

The ether complexes are less stable than the corresponding aluminum bromide complexes in this solvent.

3. With trimethylamine, the conductance increases appreciably at first and then levels off somewhat as the molar ratio approaches unity. For molar ratios beyond 1.0 the curves for the bromide solutions are particularly complex.

4. On addition of ammonia the conductance increases tremendously at first and slowly levels off at a molar ratio of 1.0.

5. The conductance curves are explained qualitatively by assuming the formation of several coordination complexes.

6. Trimethylamine and ammonia are completely combined with the gallium halides up to a molar ratio of unity. For molar ratios beyond unity, there is a measurable concentration of free amine. With dimethyl ether there is a measurable concentration of free ether from the first addition.

7. The molecular weight of gallium bromide in nitrobenzene has been determined. The results indicate a monomeric structure in this solvent.

8. The solubility of trimethylamine in nitrobenzene has been determined at 25°.

BALTIMORE, MARYLAND

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

## Some Coordination Compounds of Aluminum and Gallium Halides

BY ROSS E. VAN DYKE AND HARRY E. CRAWFORD

### I. Introduction

During the course of some recent investigations of the electrolytic properties of solutions of aluminum and gallium halides, it was decided to examine some properties of various complexes of these compounds which have not been reported heretofore. In particular, the complexes of these halides with dimethyl ether and trimethylamine were considered.

Menzel<sup>1</sup> reports the preparation of the compound  $\text{AlCl}_3 \cdot 2(\text{CH}_3)_2\text{O}$  as well as similar ethyl ether complexes of aluminum chloride and bromide. Jacober and Kraus<sup>2</sup> report a very stable monoetherate of aluminum bromide  $\text{AlBr}_3 \cdot (\text{CH}_3)_2\text{O}$ . In this paper are reported vapor pressure-composition studies for the chlorides and bromides of aluminum and gallium with dimethyl ether and trimethylamine as well as investigations of the stability of some of the resultant complexes.

### II. Experimental

**Materials.**—Anhydrous aluminum chloride was prepared by reaction of a very pure sample of metallic aluminum<sup>3</sup> with chlorine at 300°. The salt was then sublimed several times in a closed system and finally collected in a long manifold to which numerous fragile ampules were attached. The product was sublimed into these ampules which were then sealed off. *Anal.* % Al, calcd. 20.22; found 20.10; % Cl, calcd. 79.78; found 80.03. Anhydrous aluminum bromide<sup>4</sup> and the gallium halides<sup>5</sup> were prepared and handled as previously described. Trimethylamine and dimethyl ether were dried as reported previously.<sup>5</sup>

(1) Menzel and Froehlich, *Ber.*, **75B**, 1055 (1942).

(2) Jacober and Kraus, *THIS JOURNAL*, **71**, 2409 (1949).

(3) Kindly donated by The Aluminum Company of America.

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

(5) Van Dyke, *ibid.*, **72**, 2823 (1950).

**Apparatus and Procedure.**—The apparatus consisted of a large test-tube equipped with a large ground glass cap which was arranged with appropriate stopcocks and another ground joint to connect with the vacuum system. A fragile ampule filled with salt was introduced through the large ground cap; the system was then exhausted and the bulb was carefully broken. The complexing agent now was condensed on the salt by means of a Dry Ice-acetone-bath. The weight of complexing agent withdrawn from the system was determined by adsorption on activated silica gel<sup>6</sup> which was contained in a large evacuated tube. The tube was provided with a stopcock and ground joint connection to the solution vessel.

Pressures were measured on a closed end manometer with the aid of a cathetometer. Temperatures were read by means of a seven-junction copper-constantan thermocouple which was calibrated using the freezing points of water and mercury and the sublimation point of carbon dioxide.

### III. Results

Vapor pressure-composition diagrams were determined for solutions of the chlorides and bromides of aluminum and gallium in dimethyl ether and in trimethylamine. These data are presented graphically in Figs. 1 and 2.

**Variation of Vapor Pressure with Temperature.**—The vapor pressures of the solid gallium halide monoetherates as a function of temperature were determined. The dissociation pressure of the solid, 2:1 addition compounds of the aluminum halides as a function of temperature have been determined. These data are presented in Table I.

(6) Kindly donated by the Davison Chemical Company.

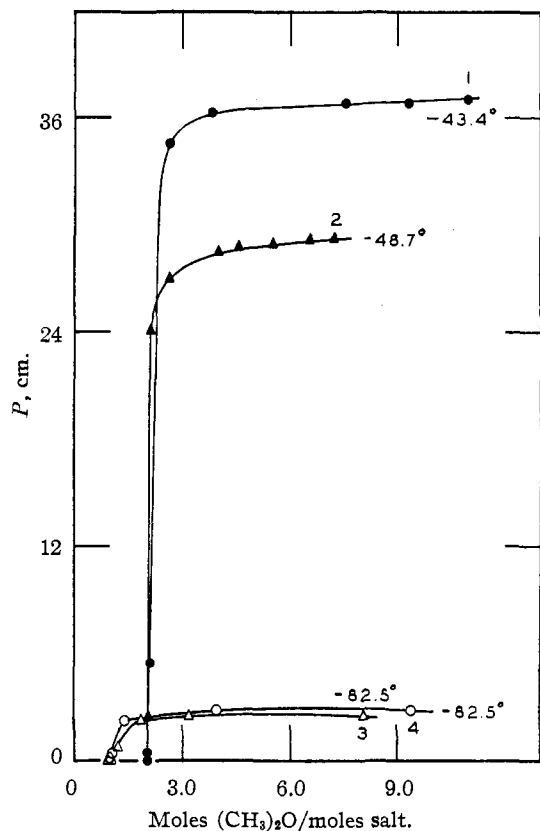


Fig. 1.—Vapor pressure–composition diagram for dimethyl ether solutions: (1)  $\text{AlBr}_3$ , (2)  $\text{AlCl}_3$ , (3)  $\text{GaCl}_3$ , (4)  $\text{GaBr}_3$ .

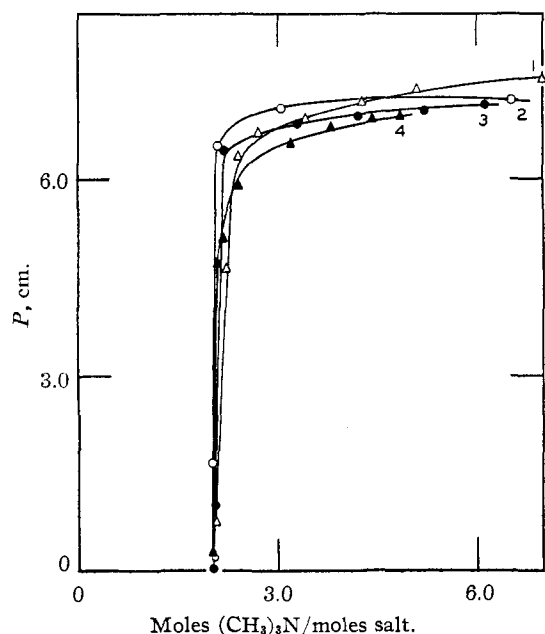


Fig. 2.—Vapor pressure–composition diagram for trimethylamine solutions at  $-48.7^\circ$ : (1)  $\text{GaCl}_3$ , (2)  $\text{GaBr}_3$ , (3)  $\text{AlBr}_3$ , (4)  $\text{AlCl}_3$ .

TABLE I

$P_{\text{mm.}}$	$1/T \times 10^3$	$P_{\text{mm.}}$	$1/T \times 10^3$
A. $\text{AlCl}_3 \cdot 2(\text{CH}_3)_2\text{O}$		C. $\text{AlBr}_3 \cdot 2(\text{CH}_3)_2\text{O}$	
4.95	3.663	6.90	3.660
8.30	3.580	19.15	3.521
18.75	3.445	38.65	3.425
31.90	3.363	73.65	3.332
B. $\text{AlCl}_3 \cdot 2(\text{CH}_3)_3\text{N}$		D. $\text{AlBr}_3 \cdot 2(\text{CH}_3)_3\text{N}$	
24.10	3.645	7.95	3.662
37.80	3.556	22.90	3.528
75.85	3.413	51.40	3.423
153.5	3.303	84.90	3.360

#### IV. Discussion

**Gallium Halide–Ether Complexes.**—As shown in Fig. 1, the gallium halides form 1:1 addition compounds with dimethyl ether. The flat portion of curves 3 and 4 corresponds to a saturated solution of these compounds in ether. As the liquid phase disappears the vapor pressure drops to that of the 1:1 complex. These compounds are stable in the absence of moisture at temperatures below  $100^\circ$ . The chloride monoetherate melts at  $3.0^\circ$  while the bromide complex melts at  $8.5\text{--}9.0^\circ$ . The vapor pressure of gallium chloride monoetherate is given by the equation  $\log_{10} P_{\text{mm.}} = -1956/T + 6.52$ . At 43, 82 and  $123^\circ$ , the vapor pressure is 2.1, 8.8 and 39.3 mm., respectively. The average deviation of the experimental points from the values computed from the empirical equation is 2.7%. The molal heat of vaporization as calculated from the vapor pressure curve is 8,950 cal. The vapor pressure of the bromide monoetherate is given by the equation  $\log_{10} P_{\text{mm.}} = -1205/T + 4.61$ . At 26, 60, 72 and  $88^\circ$  the vapor pressure is 3.4, 10.1, 12.7 and 18.2 mm., respectively. The average deviation of the experimental points from the calculated values is 2.5%. The molal heat of vaporization as calculated from the vapor pressure curve is 5,514 cal. It is an interesting fact that while the gallium halides appear to complex with only one molecule of ether in dimethyl ether, the salts when dissolved in nitrobenzene coordinate to some extent a second molecule of ether.<sup>5</sup>

**Gallium Halide–Trimethylamine Complexes.**—According to Fig. 2 the gallium salts form complexes with trimethylamine containing two moles of amine per mole of salt. The flat portion of curves 1 and 2 corresponds to a saturated solution of the respective 2:1 addition compounds in trimethylamine. As the liquid phase disappears the vapor pressure drops sharply to zero at a molar ratio of 2.0. The compound  $\text{GaCl}_3 \cdot 2(\text{CH}_3)_3\text{N}$  decomposes slowly under vacuum at  $-48.7^\circ$  but is unstable at  $0^\circ$ . The compound  $\text{GaBr}_3 \cdot 2(\text{CH}_3)_3\text{N}$  decomposes rapidly with pumping at  $-48.7^\circ$ . The 1:1 amine complexes are chalky powders which are quite stable in the absence of moisture at temperatures up to  $200^\circ$ .

**Aluminum Halide Complexes.**—Aluminum chloride and bromide form complexes with tri-

methylamine and dimethyl ether containing two molecules of complexing agent per mole of salt. Using J. T. Baker C. P. aluminum chloride which was sublimed several times approximately 1.9 moles of ether or amine react. However, using salt prepared from very pure aluminum as previously described the reaction with two moles of complexing agent was quantitative.

The dietherates and diamine complexes of the aluminum halides decompose with pumping at room temperature to the respective 1:1 addition compounds. These complexes are all solids; hence the dissociation pressures of Table I may be treated as equilibrium constants  $K_p$  for the general reaction  $AB_2(s) \leftrightarrow AB(s) + B(g)$  where  $AB_2(s)$  is the 2:1 addition compound,  $AB(s)$  is the 1:1 complex, and  $B(g)$  is the complexing molecule. The dissociation pressure of aluminum chloride dietherate is given by the equation  $\log_{10} P_{mm.} = -2462/T + 9.75$ . The heat of reaction as calculated from the equation is 11.27 kcal. The dissociation pressure of the 2:1 complex of trimethylamine with aluminum chloride is given by the equation  $\log_{10} P_{mm.} = -2280/T + 9.70$ . The heat of reaction as computed from the vapor pressure equation is 10.43 kcal. The dissociation pressure of aluminum bromide dietherate is given by the equation  $\log_{10} P_{mm.} = -3111/T + 12.25$ . The heat of reaction as calculated from the equation is 14.24 kcal. The dissociation pressure of the 2:1 complex of trimethylamine with aluminum bromide is given by the equation  $\log_{10} P_{mm.} = -3318/T + 13.05$ . The heat of reaction as calculated from the equation is 15.18 kcal. The average deviation of the experimental data in Table I from the values computed from the empirical equations is 1.0% for the aluminum chloride complexes, 1.3% for aluminum bromide dietherate and 0.95% in the case of the diamine complex of aluminum bromide.

A comparison of the heats of reaction is of considerable interest. The value of  $\Delta H$  for the reaction of  $AlBr_3 \cdot (CH_3)_2O$  with ether to produce the dietherate is approximately 3.0 kcal./mole greater than the value for the corresponding reaction of  $AlCl_3 \cdot (CH_3)_2O$ . A similar comparison in the case of amine complexes shows that the formation of  $AlBr_3 \cdot 2(CH_3)_3N$  involves 4.75 kcal./mole in excess of heat of reaction of the chloride complex with amine. On the other hand, the  $\Delta H$  values for the formation of  $AlCl_3 \cdot 2(CH_3)_2O$  and  $AlCl_3 \cdot 2(CH_3)_3N$  from the 1:1 complexes differ by only 0.84 kcal./mole. A similar comparison in the case of the bromide complexes shows a difference of 0.94 kcal./mole. These results suggest that the 1:1 aluminum bromide complexes are stronger acids than the corresponding chloride addition compounds. However, a complete discussion of these results must await further investigation, particularly, the determination of the  $\Delta H$  values for the addition of the first mole of complexing agent to the aluminum halides.

## V. Summary

1. Dimethyl ether addition compounds of the gallium halides  $GaBr_3 \cdot (CH_3)_2O$ , and  $GaCl_3 \cdot (CH_3)_2O$  have been prepared and their vapor pressure curves determined.
2. Trimethylamine addition compounds of the gallium halides containing 2 moles of amine per mole of salt are reported.
3. 2:1 complexes of aluminum chloride and bromide with trimethylamine and dimethyl ether are reported.
4. Heats of reaction for the addition of the second mole of complexing agent to the 1:1 aluminum halide complexes have been determined from the vapor pressure curves.

BALTIMORE, MARYLAND

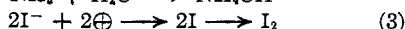
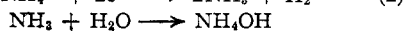
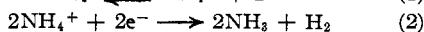
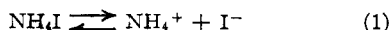
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[CONTRIBUTION FROM THE LABORATORIES OF THE BENZIMA FACTORIES, NATIONAL ENTERPRISE]

## The Electrolysis of Aqueous Solutions of Ammonium Iodide

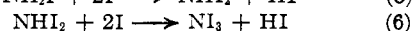
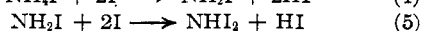
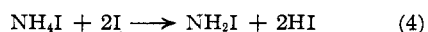
BY FRANK JIRSA

The electrolysis of aqueous solutions of ammonium iodide is characterized by the following primary reactions



At the cathode, hydrogen gas is liberated together with the formation of aqueous ammonia, while iodine is formed at the anode. In a separate compartment secondary processes can take place, reactions which normally do not occur because io-

dine itself is a very weak iodinating agent, but which are possible during the electrolysis when iodine is present in the nascent state, *i. e.*, in a more active form than is its molecular one



When solid iodine is caused to react with a concentrated solution of ammonium iodide, none of the above amines will be obtained. An addition compound, ammonium triiodide  $NH_4I_3$ , will result, forming nice crystals which are easily