[CONTRIBUTION NO. 624 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

The Lower Oxidation States of Gallium. III. The Constitution of Ga_2Cl_4 and its Analogy with $Ga(AlCl_4)$

BY RICHARD K. MCMULLAN[1] AND JOHN D. CORBETT

RECEIVED APRIL 4, 1958

Dielectric constant measurements on benzene solutions of Ga_2Cl_4 give a dipole moment of 8.9 Debye units for this solute at infinite dilution. The same Raman spectrum is observed for benzene solutions of Ga_2Cl_4 and $Ag(GaCl_4)$. These results together with molecular weight data lead to the conclusion that Ga_2Cl_4 exists in benzene as the solvated ion pairs $Ga^+(GaCl_4)^-$ which aggregate with increasing concentration. Consideration of the absence of a stable gallium(I) chloride and the acid-base interaction resulting in the formation of $Ga(GaCl_4)$ leads to the concept of stabilization of lower oxidation states toward disproportionation by strong Lewis acids and to the preparation of $Ga(AlCl_4)$. The similarity of $Ga(GaCl_4)$ and $Ga(AlCl_4)$ is discussed.

Introduction

Until recently, gallium "dichloride" had received insufficient study to clarify the problem of valency suggested by its empirical formula, $GaCl_2$, *viz.*, the apparent presence of a divalent metal of representative group III where the valencies are commonly 1 and 3. Two structural formulations have been proposed to account for this and the observed diamagnetism[2]; both are based on the dimeric unit Ga_2Cl_4. One[2] involves a Ga–Ga bond such as those reportedly present in crystalline GaS[3] and GaSe[4] and those found in the crystal of metallic gallium.[5] This formulation then suggests a symmetric molecular unit, $Cl_2Ga–GaCl_2$, with three bonds trigonally disposed around each gallium atom. The alternate formulation involves an ionic unit $Ga(I)[Ga(III)Cl_4]$, similar to those proposed for the analogous indium and thallium "dihalides." Previous objection to this ionic unit was based on the apparent non-existence of the gallium(I) halides.[6] However, with the recent preparation of GaI[7] and GaBr[8] and studies of gallium–gallium chloride systems,[9–11] this objection has been removed. Simultaneously with the studies reported herein, Woodward, Garton and Roberts[12] have inferred the presence of the $GaCl_4^-$ ion in fused Ga_2Cl_4 from an examination of the Raman spectrum of the salt, and Garton and Powell[13] have established $Ga(GaCl_4)$ as the structure of the crystalline state from X-ray investigation. The present studies establish the nature of gallium "dichloride" in benzene and characterize the behavior of this solute in this low dielectric medium.

Experimental

A. **Materials.**—"Baker Analyzed" Reagent Grade benzene (thiophene-free) was distilled through a thirty-plate Oldershaw column at a 30–1 reflux ratio. The distillate was stored *in vacuo* over calcium hydride, from which it was redistilled before use. Chlorobenzene (Eastman Kodak Co. "White Label") was purified in a similar manner.

Gallium (99.95%, Aluminum Company of America) was oxidized to the trichloride by gentle heating in a stream of dry chlorine diluted with helium. The product was triply sublimed *in vacuo*, the last sublimation being into a fragile bulb of approximately 10-g. capacity. The bulb was weighed to the nearest mg., placed in a tube which was sealed to a break-off tube and the entire apparatus then thoroughly evacuated and sealed off. The fragile bulb was punctured with a glass-encased magnet and the contents of the bulb then sublimed into the break-off tube. The fractured bulb was recovered and weighed so as to determine the weight of the trichloride sample. The tube containing the trichloride was sealed to another tube into which was placed the requisite amount of metallic gallium required for the quantitative reduction of the trichloride to the "dichloride." After the apparatus was thoroughly evacuated, the break-off bulb was crushed with a magnetic bar and the trichloride sublimed into the tube containing the gallium. The reaction vessel, after being sealed off from the other parts of the apparatus, was placed in a furnace and maintained at 180° for 12 hr. by which time the metal was completely consumed. The high purity of materials obtained by this method has been discussed previously.[7,8]

By a similar procedure $Ga(I)[Al(III)Cl_4]$ was prepared from gallium trichloride using metallic aluminum (A. D. MacKay, 99.99%) as the reducing agent. The mixture was maintained in the fused state at 190° for three days after which time the metal phase produced was separated from the salt. The melting point of the metal, as well as its "inertness" toward water indicated that it was pure Ga and not an alloy containing Al. In addition, the mole ratios $GaCl_3/Ga = 4.009$ and $Al/Ga = 3.003$, as calculated from the weights of the materials used and the weight of the gallium produced, compared favorably with those expected for the quantitative reduction of Ga(III) to Ga(I) as shown by the reaction

$$4GaCl_3 + 3Al = 3Ga(I)[Al(III)Cl_4] + Ga$$

Since gallium metal does not reduce $AlCl_3$ the oxidation states are unambiguous.

$Ag(I)[Ga(III)Cl_4)$ was prepared in the fused state at 180° from AgCl (Baker Reagent Grade, vacuum-dried) and $GaCl_3$. These were combined in equimolar amounts by a procedure similar to that described above.

B. **Apparatus and Experimental Procedure.**—1. **Molecular Determinations.**—The apparatus and procedure for the cryoscopic measurements were essentially those previously described.[14] Rather stringent conditions, however, were imposed on the measurements described herein because of the extreme sensitivity of the salts and the solutions, particularly to moisture. Anhydrous and anaerobic conditions were maintained throughout the experiments by performing all solvent transfers in a vacuum system and all salt transfers in a dry box under an atmosphere of helium. The benzene, prior to transfer into the cryoscopic cell, was distilled from calcium hydride into a tared flask which was then

---

[1] Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

[2] W. Klemm and W. Tilk, *Z. anorg. allgem. Chem.*, **207**, 161 (1932).

[3] H. Hahn and G. Frank, *ibid.*, **278**, 333 (1955).

[4] K. Schubert and E. Dorre, *Naturwiss.*, **40**, 604 (1953).

[5] A. J. Bradley, *Z. Krist.*, **91A**, 302 (1935).

[6] N. V. Sidgwick, "Chemical Elements and their Compounds," Oxford Press, London, England, 1950, p. 477.

[7] J. D. Corbett and R. K. McMullan, THIS JOURNAL, **77**, 4217 (1955).

[8] J. D. Corbett and A. Hershaft, *ibid.*, **80**, 1530 (1958).

[9] J. D. Corbett and S. von Winbush, *ibid.*, **77**, 3964 (1955).

[10] J. D. Corbett and R. K. McMullan, *ibid.*, **78**, 2906 (1956).

[11] E. Gastinger, *Angew. Chem.*, **67**, 103 (1955).

[12] Woodward, Garton and Roberts, *J. Chem. Soc.*, 3623 (1956).

[13] G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

[14] R. K. McMullan and J. D. Corbett, *J. Chem. Educ.*, **33**, 313 (1956).

accurately weighed on a solution balance. After the benzene was transferred quantitatively to the cryoscopic cell, its freezing point was determined several times and an average of these values taken. Solutions of either Ga_2Cl_4 or $Ga(AlCl_4)$ were prepared and successively concentrated by the addition of salt samples from tared ampoules that were constructed from standard taper joints. During the additions the benzene in the cell was protected from the atmosphere by a blanket of argon and the salt in the inverted half-ampoule by helium. After each salt addition, freezing points reproducible to 1 millidegree were determined. In this manner thermistor resistances at the freezing point of these benzene solutions were determined at various concentrations over an extensive concentration range. From these data average molecular weights were calculated using the previously established relationship between thermistor resistance and molality.[14]

2. **Solution Dielectric Constant Measurements.**—The dielectric constants of solution of Ga_2Cl_4 in benzene relative to pure benzene as a standard were determined with an apparatus which employed the resonance method of capacitance measurement.[15] Because of the unusually large increase in dielectric constant with increasing solute concentration, measurements for the purpose of dipole moment determinations were necessarily made in a very dilute concentration range of 0.01 to 0.05 mole %. These solutions were prepared from weighed components using the technique described in the cryoscopic measurements; in addition their compositions were checked after the measurements by spectrophotometric determination of the total gallium as the tris-5,7-dibromo-8-hydroxyquinolate in chloroform. Transfers of solutions into the capacitance cell were made in the vacuum system and the cell sealed off under vacuum for each measurement. In order to thermostat the solutions at 25° during the measurements, the cell and its holder were placed on an insulating support, surrounded by a helix of copper tubing and enclosed by an inverted Dewar flask. Water from a constant temperature bath was drawn through the copper tubing. When the temperature of the dead air space was established at 25°, as determined by a thermocouple, the capacitance measurements showed no drift with time. Dielectric constant values were determined for solutions of chlorobenzene in benzene in a similar manner.

3. **Solution Density Measurements.**—Density data were obtained for solutions of Ga_2Cl_4 in benzene by a differential buoyance method, employing a magnetically compensated balance of the type described by Edwards and Baldwin.[16] The balance was enclosed in a glass tube which was sealed to the vacuum system so that the introduction of the benzene and subsequent density measurements could be made *in vacuo*. A small silica-encased Alnico magnet was mounted vertically in the balance beam at the point of its suspension. The balance case was wrapped with insulated copper wire to form a solenoid, the field of which acted on the magnet. Balance was achieved by varying the current passed through the solenoid until a pointer viewed by a fixed telescope returned to the reference point. The reproducibility of the balance was 0.1 mg., which corresponded to less than 2×10^{-5} g. cm.$^{-3}$ uncertainty in the density. Benzene was introduced and the solutions prepared as described above. The solutions were stirred magnetically and then placed in a large Dewar flask through which water thermostated at 25 ± 0.02° was circulated. From the current necessary to re-establish balance after benzene was replaced by the solutions, the differential densities of these solutions were calculated using a previously established current-weight proportionality.

4. **Raman Spectrum Measurements.**—Benzene solutions of Ga_2Cl_4 and of $AgGaCl_4$ were prepared for Raman spectral examinations by a procedure similar to those described above. For both solutions, the concentrations were approximately one mole per cent. based on the formula weights of Ga_2Cl_4 and $AgGaCl_4$; the solubility of the former is 1.23 mole %. The spectra were recorded photographically with a Lane–Wells high-speed Raman spectrograph.

Results and Discussion

The dependence of the apparent molecular weight of gallium "dichloride" on concentration is shown in Fig. 1. An extrapolation of these data to zero concentration gives a molecular weight of 280 ± 5 as compared to the theoretical value of 281.2 expected for the unit Ga_2Cl_4. In the concentration range studied, the data reveal that Ga_2Cl_4 undergoes no dissociation into smaller units but rather undergoes rapid association with concentration, producing aggregated species which, in the higher concentration range, approximately triple the apparent molecular weight. The cause for this association is revealed upon examination of Fig. 2 where the dielectric constant increase, $\Delta\epsilon$, is plotted against concentration of Ga_2Cl_4, together with similar data obtained for chlorobenzene in this Laboratory and for silver perchlorate by Hooper and Kraus.[17] These data indicate that gallium "dichloride," like silver perchlorate and in contrast to the simple polar molecule chlorobenzene, possesses an unusually large dipole moment in benzene. From this observation it is inferred that gallium "dichloride" exists in benzene as the ion-pair $Ga^+(GaCl_4)^-$ rather than the symmetric unit $Cl_2Ga–GaCl_2$ and is in this respect similar to silver perchlorate. Therefore, the association observed in the molecular weight data is attributed to aggregation of the ion-pairs into multipolar units.

In order to estimate the dipole moment of gallium dichloride in benzene, the molar polarization of the solute at infinite dilution was determined from the dielectric constant and density data by the method of Halverstadt and Kumler[18] using values of the dielectric constant and density of the pure solvent taken, respectively, from a literature review by Treiber, *et al.*,[19] and from the American Petroleum Institute Tables.[20] The value so obtained was 1600 cm.^{3}. The dipole moment of gallium dichloride calculated from this value using the Debye equation was 8.9 Debye units, assuming that the value of the deformation polarization was within the limits of error (5%) placed on the total polarization and thus could be neglected without affecting the validity of the results.

Comparison of the Raman spectra of benzene solutions of Ga_2Cl_4 and $Ag(GaCl_4)$ further substantiates the ion-pair model proposed for the gallium dichloride species. Observation of a single frequency at 341 ± 5 cm.$^{-1}$ in both solutions indicates that the polyatomic units are isostructural. If it is reasonably assumed that the $GaCl_4^-$ ion exists in the $Ag(GaCl_4)$ solution, then it is inferred that this anion is also present in the gallium dichloride solutions. The above line is in close agreement with the most intense and sharpest line observed at 346 cm.$^{-1}$ in the Raman spectrum of fused Ga_2Cl_4 by Woodward, *et al.*[12] The other three frequencies predicted for a tetrahedral ion belonging to point group T_d and observed as weaker, more diffuse lines by Woodward were not found, probably because the solutions were too dilute.

This study, aside from the structural information

---

[15] Model V Oscillometer with Cell Compensator, E. H. Sargent and Co., Chicago, Ill.

[16] F. C. Edwards and R. P. Baldwin, *Anal. Chem.*, **23**, 357 (1951).

[17] G. S. Hooper and C. A. Kraus, THIS JOURNAL, **56**, 2265 (1934).

[18] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942)

[19] E. Treiber, J. Schurz and H. Koren, *Monatsh.*, **82**, 32 (1951).

[20] American Petroleum Institute, "Selected Values of Properties of Hydrocarbons and Related Compounds," Research Project 44, Carnegie Institute of Technology, Pittsburgh, Penn., 1952, 3, Part 1, Table 21a.

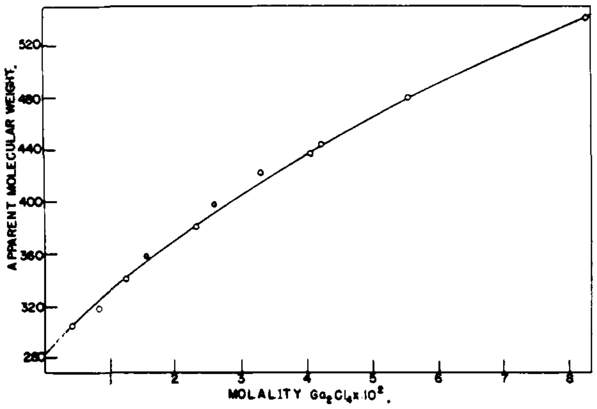

Fig. 1.—Apparent molecular weight of Ga_2Cl_4 in benzene at 5°.

it provides, reveals a type of solution arising from rather unusual solvation forces. As with $AgClO_4$ and $Ag(GaCl_4)$, the dissolution of $Ga(GaCl_4)$ and $Ga(AlCl_4)$ in benzene must depend on a rather strong solvation of the unipositive cation. This interaction appears to be of the charge transfer type described by Mulliken,[21] involving the lowest acceptor p-orbitals of the Ga^+ ion and the pi electron system of the benzene. Such bonding, coupled with the low lattice energies indicated by the low melting points of these compounds, would account for the enhanced solubilities of the gallium(I) salts as ion pairs as well as those of other polarizing cations of post-transition metals revealed by current studies.[22] It is interesting to note that all these salts separate from solution with benzene of crystallization,[22,23] a monobenzene complex having been reported for Ga_2Cl_4 and Ga_2Br_4.[24] This solvation also allows the preparation of benzene solutions of Ga_2X_4 by the novel reaction of gallium and the mercury halides.[24] The reactions of such Ga_2Cl_4 solutions with hydrogen sulfide[24] and with pyridine[22] are also consistent with the ion-pair formulation.

In light of this study, as well as those already cited,[7-13] it is clear that there is no evidence for gallium(II) in halide systems and that only the uni- and tri-positive states should be considered. In this connection it should be mentioned that the vapor density data that led Laubengayer and Schirmer[25] to infer the presence of the gaseous monomer $GaCl_2$ when Ga_2Cl_4 is heated to near 500° can be accounted for equally well by vaporization as GaCl and $GaCl_3$. In view of the similar behavior of the aluminum(I) halides at elevated temperatures, this would not be unexpected; some evidence for this mechanism has been noted in the gallium bromide system.[26]

It is evident that the so-called gallium dihalides are simple 1:1 complexes produced in the $Ga-GaX_3$ systems by an acid-base interaction between the acidic gallium(III) halide molecule and the basic halide ion of the gallium(I) halide formed in the reaction. Because of the additional stability of these GaX_4^- complexes, further reduction of the Ga(III) therein becomes more difficult, and only partial reduction to GaX occurs, increasing from chloride to iodide[8] in agreement with the expected decrease in stability of the GaX_4^- ion.[26] Conversely, disproportionation of the unstable monochloride, formed in small amounts in the molten $Ga-Ga_2Cl_4$ system,[9] proceeds on solidification only to the point where sufficient gallium(III) is produced to neutralize the basic chloride ion, thus yielding $Ga(GaCl_4)$ as the solid product. From this viewpoint the stabilization of gallium(I) chloride by a strong acid evident in $Ga(GaCl_4)$, where some ambiguity in oxidation states has existed, should also be possible with the distinctive acid $AlCl_3$. Experimental verification of this in the preparation of $Ga(AlCl_4)$ readily allows identification of GaCl as the other component and affords additional evidence concerning the nature of the gallium subhalides. Application of this concept for the stabilization of lower oxidation states toward disproportionation also has been successful in other systems.[10]

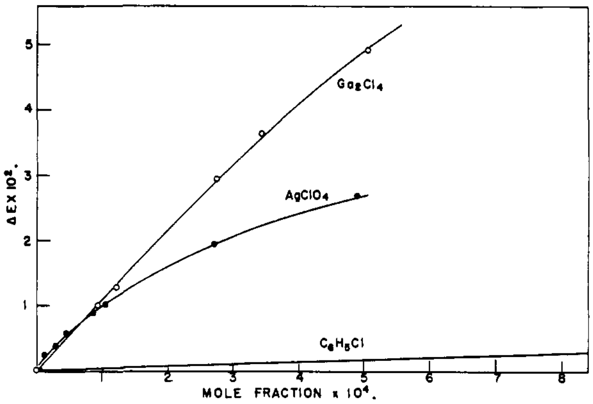

Fig. 2.—Change in dielectric constant for benzene solutions of Ga_2Cl_4, $AgClO_4$ and C_5H_5Cl.

That $Ga(GaCl_4)$ and $GaAlCl_4$ are structural and chemical analogs is shown by the similarity in their properties. In benzene $Ga(AlCl_4)$, like $Ga(GaCl_4)$, dissolves with the apparent formation of ion pairs and aggregates thereof inasmuch as the average molecular weight of the solute shows the same large concentration dependence that characterizes the Ga_2Cl_4 solutions. $Ga(GaCl_4)$ melts at 171°, while $Ga(AlCl_4)$ melts at 175°. Although the X-ray powder diffraction patterns show a marked similarity, isomorphism cannot be determined with any degree of certainty because of the complexity of the patterns, although such a structural relationship has been found between the corresponding bromides.[8] In the reaction with water both compounds form a characteristic orange-brown precipitate from which hydrogen slowly evolves. This reaction can be attributed to hydrolysis of the unipositive gallium ion with the attendant oxidation of the product by water. A small amount of gallium is also produced during the reaction as a result of disproportionation which accompanies the initially vigorous solvation and hydrolysis.

---

(21) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

(22) R. K. McMullan, unpublished research.

(23) R. E. Rundle and J. D. Corbett, THIS JOURNAL, **79**, 757 (1957).

(24) R. Carlston, E. Griswold and J. Kleinberg, *ibid.*, **80**, 1532 (1958).

(25) A. W. Laubengayer and F. B. Schirmer, *ibid.*, **62**, 1578 (1940).

(26) J. Corbett, S. von Winbush and F. Albers, *ibid.*, **79**, 3020 (1957).

Acknowledgments.—The authors are indebted to Prof. Charles V. Banks and the Analytical Service Group of the Ames Laboratory for spectrophotometric determinations in conjunction with the dielectric constant measurements and to Miller Layton for his assistance in obtaining the Raman spectra.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Some Observations on Lower Halides of Indium

BY RONALD J. CLARK, ERNEST GRISWOLD AND JACOB KLEINBERG

RECEIVED APRIL 12, 1958

Indium monohalides and dihalides have been prepared conveniently by reaction of the metal with appropriate quantities of mercury(I) or mercury(II) halides. A phase study of the system InCl–$InCl_3$ has demonstrated the unlikelihood of the existence of $InCl_2$; the most stable species found in the system has a composition In_2Cl_3 and is reasonably formulated as $In_3^{I}[In^{III}Cl_6]$. The compound $In[AlCl_4]$ has been prepared and characterized.

Recent work[1-3] has provided strong evidence that in gallium dichloride two oxidation states of gallium are exhibited and that the compound is best formulated as $Ga^{I}[Ga^{III}Cl_4]$. The present investigation was undertaken to obtain information which might shed light on the oxidation state(s) in the substance reported to have the composition $InCl_2$.

In the course of this work, it was found that the method developed in this Laboratory for the preparation of gallium dihalides,[4] namely, reaction of the metal with mercury(I) or mercury(II) halide, was applicable to the synthesis of both indium monohalides and dihalides. Moreover, a similar reaction carried out in the presence of elemental aluminum yielded the indium(I) compound $In[AlCl_4]$. In view of conflicting reports in the literature on the melting behavior of $InCl_2$, a phase study of the system InCl–$InCl_3$ was undertaken. The results of this study showed that it is highly doubtful that $InCl_2$ exists as a definite compound.

Preparation of Lower Halides of Indium.—Methods previously reported for the preparation of the dihalides include reduction of trihalides with indium metal,[5,6] reaction of metal with hydrogen halide,[7] direct union of the elements[8,9] and reduction of trihalide with hydrogen in the presence of hydrogen halide.[10] Monohalides have been obtained by reduction of trihalide[6] or dihalide[7,11] with the metal and by direct combination of the elements.[8,9] The lower halides can be prepared in a much more convenient fashion by reaction in appropriate stoichiometric quantities between mercury(I) or mercury(II) halide with indium metal as described below.

Experimental

The indium metal employed was obtained from the Fairmount Chemical Company and had a reported purity of 99.97%. Mercury(I) chloride, for the preparation of the lower indium chlorides, and mercury(II) bromide and iodide, for the synthesis of lower bromides and iodides, were of reagent grade, meeting ACS specifications. The reaction vessel used in all preparations consisted of a 20 × 0.8 cm. thick-walled Pyrex tube with a one cm. well located about 6 cm. from the closed end of the tube. Throughout the work described in this paper, transfers of moisture- or oxygen-sensitive materials were carried out in a dry box under nitrogen.

Essentially stoichiometric proportions of mercury halide and indium metal were employed in all preparations, except that of the monochloride. When the theoretical quantities of indium and mercury(I) chloride were taken, a product of the composition $InCl_{1.19}$ was obtained. A large excess of the metal was necessary in order that a product approximating InCl in composition be formed.

The preparative procedure described below for indium monoiodide may be regarded as typical. To the reaction tube, 1.2214 g. (0.00269 mole) of mercury(II) iodide and 0.6266 g. (0.00546 mole) of indium metal were added. The tube was then evacuated to a pressure of 10–15 μ and sealed. Reaction was effected by heating to about 400° in a muffle furnace for about 30 min., after which the tube was tilted to allow the mercury formed in the reaction to collect in the well. To ensure complete removal of mercury, the end of the tube containing the indium product was heated at about 350° for 2 hr. in a tube furnace, while the portion to which the well was attached was maintained at room temperature.

Reaction temperatures for the preparation of the other halides were as follows: monochloride, 325°; monobromide, 350°; the dihalides, 350°.

For analysis of the chlorides, the products were dissolved in dilute nitric acid. Indium was determined on a portion of the solution by precipitation with 8-hydroxyquinoline.[12,13] Chloride was titrated with standard silver nitrate solution, using a Beckman Model K Automatic Titrator, the electrode system consisting of a silver indicator electrode and a calomel reference electrode equipped with saturated potassium nitrate bridge. Dissolution of the bromide samples required somewhat more concentrated nitric acid and it was necessary to provide for the collection and reduction of elementary bromine formed in the dissolving process. The method of Spitzer[14] was utilized for this purpose. Indium and halide were determined as described above for the chlorides. Analysis for indium and halogen in the iodides was performed on separate samples of the solid products. For the determination of indium, a sample was heated with dilute nitric acid until iodine was no longer evolved and then the indium was precipitated with 8-hydroxyquinoline as before. In the analysis for iodide, a sample was heated for 2 hr. on a steam-bath with an excess of standard silver nitrate solution in the presence of nitric acid. The precipitated silver iodide was collected, washed with dilute nitric acid, dried at 110° and weighed.

---

(1) G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

(2) L. A. Woodward, G. Garton and H. I. Roberts, *J. Chem. Soc.*, 3723 (1956).

(3) R. K. McMullan and J. D. Corbett, to be published.

(4) R. C. Carlston, E. Griswold and J. Kleinberg, THIS JOURNAL, **80**, 1532 (1958).

(5) W. Klemm, *Z. anorg. allgem. Chem.*, **152**, 252 (1926).

(6) W. Klemm and F. Dierks, *ibid.*, **219**, 42 (1934).

(7) L. F. Nilson and O. Pettersson, *Z. physik. Chem.*, **2**, 657 (1888).

(8) A. Thiel, *Z. anorg. Chem.*, **40**, 280 (1904).

(9) A. Thiel and H. Koelsch, *ibid.*, **66**, 288 (1910).

(10) J. K. Aiken, J. B. Haley and H. Terrey, *Trans. Faraday Soc.*, **32**, 1617 (1936).

(11) M. Wehrli and E. Miescher. *Helv. Phys. Acta*, **7**, 298 (1934).

(12) W. Geilmann and Fr. W. Wrigge, *Z. anorg. allegem. Chem.*, **209**, 129 (1932).

(13) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier Publishing Co., New York, N. Y., 1953.

(14) L. Spitzer, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 465 (1936).