, 1950

(10) Ulich, *Z. physik. Chem.*, Bodenstein Festband, 323 (1931).

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

Polarographic Acetamide–Formaldehyde and Benzamide–Formaldehyde Kinetic Studies

BY GEORGE A. CROWE, JR.,(1) AND CECIL C. LYNCH

In previous papers[2,3] we showed polarographically that the reaction between urea and formaldehyde to form monomethylolurea was reversible, and studied the effects of change in temperature and *p*H on the reaction. A study of the initial reaction kinetics of formaldehyde with amides having only one amino group (to form methylolamides) seemed desirable. Acetamide and benzamide were selected as typical amides.

The kinetic studies described here indicate that in the initial reaction of formaldehyde with acetamide or benzamide, the equilibrium constant and the energy of activation are about the same as for urea–formaldehyde.[3] The first part of the reaction is second order. The reaction rates at high *p*H values of formaldehyde with acetamide and with urea are about the same, but the reaction of formaldehyde with benzamide is several times as rapid, due to the activating influence of the phenyl group and consequent increase in rate of anion formation of the amide.

Experimental

The apparatus, general technique and most of the chemicals were as described previously.[2,3] The acetamide was Baker and Adamson, Reagent, m. p. 81°. The benzamide was Eastman Kodak Co., white label, m. p. 130°. The supporting electrolytes consisted of 0.05 *N* lithium hydroxide (*p*H 12.7), 0.1 *M* sodium carbonate (*p*H 11.2) and 0.1 *M* sodium bicarbonate (*p*H 8.6). The supporting electrolyte solutions were made up to twice the concentrations given above. For the test solutions, 3 ml. of the supporting electrolyte was diluted with 1 (or 2) ml. of the amide solution and 2 (or 1) ml. of the formaldehyde solution. The rate constants and equilibrium constants were determined by following the concentration of unreacted formaldehyde with time, using the polarograph.

Reaction rates and equilibrium constants for the reversible amide-formaldehyde reactions are given in Tables I and II. The reactions were found to be second order.

Effect of Temperature Change.—The energy of activation for the acetamide–formaldehyde reaction was found to be 13,850 cal. per mole at *p*H 12.7. For the benzamide–formaldehyde reaction the activation energy was 14,950 cal. per mole at *p*H 11.2. It is felt that the energies of activation are accurate to ±1 kcal. per mole. These values are in the same range as the energy of activation for the urea–formaldehyde (to monomethylolurea) reaction, for which Crowe and Lynch[3] obtained 15,900 cal. per mole at *p*H 12.7, and Smythe[4] found 14,700 cal. per mole in neutral solution. Thus it appears, as postulated earlier,[3] that the increase in reaction rate with increase in temperature is not dependent on the kind of amide to any appreciable extent, but instead upon the increased rate of dehydration of methylene glycol (hydrated formaldehyde) with increasing temperature.

Effect of *p*H Change.—In the *p*H range between 8.6 and 12.7, the reaction rate increases with hydroxyl ion concentration, although the equilibrium constant remains at about the same

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(1) Hercules Powder Company, Hercules Experiment Station, Wilmington, Delaware.

(2) Crowe and Lynch, THIS JOURNAL, **70**, 3795 (1948).

(3) Crowe and Lynch, *ibid.*, **71**, 3731 (1949).

(4) Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).