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BASIC CHEMISTRY OF GALLIUM:
A STUDY OF THE CHLOROGALLATES

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Personnel

This report covers work performed by Mr. Harold L. Friedman in the period August, 1947 to June, 1949. The work was begun under the supervision of Warren C. Johnson and was continued under Henry Taube beginning January, 1948.

Some of the work on ammonium chloro ferrate and chloro aluminate were performed by Messrs. Wesley K. Lind and Robert A. Plane as laboratory work for a course in advanced inorganic chemistry.

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A. INTRODUCTION

In this report observations on the chlorogallates NH_4GaCl_4 , CsGaCl_4 , KGaCl_4 , LiGaCl_4 and some related compounds are described. These chlorogallates are members of a larger class of compounds of the general formula $\text{M}'\text{M}'''\text{Cl}_4$, in which M' represents a monovalent ion (NH_4^+ , alkali metal ion or others) and M''' represents a trivalent ion (Al^{+++} , Fe^{+++} , Ga^{+++} , Tl^{+++} or others). For comparison with results obtained with the chlorogallates, some experiments have been carried out with the aluminum and iron analogues, and these are also described in the report.

The literature on the chemistry of the substances of the class $\text{M}'\text{M}'''\text{Cl}_4$ is meager. Three of the chlorogallates which were studied, namely CsGaCl_4 , KGaCl_4 and LiGaCl_4 , have in fact not previously been prepared. The present work presents a survey of the preparation and properties of some of these compounds, emphasis being placed on the gallium compounds. Several methods of preparation have been tested and compared, and physical properties such as melting points, densities and solubility in ether measured for some. Ammonium chlorogallate has been investigated most intensively. It vaporizes at a lower temperature than do the other chlorogallates, and the liquid-vapor equilibrium has been studied in some detail. The constitution of the ether solutions of this substance has also been investigated. There is no evidence that the substance behaves atypically in ether, and the results obtained in a study of the colligative properties and of the conductivity are probably representative for the ether solutions of the other compounds of this type.

An important direction of interest in the compounds of formula $\text{M}'\text{M}'''\text{Cl}_4$ is toward investigation of the stability with respect to the change:

Observations on the affinity of $\text{M}'\text{Cl}$ for $\text{M}'''\text{Cl}_3$ would lead to conclusions about the relative basicities of the substances $\text{M}'\text{Cl}$ and the relative acidities of the substances $\text{M}'''\text{Cl}_3$. Only a few qualitative conclusions in this connection can be drawn from the work thus far, but the research does lay the groundwork for future intensive investigations of stability.

B. A GENERAL DESCRIPTION OF THE EXPERIMENTAL
FACILITIES USED

All of the compounds studied in this work are sensitive to moisture and consequently must be handled in a vacuum system or in a good dry box. A brief description of these facilities and some other experimental procedure is given here in order to avoid repetition throughout the report.

A schematic representation of the essential part of the vacuum system is presented in Fig. 1. Manifold B was used with apparatus which was sealed directly to the vacuum line while manifold C was used with apparatus which was connected to the line by a standard taper ground joint. Manifold D was used chiefly to handle the reagents which were stored in the large reservoirs. Reservoir W contained thiophene-free benzene which was stored over P_2O_5 . Reservoir X contained diethyl ether (Mallinckrodt Reagent Grade, not further purified) which was stored over lithium aluminum hydride, or less frequently, over lithium hydride. Reservoir Y contained dry hydrogen chloride and reservoir Z, dry ammonia.

The stopcocks on Manifold A were greased with Apiezon N. Dow-Corning Silicone high vacuum grease was used on the other stopcocks. Satisfactory results were obtained with Silicone only on very well fitted stopcocks of less than six millimeter bore. Mercury cut-offs were used where stopcocks could not conveniently be regreased or where they might come in contact with liquid ether.

The dry box, built in collaboration with Mr. J. Halperin, was constructed of 16 gauge galvanized iron with windows of plexiglas, and enclosed in a space of $1 \times 0.7 \times 0.8$ m. It had a brass air lock 31 cm. in diameter and 47 cm. long, which could be evacuated and could be entered either from the outside or from the inside of the dry box. An analytical balance, sensitive to about one milligram, and on which all of the wooden parts had been replaced by metal, was mounted within the dry box. An atmosphere of carbon dioxide was maintained at several milliliters over the outside pressure, and was dried by a phosphorus pentoxide tube in the inlet and by a large dish of phosphorus pentoxide within the box. A small fan served to keep the atmosphere within the box circulating over the drying agent.

Iron-constantan thermocouples were used for temperature measurements between 200° and $500^\circ C$. These were prepared from Leeds and Northrup fiber-glass insulated #30 B. & S. iron constantan pair. They were occasionally

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Fig. 1. -- Vacuum system

calibrated against the melting points of National Bureau of Standards samples of tin, lead, and zinc. The corrections were used when the deviations were greater than 1° . Thermometers were used for measuring temperatures below 200° , and uncalibrated chromel-alumel thermocouples were used above 500° .

The following analytical methods were used throughout this work. All gallium analyses were performed by precipitating and weighing gallium tris (8-hydroxyquinolate). This compound was precipitated from ammoniacal tartrate solution as described by Geilman and Wrigge.¹⁾ All nitrogen analyses were performed by the Kjeldahl method using boric acid.²⁾ The chloride analyses were performed either by precipitating and weighing silver chloride, or by a Volhard titration using nitrobenzene.³⁾ Equally good results were obtained by either method, but the latter was faster.

The densities of the solid compounds prepared were determined by means of two pycnometers which were constructed of Pyrex tubing, and had the form of Florence flasks of one milliliter capacity. The kerosene which was used in the density determinations was a highly purified product consisting only of paraffin hydrocarbons. The density determinations were all made in the dry box. Between 0.5 and 1.0 g. of the solid was weighed into the pycnometer, the solid was covered with kerosene, the pycnometer was evacuated in order to remove entrapped air, and finally the pycnometer was filled to the mark with kerosene and weighed again. A correction was made for the variation in density of the kerosene with temperature.

C. METHOD OF PREPARATION

Observations on the preparation of a number of substances of the type $M'M''Cl_4$ are described in the following section. The particular substances

¹⁾Geilman and Wrigge, Z. Anorg. Ch., 209, 129 (1932).

²⁾Pierce and Haenisch, "Quantitative Analysis," 2d ed., John Wiley & Sons, Inc., New York, 1940, p. 127.

³⁾Ibid., p. 256

prepared were the gallium compounds NH_4GaCl_4 , CsGaCl_4 , KGaCl_4 , LiGaCl_4 and, for comparison, the aluminum compounds NH_4AlCl_4 , KAlCl_4 , LiAlCl_4 , and the iron compound NH_4FeCl_4 . Of these substances, NH_4GaCl_4 , NH_4AlCl_4 , KAlCl_4 , LiAlCl_4 and NH_4FeCl_4 have been prepared before. Kraus and Toonder⁴⁾ prepared NH_4GaCl_4 by the reaction of HCl with $\text{NH}_3\text{Ga}(\text{CH}_3)_3$. More recently, R. P. Hammond,⁵⁾ using the methods: heating Ga_2O_3 with NH_4Cl in a vacuum or in an atmosphere of HCl , and evaporating an aqueous solution containing gallium chloride, hydrochloric acid and ammonium chloride, also obtained the compound, but in impure form. The compounds NH_4AlCl_4 ,⁶⁾ KAlCl_4 ,^{6,7)} LiAlCl_4 and NH_4FeCl_4 ⁸⁾ have been formed by heating together the components $\text{M}'\text{Cl}$ and $\text{M}'''\text{Cl}_3$. Their existence as pure substances was established by thermal analysis of the systems $\text{M}'\text{Cl} + \text{M}'''\text{Cl}_3$.

In the present work three methods for the preparation of the compounds of type formula $\text{M}'\text{M}'''\text{Cl}_4$ have been tested: (1) preparation by heating $\text{M}'\text{Cl}$ and $\text{M}'''\text{Cl}_3$, (2) preparation by treating solid $\text{M}'\text{Cl}$ with an ether solution of $\text{M}'''\text{Cl}_3$, and (3) preparation from aqueous solution. Since the greatest amount of work has been done with NH_4GaCl_4 , the observations made with it will be presented first in the discussion of each method. Included also in this section is a description of the preparation of NH_3GaCl_3 .

1. Preparation by heating $\text{M}'\text{Cl}$ with $\text{M}'''\text{Cl}_3$. The reports in the literature of the preparation of compounds of the class $\text{M}'\text{M}'''\text{Cl}_4$ by heating the components $\text{M}'\text{Cl}$ and $\text{M}'''\text{Cl}_3$ have already been mentioned. In the present work, three variations of this general method of preparation have been used: (i) mixing the components in equivalent amounts and then heating them to bring about reaction (used for NH_4FeCl_4), (ii) adjusting the composition of the mixture in the neighborhood of one mole $\text{M}'\text{Cl}$ to one mole $\text{M}'''\text{Cl}_3$ to

⁴⁾Kraus and Toonder, Proc. Nat. Acad. Sci. U.S.A., 19, 292 (1933).

⁵⁾R. P. Hammond, "Contributions to the Chemistry of Gallium," Ph.D. Dissertation, University of Chicago, 1947.

⁶⁾Kendall, Crittenden and Miller, J.A.C.S. 45, 976 (1923).

⁷⁾Baud, Ann. Chim. Phys. (8) 1, 46 (1904).

⁸⁾Hachmeister, Z. anorg. allgem. Chem., 169, 179 (1920).

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maximum melting point (used for KGaCl_4 and CsGaCl_4), and (iii) using an excess of $\text{M}'''\text{Cl}_3$ and heating in vacuum to remove the excess (used for KGaCl_4 and KAlCl_4). Method (i) involves the difficulty of weighing and handling the moisture sensitive component $\text{M}'''\text{Cl}_3$. Method (ii) can be applied conveniently only when the product $\text{M}'\text{M}'''\text{Cl}_4$ is itself non-volatile. Method (iii) avoids the necessity of weighing $\text{M}'''\text{Cl}_3$; it also can be applied only when the product is non-volatile and when the affinity of $\text{M}'\text{Cl}$ for $\text{M}'''\text{Cl}_3$ is great.

a) NH_4GaCl_4 . Method (ii), applying thermal analysis, was tested as a method of preparation of NH_4GaCl_4 as described below for CsGaCl_4 . At the temperature required, HCl is formed and the composition of the reaction mixture is difficult to control and the method proved to be unsuitable for the preparation of pure NH_4GaCl_4 . The experiment does, however, justify the conclusion that NH_4Cl and GaCl_3 do react directly at temperatures high enough to provide a liquid phase.

b) CsGaCl_4 . Thermal analysis of the system $\text{CsCl} + \text{GaCl}_3$ shows that a maximum in the freezing point occurs at the composition corresponding to CsGaCl_4 . GaCl_3 becomes much more difficult to remove from the mixture by distillation just at the composition corresponding to CsGaCl_4 . Thus CsGaCl_4 can be freed from excess GaCl_3 by heating the system at the melting point and pumping on it. Further GaCl_3 can be removed, however, by heating the substance above 450° in a vacuum.

Experimental. The apparatus of Fig. 2 was used to find the composition of the mixture of CsCl and GaCl_3 near 50 mole percent having the highest melting point. At the beginning of the experiment, tube C contained 30 millimoles of CsCl and H contained about 60 millimoles of GaCl_3 . The apparatus was evacuated through A and then, after the break-off seal was opened, the apparatus was sealed off at A. All of the GaCl_3 was distilled into E and the apparatus was sealed off at F. Tube C was heated in a small tube furnace to 400° and then GaCl_3 was distilled into C until the contents of C were liquid at this temperature. Then the heating current of the furnace was decreased, a thermocouple was inserted into B, and the temperature was recorded at frequent intervals as the material in C cooled. A typical series of readings of the thermocouple potential, taken at 15 sec. intervals, is shown by the cooling curve of Fig. 3. From this series of readings, 21.02 millivolts was taken as

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Fig. 2.-- Apparatus for observing freezing points

Fig. 3.-- Cooling Curve

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the potential corresponding to the freezing point of this mixture. The freezing point was varied by increasing or decreasing the amount of GaCl_3 in the mixture by distilling GaCl_3 into or out of tube C. In this way a maximum freezing point was observed at 385° . The range of freezing points observed extended from 384° on the GaCl_3 rich side to 381° on the GaCl_3 poor side. It was difficult to observe the freezing points of mixture rich in GaCl_3 because the excess distilled out of C before the mixture was all melted. In contrast to this, in order to decrease the amount of GaCl_3 below that at the maximum melting point, it was necessary to cool E to -80° while heating C to 500° for 30 minutes.

After the composition was once more adjusted until the material had a freezing point of 385° , the apparatus was sealed off at D and tube C was opened in a dry box. Found: percentage Cl, 40.85, 40.93. Calculated for CsGaCl_4 : percentage Cl, 41.17.

c) KGaCl_4 . Potassium chlorogallate may also be prepared from anhydrous GaCl_3 and KCl by adjusting the composition until the maximum freezing point is obtained, just as described above for CsGaCl_4 . The lowest freezing point observed on the GaCl_3 rich side of the composition range was 247° , on the GaCl_3 poor side, 251° , and a maximum of 258.8° was observed between these limits. It was further observed that most of the excess GaCl_3 is driven from a GaCl_3 rich mixture without decomposing KGaCl_4 by heating the sample at 350° for one or two hours. At the conclusion of the experiment the composition of the material was adjusted until a freezing point of 258.3° was obtained and then the sample was analyzed. Found: percentage Cl, 56.48. Calculated for KGaCl_4 : percentage Cl, 56.59.

d) KAlCl_4 . Potassium chloroaluminate may be prepared by mixing KCl with excess AlCl_3 and distilling off the excess AlCl_3 in a vacuum.

Experimental. About 0.2 mole of reagent grade AlCl_3 was purified by vacuum sublimation. It was collected in a vessel containing 0.1 mole of KCl . The whole apparatus was then heated to 170° overnight to allow the materials to react. Then the vessel containing the mixture was slowly heated to 420° while the other end of the apparatus was cooled in liquid nitrogen. The residue was then analyzed. Found: percentage Cl, 68.2, 68.2. Calculated for KAlCl_4 : percentage Cl, 68.22.

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e) LiAlCl_4 . An attempt was made to prepare this compound by a method exactly analogous to the preparation of KAlCl_4 just described. When the mixture of AlCl_3 and LiCl was heated, the distillation of AlCl_3 did not stop at a composition corresponding to LiAlCl_4 , but continued until a residue of LiCl remained. The compound has been identified by thermal analysis⁶⁾.

f) NH_4FeCl_4 . Ammonium chloroferrate was prepared by heating together equivalent amounts of NH_4Cl and FeCl_3 . The melting point of the sample was $294^\circ\text{--}295^\circ$. Hachmeister⁸⁾ has reported 297° .

2. Treating $\text{M}'\text{Cl}$ with an ether solution of $\text{M}'''\text{Cl}_3$. A number of preparations have been made which are based on the fact that the products $\text{M}'\text{M}'''\text{Cl}_4$ in question are soluble in ether, while the reactant $\text{M}'\text{Cl}$ is only sparingly soluble. The reaction mixture containing $\text{M}'\text{Cl}$ and $\text{M}'\text{M}'''\text{Cl}_4$ is prepared by heating $\text{M}'''\text{Cl}_3$ with excess $\text{M}'\text{Cl}$, and is then extracted with ether. The substance $\text{M}'\text{M}'''\text{Cl}_4$ is recovered by evaporating the solution in vacuo, finally heating the product gently to remove the last traces of ether. A modification of this method is to treat excess $\text{M}'\text{Cl}$ with a solution of $\text{M}'''\text{Cl}_3$ in ether. As a preparative method, it has the disadvantage that the solvent is exposed to the action of the acidic component $\text{M}'''\text{Cl}_3$. It is of interest though in showing that equilibrium in the reaction. $\text{M}'\text{Cl}_s + \text{M}'''\text{Cl}_3 (\text{ether}) \rightarrow \text{M}'\text{M}'''\text{Cl}_4 (\text{ether})$ is established fairly rapidly at room temperature.

Neither modification of the ether solution method involves the troublesome step of weighing $\text{M}'''\text{Cl}_3$ accurately. However, not all of the compounds $\text{M}'\text{M}'''\text{Cl}_4$ can be prepared by this method. The obvious condition for success which involves the difference in solubility of $\text{M}'\text{Cl}$ and $\text{M}'\text{M}'''\text{Cl}_4$ has already been mentioned. Another necessary condition is that the equilibrium in the reaction above is far to the right. This condition is fulfilled by $\text{NH}_4\text{Cl} + \text{GaCl}_3$ and $\text{NH}_4\text{Cl} + \text{AlCl}_3$, for example, but not by $\text{LiCl} + \text{GaCl}_3$.

a) NH_4GaCl_4 . Ammonium chlorogallate has been prepared by both modifications of the ether solution method. Equilibrium in the reaction

appears to be far to the right, and the product recovered from the ether solution is about 99 percent NH_4GaCl_4 .

Experimental.

(i) Treatment of NH_4Cl with an ether solution of GaCl_3 . The apparatus for filtration under anhydrous conditions is shown in Fig. 4. For this experiment about 0.1 mole of GaCl_3 was placed in A and 0.3 mole of NH_4Cl in B. After the apparatus was evacuated and heated to dry the glass and the NH_4Cl , about 70 ml. of anhydrous ether was distilled in and condensed in B. The internal break-off seal between B and A was broken by means of the magnetic breaker, D, and then the cold ether was poured into A. Gallium trichloride dissolves in ether with the evolution of much heat, and it was necessary to cool A with dry ice in order to keep the temperature down and avoid side reactions. In spite of this precaution, a very small amount of charring occurred in this step. Then the solution was occasionally poured back and forth from A to B for three hours to allow all of the solution to come in contact with NH_4Cl . Finally, the solution was filtered into C and evaporated, first just by pumping off the ether, and then by warming to $70-100^\circ$ while pumping.

A sample of this product melted from 295 to 308° . On analysis the composition was found to be: percentage N, 6.06, 6.04, 6.08; percentage Ga, 30.56, 30.56, 30.60; percentage Cl, 61.50, 61.56, 61.60. Calculated for NH_4GaCl_4 : percentage N, 6.10; percentage Ga, 30.37; percentage Cl, 61.78. Another sample of this product was distilled under a 15 cm. pressure of HCl. The distillate melted in the range $301.5-305.5^\circ$.

(ii) Extracting NH_4GaCl_4 from a mixture of NH_4Cl . About 0.1 mole of GaCl_3 was distilled onto 0.2 mole of carefully dried NH_4Cl in a tube bearing an internal break-off seal. Then this tube was sealed off, heated at 100° for several hours, and was sealed in place of tube A in the apparatus of Fig. 4. After this apparatus was evacuated, the break-off seal was opened and dry ether was distilled into B. The ether was run back and forth from B to A for an hour and then the solution was filtered into C. The solution was evaporated to dryness at room temperature and then was heated to 100° in a vacuum for two hours. The vessel C was sealed off at E and connected to another apparatus by F. Then the residue was distilled from C under a pressure of 15 cm. of HCl. Finally, the distillate was heated to 275° for several days while the hydrogen chloride pressure was maintained above 15 cm. in order to convert all of this distillate to NH_4GaCl_4 . These

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Fig. 4. -- Apparatus for filtration in a vacuum

precautions were necessary because, as will be shown below, ammonium chlorogallate decomposes into HCl and NH_3GaCl_3 in the vapor phase and when vapor of this composition is cooled rapidly the NH_3GaCl_3 may condense without reacting with HCl. The product was melted and poured into a "cow" which had five side tubes, each of which had an internal break-off seal. The side tubes were then sealed off from the "cow" and the melting point of their contents was determined by heating them in a salt bath. All of the samples melted in the range 302 to 304°. It must be emphasized that in this whole process the gallium compounds were handled in all glass vessels and not allowed to come in contact with any substances other than those mentioned.

b) LiGaCl_4 . Mention has already been made of the fact that, in contrast to the behavior with NH_4Cl , GaCl_3 in ether does not pick up an equivalent amount of LiCl. The ratio GaCl_3 in ether to LiCl in ether increases as the concentration of GaCl_3 increases. When an ether solution of LiGaCl_4 is evaporated, the solid which separates from the saturated solution is intermediate in composition between LiCl and LiGaCl_4 . The ether solution method is thus not suitable for the preparation of LiGaCl_4 . The behavior of this system is discussed further in section G.

c) NH_4AlCl_4 .

Experimental. The procedure is entirely analogous to that for the preparation of NH_4GaCl_4 from GaCl_3 and excess NH_4Cl , except that the residue from evaporation of the ether solution was not purified by distillation. The residue was analyzed for chlorine. Found: percentage Cl, 75.85, 75.85. Calculated for NH_4AlCl_4 : percentage Cl, 75.91.

3. Preparation from aqueous solution. Replacement by Cl^- of H_2O , OH^- or O^{2-} coordinated to gallium ion is in general difficult to accomplish. Thus, evaporation of a solution containing Ga^{+++} , H^+ and Cl^- leads to the formation of Ga_2O_3 . One method of bringing about the substitution is to pass CCl_4 over Ga_2O_3 at about 500°⁹⁾ A method developed in the present research depends on the fact first observed by Hammond⁵⁾ that NH_4GaCl_4 is formed when an aqueous solution containing Ga^{+++} , Cl^- and NH_4^+ is evaporated

⁹⁾ Klemm and Tilk, Z. Anorg. Ch., 207, 163 (1932)

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and heated strongly. NH_4GaCl_4 can be regarded as an intermediate step in the preparation of anhydrous GaCl_3 from Ga^{+++} aq, for as is described in greater detail in section F, NH_4GaCl_4 is readily oxidized by chlorine, forming GaCl_3 , HCl and N_2 .

The observation that the replacement of water by Cl^- can be accomplished with NH_4Cl leads naturally to the investigation of other alkali halides for similar behavior. Experiments have shown that with CsCl and KCl the corresponding chlorogallates are not formed. A surprising observation is that when NH_4Cl is also present, and the resulting mixtures strongly heated, both KGaCl_4 and CsGaCl_4 can be formed from water solutions. However, LiGaCl_4 is not formed from aqueous solution, even when NH_4Cl is present.

It is of interest to note that NH_4FeCl_4 , but not NH_4AlCl_4 can be formed from aqueous solution by a method analogous to that used for NH_4GaCl_4 .

a) NH_4GaCl_4

Experimental. A solution containing 0.13 mole of Ga in 10 ml. of hydrochloric acid was transferred into a 25 ml. distilling flask. Then 0.15 mole of NH_4Cl was added to the solution and the neck of the flask was washed down with a few ml. of concentrated hydrochloric acid. A stream of dry HCl was passed in through the side arm of the distilling flask and the flask was heated with an electric heater, the rate of heating being slowly increased manually until the end of the experiment.

As the solution was heated the temperature of the liquid rose slowly to 120° , at which temperature a solid phase began to separate and the temperature of the boiling solution began to increase much more rapidly. The solution was slightly yellow, and it is believed that this color, which was always observed no matter how carefully the materials were purified, is due to an interaction of gallium ions and chloride ions in water. At 185° , all of the liquid was gone and the white solid immediately started to melt, evolving much gas. At 320° the materials in the flask had melted to a clear colorless liquid which boiled as the temperature increased. The neck of the flask was flamed occasionally to drive off the NH_4Cl which condensed there. The temperature of the boiling liquid became constant at 444° , evidently the boiling point under these conditions.

The heater was removed and the flask was allowed to cool while the stream of dry HCl was maintained in order to keep the product dry. The

product froze between 291 and 289°. As soon as the bulb of the flask was cool, it was sealed off from the neck and put into the dry box and opened. The yield, calculated from the amount of gallium taken, was 64%, and the product was about 97-99% NH_4GaCl_4 . The remainder of the gallium was no doubt distilled off as ammonium chlorogallate with the excess NH_4Cl , and was usually recovered from a condenser and scrubber which was attached to the neck of the distilling flask during the distillation.

b) CsGaCl_4 . Cesium chlorogallate can not be prepared by evaporating a solution containing equimolar amounts of gallium ion and cesium ion in excess hydrochloric acid; if the residue is heated until it melts at 200-300° the melt contains very much suspended solid, and when allowed to cool the material is only partially soluble in water. If, however, the process is repeated with slightly more than one mole of ammonium chloride added to the solution, cesium chlorogallate is formed which is over 95% pure.

Experimental. A solution was prepared which contained 32 millimoles of Ga, 25 millimoles of Cs, and 35 millimoles of NH_4Cl in excess HCl. The material was contained in a 25 ml. distilling flask and dry HCl was passed in through the side tube of the flask. A condenser was connected to the neck of the flask to make it possible to recover the volatile gallium compounds, and then the bulb was heated with an electric heater. Heating was continued as the solution boiled to dryness, and the residue melted and began to boil. When the melt had practically ceased to boil, the neck of the flask was heated strongly to drive off the NH_4GaCl_4 which collected there, and then the apparatus was allowed to cool. As soon as it was cool the bulb was sealed off and opened in the dry box. Found: percentage Cl, 41.98, 42.12; percentage N, 0.30. Calculated for a mixture of 95.8% CsGaCl_4 and 4.2% NH_4GaCl_4 : percentage Cl, 42.05; percentage N, 0.25.

c) KGaCl_4 . The method of preparation with NH_4Cl added is entirely analogous to that used for CsGaCl_4 . The melting point of the best sample prepared from aqueous solution was about 250°, while the melting point of pure KGaCl_4 is 259°. A sample of the preparation from aqueous solution gave the analysis: percentage Ga, 27.7; percentage Cl 56.4. Calculated for KGaCl_4 : percentage Ga, 27.8; percentage Cl, 56.6.

d) LiGaCl₄. For LiGaCl₄ the method used for CsGaCl₄ was again followed, using LiCl in place of CsCl. The appearance and behavior of the melt finally obtained are very different from those found for KGaCl₄ and CsGaCl₄. After the melt had boiled for a few minutes, it was allowed to cool and was analyzed for Cl, Ga and N. The composition of the melt may be expressed as; 57 mole percent LiCl, 37 mole percent NH₄GaCl₄, the remainder NH₃GaCl₃ and LiGaCl₄.

4. Preparation of Gallium Trichloride Monamine. The interpretation of data on the vapor pressure of NH₄GaCl₄ required some experiments with NH₃GaCl₃. This substance was first described by Klemm, Tilk, and Jacobi¹⁰⁾. The method of preparation used by them--heating equimolar amounts of GaCl₃ and NH₃ together--was adopted for the present work.

Experimental. Previous experience had shown that GaCl₃ could not be handled in the dry box. Even when the atmosphere in the dry box was at its driest the GaCl₃ fumed strongly, especially when it was transferred from one vessel to another. Therefore the GaCl₃ was weighed by the following procedure.

A sealed sample tube containing GaCl₃ and bearing an internal break-off seal was weighed and was then sealed into the apparatus shown in Fig. 5. The apparatus was evacuated through A and flamed and finally was sealed off at A. Then the apparatus was shaken to break the inner seal, and the GaCl₃ was distilled into D. Finally, the tube at C was fused in two, E was opened, and the empty sample tube and the bits of glass from the break-off seal were weighed. In this way the amount of GaCl₃ in C was found to be 0.0721 moles.

An equivalent amount of NH₃ was measured out by adjusting the pressure of this gas in a known volume. Then the apparatus was connected to the line at F, and connection was evacuated, the inner seal was broken, and the ammonia was distilled into D. When the reaction was complete the vessel was sealed off at F and slowly heated in an oven to 130° to allow the mixture of GaCl₃ and higher amines of GaCl₃ to react to form GaCl₃ to react to form GaCl₃NH₃. The entire product was then distilled once in a vacuum, and the fraction condensing at 100° was collected. This product will be designated as Preparation A.

Part of Preparation A was subjected to a second vacuum distillation.

¹⁰⁾ Klemm, Tilk and Jacobi, Z. Anorg. Allgem. Chem. 207, 200 (1932).

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Fig. 5.-- Apparatus for weighing GaCl_3

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Three-fourths of the material taken was distilled, and the fraction which condensed at 100° was collected. This is designated as Preparation B.

Samples of each preparation were analyzed. Found: Preparation A, percentage Cl, 54.80, 54.89; Preparation B, percentage Cl, 54.71, 54.81; percentage N, 7.10, 7.12. Calculated for NH_3GaCl_3 : percentage Cl, 55.08; percentage N, 7.25.

Preparation A melted in the range $120-123^{\circ}$. Klemm¹⁰⁾ et al reported $121-124^{\circ}$.

NH_3GaCl_3 above its melting point reacts fairly rapidly with HCl to form NH_4GaCl_4 . Even with an excess of HCl, the composition of the condensed phase remains that corresponding to NH_4GaCl_4 . A sample of ammonium chlorogallate was prepared in this way. Its melting point was 304° , which is the melting point of the pure NH_4GaCl_4 .

D. GENERAL PROPERTIES OF THE CHLOROGALLATES AND RELATED COMPOUNDS

Some physical properties of the substances which were prepared are summarized below. References are given to all data from the literature. Data for which no references are cited have been obtained in the present study.

Table I

	m.p., $^{\circ}\text{C}$	density at 25° , g./ml.	molar vol., ml.	Sol'y in ether* at 25° (weight %)
NH_4GaCl_4	304	$2.08 \pm .02$	110	58.
CsGaCl_4	385	$2.85 \pm .03$	121	< .004
KGaCl_4	259	$2.38 \pm .01$	105	> 30.
LiGaCl_4	---	-----	---	> 30.
NH_4AlCl_4	$304^{6)}$	$1.73 \pm .02$	108	soluble
KAlCl_4	---	-----	---	-----
LiAlCl_4	$143, 5^{6)}$	-----	---	-----
NH_4FeCl_4	$294-5, 297^{8)}$	$1.97 \pm .02$	110	44.
NH_3GaCl_3	$123, 124^{10)}$	$2.20, 2.189^{10)}$	88	soluble

*These data are discussed in more detail in the text following.

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For NH_4GaCl_4 , NH_4AlCl_4 and NH_4FeCl_4 , the solid phases which separate from the ether solutions contain the components $\text{M}'\text{Cl}$ and $\text{M}'''\text{Cl}_3$ essentially in the mole ratio 1:1. By contrast, the first solid which separates from the solutions of KGaCl_4 and LiGaCl_4 , somewhat more concentrated than 30% by weight, is the component $\text{M}'\text{Cl}$, and the solution is left enriched in GaCl_3 . The wet solids separated from the saturated solutions of NH_4GaCl_4 and NH_4FeCl_4 have been analyzed for content of solvent. For NH_4GaCl_4 the mole ratio ether to solute was found to be about 0.85 (variable); for NH_4FeCl_4 , about 0.45 (variable). It is very likely that the solvent is retained mechanically, and the solid phase is not a true solvate.

In all solubility determination, the substances were kept from contact with moisture, air, grease, or any materials that might introduce impurities. The solid and liquid in contact were shaken for a period of at least 12 hours in a thermostat kept at 25° . For NH_4FeCl_4 , equilibrium was approached from both sides, and a period of 12 hours was found to be more than adequate for reaching equilibrium.

Except for an experiment with NH_4FeCl_4 in benzene, the solubilities of the compounds in organic solvents other than ether have not been investigated. NH_4FeCl_4 imparts a faint yellow color to benzene, but the concentration of the saturated solution is less than 10^{-3} molal at 25° .

All of the compounds studied dissolve in water with the evolution of heat. As has already been discussed in Section C, only NH_4GaCl_4 and NH_4FeCl_4 are reformed when the aqueous solutions are heated. All the compounds are sensitive to moisture from the air, but much less sensitive than are the corresponding compounds AlCl_3 , FeCl_3 , GaCl_3 .

Except for NH_4FeCl_4 , all of the compounds studied are white solids. NH_4FeCl_4 is also solid at room temperature; in massive condition it is purple-black in color, but the color of the finely ground solid is yellow. Most of the compounds are formed, following the methods of preparation outlined, as well defined crystals. NH_4GaCl_4 appears from ether solution as very fine, poorly formed crystals. Larger crystals have been grown by leaving a large sealed evacuated vessel containing some NH_4GaCl_4 in an oven at 250° for a few weeks. These crystals were submitted to Dr. William H. Zachariasen of the Department of Physics, University of Chicago, for X-ray analysis. Examination of NH_4GaCl_4 , KGaCl_4 and CsGaCl_4 under the microscope

has shown them to be anisotropic.

E. OBSERVATIONS ON STABILITY

Some of the observations made in connection with the preparative work imply differences in stability with respect to the reactions:

Another problem of interest is investigation of the systems to establish whether $M'Cl$ and $M''Cl_3$ associate in the gas phase, Baud¹¹⁾ has reported that $KAlCl_4$ distills without decomposition an observation which implies that $KAlCl_4$ exists in the gas phase. A high temperature distillation was carried out for $KGaCl_4$ and the result obtained suggested reinvestigation of the $KAlCl_4$ distillation. It was found that in both cases considerable decomposition occurs, the condensate being enriched in $M''Cl_3$.

Experimental. About 100 g. of $KGaCl_4$ was prepared by heating KCl and $GaCl_3$ together in an evacuated quartz vessel. The potassium chlorogallate was then heated slowly to about 700° while a connected pyrex vessel was cooled in liquid nitrogen to maintain the vacuum in the system. Decomposition is exceedingly slow below 500° . At about this temperature, $GaCl_3$ is lost, and at the higher temperatures KCl was also transported, $KGaCl_4$ being collected in the condenser. Above 650° material refluxed rapidly near the mouth of the furnace.

$KAlCl_4$ behaves in a very similar manner.

Unfortunately, the observations on the distillation do not lead to any definite conclusions about the stability of the species $KGaCl_4$ or $KAlCl_4$ in the gas phase. The refluxing of material observed cannot be accounted for by $GaCl_3$, and might suggest condensation of $KGaCl_4$. It seems possible, however, to account for it also by evaporation of KCl as such, with $GaCl_3$; these substances recombine on condensing and flow down the sides of the tube. A more definite conclusion can probably be reached by measurements of the density of vaporized $KGaCl_4$ or $KAlCl_4$. Several efforts were made to construct a quartz gauge suitable for such measurements, but were unsuccessful.

It also seemed of interest to discover whether $HGaCl_4$ exists in the gas

¹¹⁾ Baud, Ann. Chém. Phys. (8) 1, 46 (1904).

phase. This was done by investigating the additivity of GaCl_3 and HCl pressures. Although the experimental error in this determination was large, it is possible to conclude that this compound is not very stable. At 450°C a maximum limit of 10^{-6} may be put on the constant $K = \frac{(\text{HGaCl}_4)}{(\text{HCl})(\text{GaCl}_3)}$ for a standard state of one atmosphere for each gas.

Experimental. A Bourdon gauge was employed which required optical detection of the motion of the pointer. The gauge was employed as a null instrument and the motion of the pointer was observed through a microscope. The large inaccuracy in this experiment arose because the fiduciary mark was too far from the pointer, and it was very difficult to reproduce the zero setting of the gauge.

The pressure was observed at several temperatures. Some of the data are shown in Table 2.

Table II
Additivity of Pressures of GaCl_3 and HCl

Temperature, $^\circ\text{K}$	$\text{Ga}_2\text{Cl}_6\text{-GaCl}_3$	HCl	Pressure, cm.	
			Calculated total	Experimental total
500	17.05	24.3	41.3	43.5
600	26.5	29.2	55.7	55.0
650	33.0	31.6	64.6	65.8
700	40.5	34.0	74.5	73.0

For NH_4GaCl_4 a reaction of the type described for KGaCl_4 or KAlCl_4 is not expected, since NH_4Cl itself is unstable at high temperatures. A different type of decomposition takes place, however, and in fact sets in at temperatures as low as 200° . Heated in a vacuum, NH_4GaCl_4 rapidly loses HCl , and the residue approaches NH_3GaCl_3 in composition. The system is discussed in more detail in Section F.

Experimental. A sample of NH_4GaCl_4 which melted in the range $297\text{-}301^\circ$ was heated in an evacuated vessel, the other end of which was immersed in liquid nitrogen. As the temperature increased, the sample appeared to melt and boil all at once. After boiling for a few minutes, it was allowed to cool and the apparatus was cut in half. The cold end contained much HCl .

The less volatile residue was analyzed for chlorine. Found: percentage Cl, 58.4, 58.4. Calculated for NH_4GaCl_4 : percentage Cl, 61.8. Calculated for NH_3GaCl_3 : percentage Cl, 56.6.

F. VAPOR PRESSURES AND VAPOR DENSITIES OF NH_4GaCl_4
AND NH_3GaCl_3

In this section data on the vapor pressure of solid and liquid NH_4GaCl_4 and on the density of the vapor are presented. Interpretation of the data required an investigation of the vapor pressure and vapor density of NH_3GaCl_3 , and of the miscibility of NH_4GaCl_4 and NH_3GaCl_3 in the liquid. The results of these experiments are also included in this section. The observations made confirm the conclusion, already cited, that NH_4GaCl_4 decomposes to NH_3GaCl_3 and HCl . In the gas phase, this decomposition is complete.

1. Vapor pressure of NH_4GaCl_4 . The vapor pressure was measured over the temperature range from 275 to 440° by means of a Bourdon gauge. Three experiments were performed in which the ratios of amount of ammonium chlorogallate to the volume in which it was enclosed were 4.9, 17.5, and 269 $\mu\text{mole/ml.}^*$ respectively. The data from these three experiments are presented on the Log P vs $1/T$ plot of Fig. 6. The discontinuity of slope of each curve occurs at the melting point for the ratio of $\mu\text{mole/ml.}$ The points below the curve for 4.9 $\mu\text{mole/ml.}$ at the high pressure end of the curve correspond to the unsaturated vapor and not to the vapor pressure of the liquid. The vapor density may be calculated from these data, as discussed in the next section.

The data show that the vapor pressure depends on the ratio of amount of NH_4GaCl_4 to volume as well as the temperature. Thus the liquid-vapor equilibrium system has more than one degree of freedom, and therefore the composition of the phases cannot correspond to the formula NH_4GaCl_4 . This is not surprising, in view of the observation already made that NH_4GaCl_4 loses HCl readily when heated in a vacuum. The system will be discussed more completely in relation to the phase rule and to some other data in part 5 of this section.

Experimental. The modified form of Bourdon gauge which was used to measure the pressure of ammonium chlorogallate in the experiments at 4.9 and 17.5

* $\mu\text{mole} = 10^{-6} \text{ mole.}$

Fig 6

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μ mole/ml. is shown in Fig. 7. The gauge used in the experiment for 269 μ mole/ml. was similar in construction except that the extra volume furnished by the outer envelope was omitted. In effect, the wall ABC (Fig. 7) was omitted and the wall CD was added. Both of the gauges were designed with the object of keeping the space available to the NH_4GaCl_4 as short as possible. This is necessary in order to minimize the temperature gradient in the space.

A difference in gas pressure on the two sides of the Bourdon tube, P and Q, serves to bend the Bourdon tube and open or close the switch. The balance pressure difference, abbreviated BPD, is defined as the difference in pressure between P and Q required to just open the switch. As nearly as can be measured, this is the same as the pressure difference required to just close the switch. When the adjustment is very close, stray vibrations make the switch vibrate open and shut.

In practice, the pressure in Q was controlled by a capillary leak which was attached at one end to S and, at the other end, to a three way stopcock by which it could be connected to the atmosphere or to a vacuum pump. A mercury manometer of 12 mm. bore was also connected to S and the pressure in P was then determined as the pressure in Q plus the BPD.

A thyatron relay was connected to the switch in such a way that the relay was controlled by the switch, although at most 50 μ amperes flowed through the switch. The relay controlled a signal light which indicated whether the switch contacts were open or closed.

It was found that although the BPD could be reproduced to 0.01 mm. of mercury if the experimental conditions were not widely varied, it depended strongly on the temperature and depended in a critical way upon the orientation of the gauge with respect to the gravitational field. It also was changed by straining the tube P-S and by large differences in pressure between P and Q. Annealing the gauge at 525° in the exact position in which it was used in the furnace improved the reproducibility of the BPD considerably, and clamping the gauge in position during each run also helped. Finally a calibration of BPD against temperature was made. It was found that at any temperature in the range the BPD could be reproduced within $1/2$ mm. if care was taken, and that it could be reproduced within 5 mm. in any case.

A nichrome wound tube furnace was used which had a hole 7.5 cm. in diameter and 55 cm. long. A piece of 2 $1/2$ inch iron pipe 20 cm. long and

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Fig. 7.--Bourdon Gauge

Fig. 8.--Chlorination apparatus

closed at one end was placed in the center of the tube. The ends of four thermocouples were placed along the Bourdon bulb and then this was inserted into the iron pipe, which served to decrease the temperature gradient along the bulb. With the smaller gauge it was possible to place a glass tube and a sheet iron liner within the iron pipe as additional thermal shielding before inserting the bulb of the Bourdon gauge. The remaining space in the furnace was packed with silocel or pyrex wool insulation.

The samples of ammonium chlorogallate used in this series of experiments were all from the preparation described in section C part 2. A charge of ammonium chlorogallate was introduced into the Bourdon gauge after it was evacuated and before it was put into the furnace by melting the sample in the sample tube and allowing it to flow into the gauge. It was necessary to distill the last bit of NH_4GaCl_4 into the gauge and then seal off the sample tube. Only a small amount of HCl could be lost in this way because of the small volume of the sample tubes (about 10 ml.).

As soon as the gauge was connected to the pressure adjusting and measuring apparatus by S, a pressure of several centimeters was measured inside the gauge. This was due to HCl which separated from the NH_3GaCl_3 in the vacuum distillation. Once the gauge had been heated up and then cooled slowly, it was found that there was a good vacuum within the bulb.

Pressure readings were taken both as the temperature of the furnace was slowly increased, and as it was decreased in the desired range. It was found easy to reproduce readings within 2 mm. at temperatures above the melting point, but it was necessary to maintain the furnace at the same temperature for as long as 24 hours in order to obtain equilibrium values for the pressure below the melting point, especially at the larger values of μ mole/ml. It was also found helpful in the experiment at 269 μ mole/ml. to move the gauge farther into the furnace for data below the melting point. This maintains the Bourdon tube at higher temperatures than the extremity of the gauge. The fact that this helps in obtaining equilibrium values of the pressure indicates that a large part of the difficulty below the melting point is due to the condensation of solid in the Bourdon tube which interferes with its motion. Because this difficulty was not completely avoided in any of the experiments, it is not surprising that the data below the melting point show a larger spread than above the melting point.

After the pressure-temperature data had been obtained, the bulb of the gauge was carefully opened. This was done by admitting air into P and Q at the same rate so that no large pressure difference developed across the Bourdon tube to break it. The bulb was then rinsed out and the rinsings were analyzed for chlorine to determine the amount of NH_4GaCl_4 in the bulb. These data are summarized in Table 3.

Table 3

Data for Experiments with Vapor Pressure and
Vapor Density of Ammonium Chlorogallate

Experiment	Millimoles of Ammonium Chlorogallate in Sample	Volume of Bulb of Gauge, ml.	M moles/ml.
1	2.98	170.7	17.5
2	0.837	170.4	4.90 ₇
3	4.58	17.	269.

2. Vapor density of ammonium chlorogallate. In the vapor pressure experiment at 4.9 M mole/ml. described in the previous section, several measurements of pressure were made beyond the temperature at which all the material had been vaporized. These data are presented in Table 4 and the three readings at the lowest temperatures after vaporization are shown also in Fig. 6. The plot shows clearly that the condensed phase has disappeared at these temperatures.

Table 4

Vapor Density of Ammonium Chlorogallate

Observed Temperature, °C				Average Temperature, °K	p, pressure cm.	C _T , Concentration, moles/ml	$\frac{C_T}{C_S}$	
A	B	C	D					
3	428	427	428	426	700	44.0	10.1 ₀	2.05 ₅
2	433	435	434	433	707	44.7	10.1 ₆	2.06 ₈
1	464	464	462	460	736	47.4	10.3 ₄	2.10 ₄
4	474	474	470	468	745	48.5	10.4 ₅	2.12 ₈
5	476	476	473	471	747	48.8	10.4 ₉	2.13 ₇

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The chronological order numbers indicate the order in which the measurements were made and show that the changes observed are not due to irreversible phenomena. The temperatures recorded are the temperatures indicated by four calibrated thermocouples spaced along the gauge inside of the furnace. The concentration in μ mole/ml., C_T , was calculated from the pressure in cm. by the equation:

$$C_T = \frac{10^6 n}{V} = \frac{10^6 p}{RT} = 160.5 p/T$$

where the middle equality is the perfect gas law. C_S is the stoichiometric concentration, 4.907 μ mole/ml, obtained by dividing the number of micromoles of ammonium chlorogallate in the gauge by the volume of the gauge in ml. The greatest error in these determinations is in the pressure, p , which may be in error by 0.5 cm. or 1% due to faulty calibration of the gauge. However, it is believed that the relative error within this series of measurements is only 0.2 of this, and that the relative values of C_T/C_S are accurate to 0.2%.

A value of $C_T/C_S = 2$ indicates that the equilibrium

is completely to the right in the vapor phase if the further dissociation of NH_3GaCl_3 in this temperature range is excluded. The data for the vapor density of NH_3GaCl_3 in this same temperature range which are reported below show that this compound is only slightly dissociated in this temperature range, and it is this slight dissociation which is probably responsible for the trend in the values of C_T/C_S in Table 4. It is possible to calculate an equilibrium constant for the reaction:

from these data and a value for the heat of this reaction from the change of equilibrium constant with temperature (see Fig. 10). The heat of reaction thus determined is between 30 and 60 kcal. and is consistent with the value indirectly determined from other data (Section I of this report). However, the large uncertainty in the calculated value of ΔH from these data make this calculation of little value except to indicate that our interpretation of the data is reasonable.

3. Vapor pressure and vapor density of NH_3GaCl_3 . The vapor pressure of samples of NH_3GaCl_3 has been measured over a temperature range by means of a pyrex Bourdon gauge. The method differed from that followed for NH_4GaCl_4 only in that an automatic device was used for maintaining the pressure balance. Two samples were run: 56 mg. of Preparation A for one series and 240 mg. of Preparation B for the second series. At the higher temperature for the small sample, the substance was completely vaporized, and in this run, the measurements of vapor density were made.

The experimental data are presented in Table 5 and Fig. 9. The points below the curve of Fig. 9 at the high temperature end of the scale are values of the pressure of the unsaturated vapor. The vapor densities calculated from these data are discussed below.

The following properties of NH_3GaCl_3 are readily derived from the curve of Fig. 9:

Normal boiling point: 438°C .

ΔH of vaporization of the liquid: 17.7 kcal./mole

ΔS of vaporization of the liquid: 24.9 cal./mole deg.)

The data for the vapor density of NH_3GaCl_3 obtained in the experiment above are also presented in Table 5. C_S is the stoichiometric concentration of NH_3GaCl_3 in the gauge calculated from the known weight of the sample, 56 mg., and the known volume of the gauge, 19.1 ml. C_T is the concentration calculated from the pressure and the perfect gas law. If the vapor is composed of NH_3GaCl_3 molecules and if these obey the perfect gas law and are not adsorbed on the glass walls, then the ratio C_T/C_S should be unity for the unsaturated vapor. The trend C_T/C_S with increasing temperature is probably due to dissociation of NH_3GaCl_3 , but because of the uncertainty in the volume of the gauge, the size of the charge, the magnitude of the deviations from the gas laws, and because of the limited temperature range, it is not possible to calculate reliable values for the heat of this dissociation from these data.

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Fig. 2-- Vapor pressure of NH_3GaCl_3

2+LOG K

FIG 2 (U)

DISSOCIATION OF NH_3GaCl_3 AS A FUNCTION OF TEMPERATURE

FIG 3 //

APPARATUS FOR ISOPIESTIC EQUILIBRATION

Table 5

Vapor Density and Vapor Pressure of NF_2GaCl_3

Data of First Experiment			Data of Second Experiment	
Temperature, °C	Pressure, cm. Hg	C_T/C_S	Temperature, °C	Pressure, cm.Hg
267	1.43		410	45.57
283	2.30		424	59.50
295	3.24		439	75.86
321	6.38		435	73.41
349	12.26		368	19.61
360	16.22		328	7.76
372	22.07		316	5.63
377	23.44		274	1.61
404	39.89		281	2.14
414.5	48.85		299	3.56
440	66.96	0.987	309	4.61
442	67.53	0.996	320.5	6.82
464	81.1	1.16	392	2.94
461	72.32	1.03	406	42.26
461	72.97	1.048		
464	72.97	1.045		
464.5	73.42	1.050		
460	72.37	1.041		
456.5	71.64	1.037		
455	70.75	1.025		
450	70.02	1.022		
445	68.83	1.011		
438.5	67.20	0.996		
418	53.08			
372.5	21.94			

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4. Miscibility of NH_4GaCl_4 and NH_3GaCl_3 in condensed states. Experiments already described have shown that NH_4GaCl_4 on heating loses HCl and the liquid phase becomes richer in NH_3GaCl_3 . For the interpretation of the data on the vapor pressure of NH_4GaCl_4 it was necessary to know whether NH_3GaCl_3 and NH_4GaCl_4 are miscible in the liquid. Experiments investigating this aspect of the system were made by heating NH_3GaCl_3 in the presence of HCl , to convert it in part to NH_4GaCl_4 , then observing the liquid visually and measuring the melting range of the liquid. The mixture of composition 80 mole % NH_3GaCl_3 to 20 mole % NH_4GaCl_4 had a molting range of at least from 100° to 200° . The mixture of composition 60 mole % NH_3GaCl_3 and 40 mole % NH_4GaCl_4 likewise had a long melting range. The sample was finally converted completely to NH_4GaCl_4 by excess HCl after which it no longer adsorbed HCl . Under no conditions was more than one liquid phase observed. The experiments show that NH_3GaCl_3 and NH_4GaCl_4 are miscible as liquids over wide ranges of composition. The long molting range of the mixtures indicates that the mutual solubility of NH_3GaCl_3 and NH_4GaCl_4 is low in the solid state.

5. Interpretation of the data on the vapor pressure of NH_4GaCl_4 . The vapor pressure data for ammonium chlorogallate may be expressed within the experimental error by the three equations:

$$\text{Log } p = \frac{-14.39 \times 10^3}{4.576 T} + 6.722 \text{ for } 269 \text{ } \mu\text{mole/ml.} \quad (1)$$

$$\text{Log } p = \frac{-14.96 \times 10^3}{4.576 T} + 6.515 \text{ for } 17.5 \text{ } \mu\text{mole/ml.} \quad (2)$$

$$\text{Log } p = \frac{-15.36 \times 10^3}{4.576 T} + 6.533 \text{ for } 4.9 \text{ } \mu\text{mole/ml.} \quad (3)$$

For liquid NH_3GaCl_3 the vapor pressure is given by

$$\text{Log } p = \frac{-17.74 \times 10^3}{4.576 T} + 7.333 \quad (4)$$

These equations give the pressure, p , in cm. of Hg as a function of the temperature, T , in degrees absolute.

The system having ammonium chlorogallate in liquid-vapor equilibrium evidently has two degrees of freedom because both the temperature and the stoichiometric concentration (defined as the ratio of the amount of material in the system to the volume accessible to it) must be fixed to determine the

pressure, and because the temperature, concentration, and pressure are the only variables. The phase rule requires that for a divariant system the number of phases equal the number of components. This number is at least two, because there are at least a vapor phase and one liquid phase present. Direct observations made in part 4 show that only one liquid phase exists, hence the total number of phases is only two. This fixes the number of components as two, a conclusion which is supported also by the following arguments.

Direct observations on the forward and reverse processes have shown that the reactions:

occur. The data on the vapor densities of NH_4GaCl_4 and NH_3GaCl_3 show that the reactions:

also take place, but equilibrium is far to the left below 430° . Since NH_3GaCl_3 exists as such in the gas at 430° , and since its heat of vaporization is constant to within experimental error, about 1%, between 300° and 430° , it is unlikely that it undergoes any decomposition in this whole temperature range. Hence the only substances present in the NH_4GaCl_4 are HCl and NH_3GaCl_3 , or any that may be formed by a combination of these. These two substances suffice to express the composition of each of the phases, and thus the number of components is at most two.

A number of observations support the conclusion that the vapor phase is richer in HCl than it is in NH_3GaCl_3 . Among these are the following: NH_4GaCl_4 on heating loses HCl and the condensed phase approaches NH_3GaCl_3 in composition; HCl does not dissolve appreciably in molten NH_4GaCl_4 , but NH_3GaCl_3 is very soluble in it; over a short range in the curve for 269 mole/ml., Fig. 6, between the melting point and a value of $\log p = 1.307$, the pressure of the NH_4GaCl_4 is greater than twice the pressure of pure NH_3GaCl_3 at each temperature. Thus the system in liquid vapor equilibrium is described by the reactions:

It is not possible to evaluate these equilibrium constants without knowledge of the composition of one of the phases in each system at each temperature. It would be possible to estimate them if the assumption were made that the solutions of NH_3GaCl_3 in NH_4GaCl_4 are ideal, but the concentrations of these solutions in the systems with 17.5 and 4.9 M mole/ml. are too high (greater than 10 mole %) for this approximation to have any value.

One consequence of these equilibria may be noted: It is not possible to prepare pure liquid ammonium chlorogallate, for this liquid would have an infinite pressure of HCl . The fact that ammonium chlorogallate reaches a constant boiling temperature when distilled in an atmosphere of HCl ⁵⁾ must mean that at this temperature the composition of the distillate is the same as that of the boiling liquid and both contain more NH_3GaCl_3 than HCl .

The fact that the slopes of the three curves of Fig. 6 are constant within the experimental error and are nearly the same means that the heats of reactions (1) and (2) are almost equal and are roughly independent of the composition of the solution of NH_3GaCl_3 in NH_4GaCl_4 . This is consistent with the fact that ΔH factors in equations (1) to (3) are not far different from the ΔH factor of equation (4), and approach it as the composition of the condensed phase in the ammonium chlorogallate experiments approaches the composition of NH_3GaCl_3 .

The results for the solid-vapor equilibrium are less definite owing to the larger experimental error in this region. This system may well be monovariant, in which case it is described by the equilibria:

The freezing points determined from the vapor pressure data are 285° , 295° , and 303°C . for 4.9, 17.5, and 269 M mole/ml. respectively. The trend is consistent with the interpretation given to these experiments.

G. SOME REACTIONS OF CHLOROGALLATES

Among the reactions of interest for these compounds are those in which $M^3 Cl$ is displaced from $M^3 M'^3 Cl_4$ by a basic constituent. The extraction by ether of $GaCl_3$ in excess of $LiCl$ from $LiGaCl_4$ may be regarded as a reaction in this class. Some qualitative experiments of the same type were done by treating $KGaCl_4$ with basic organic solvents such as pyridine. KCl was formed in some cases, but since the solvents were not purified (dried!) the results are inconclusive.

Experiments were also done treating $KGaCl_4$ with the base NH_3 . At temperatures between 200° and 500° , reaction takes place forming KCl and $GaCl_3 \cdot 3NH_3$. The latter compound is volatile under the conditions of the experiments. At higher temperatures, a yellow non-volatile compound of gallium and nitrogen, presumably GaN , is also formed. A yellow material of unknown composition¹⁰⁾ and a gray product of composition GaN ¹²⁾ have been reported as products of the reaction of Ga with NH_3 . More recently it has been reported that a gray GaN formed by the reaction of Ga with NH_3 and a yellow GaN formed by the reaction of $(NH_4)_3 GaF_6$ with NH_3 have the same Debye-Scherrer pattern¹³⁾.

Experimental. A sample of $KGaCl_4$ was placed in a porcelain boat which was heated in a quartz tube by an electric furnace. Dry NH_3 was passed through the tube while the temperature was slowly raised. The first distillate appeared at 200° in the form of a white solid which was largely suspended as a fog and which settled very slowly. This solid was found to have a vapor pressure of 26 mm. at 156° and is therefore probably $GaCl_3 \cdot 5NH_3$, which has a pressure of 35 mm. of NH_3 at 156° according to Klemm, Tilk, and Jacobi¹⁰⁾. However, judging by the work of these same authors, it is the tri-ammonate of $GaCl_3$ which is stable in the gas phase.

As the temperature of the furnace was increased to over 500° , the formation of the ammonate became very rapid and a yellow residue formed around the boat. The temperature was raised to 760° without any other change in the appearance of the process.

12) Johnson, Parsons and Crew, J. Phys. Chem. 36, 2651 (1932).

13) Hahn and Juza, Z. Anorg. Allgem. Chem. 244, 111 (1940).

The yellow residue was washed free of KCl with dilute acid and water. It was found to be insoluble in dilute acid but readily soluble in hot concentrated NaOH with the evolution of NH_3 , and to be difficultly and incompletely soluble in concentrated H_2SO_4 . The residue contains gallium as well as nitrogen, but no potassium or chlorine. Enough of the yellow material for a quantitative analysis was not obtained in this or in similar experiments.

A reaction of NH_4GaCl_4 of preparative interest is the oxidation by chlorine to form GaCl_3 , HCl and N_2 .

This reaction has already been mentioned (Section C) as the final step in preparing GaCl_3 from aqueous solution, the first step being the formation of crude NH_4GaCl_4 . The method is rapid and convenient but the over-all yield of GaCl_3 is only about 50%.

Experimental. The apparatus is shown in Fig. 8. It is essentially a 30 mm. diameter pyrex tube heated by two ten inch tube furnaces and connected at the exit end to a trap especially designed to collect large amounts of solid materials without blocking. Two pyrex wool plugs were placed in the tube at the locations shown in the figure to insure mixture of the gases.

After the furnaces had been brought up to the temperature 330° for the center of the first furnace and 440° for the center of the second furnace, chlorine which had been washed with H_2SO_4 and dried over P_2O_5 was passed through the apparatus. Then a pyrex boat containing 18.5 g. of NH_4GaCl_4 was inserted through the ground joint and the rate of flow of chlorine was quickly increased until no more NH_4GaCl_4 appeared at A. The trap was cooled to -20° to condense GaCl_3 and the reaction was allowed to proceed for 20 minutes, after which time the boat was empty. The chlorine was shut off and the trap was quickly sealed off at A and B. The product was then distilled in a vacuum. The yield of purified GaCl_3 , calculated from the amount of NH_4GaCl_4 taken, was 67%.

H. ETHER SOLUTIONS OF COMPOUNDS OF THE TYPE M'M'''Cl₄

One of the most interesting properties of the substances of the type M'M'''Cl₄ is the high solubility of some of them in ether. Data on the solubility in ether of a NH₄GaCl₄, LiGaCl₄, KGaCl₄, CsGaCl₄, NH₄FeCl₄ were presented in Section D. The solubilities of NH₄GaCl₄ and NH₄FeCl₄ are particularly high. With NH₄GaCl₄ the composition of the saturated solution corresponds to 2.3 moles of ether per mole of solute; for NH₄FeCl₄ this ratio is 3.8. It seemed of interest to investigate the solutions in greater detail, and in particular to learn the constitution of the solute in the ether solution. The observations would seem to have a direct bearing on the extraction by ether from aqueous solutions containing HCl of substances such as FeCl₃ and GaCl₃. It has been shown¹⁴⁾¹⁵⁾ that these are taken into the ether phase as HFeCl₄¹⁴⁾¹⁵⁾ and HGaCl₄¹⁶⁾. In composition, at any rate, the solutes in ether are analogous to the compounds under present investigation.

1. Two phase region. It has been observed that when the concentration of the solute NH₄GaCl₄ in ether is increased, a point is reached at which a new liquid phase appears. On further increase in the amount of solute, the solute rich phase grows at the expense of the more dilute phase, and eventually the dilute phase disappears completely. Analyses were made of the composition of the two liquid phases in equilibrium, at 25°, and the results are presented in Table 6.

Table 6

Two Liquid Phases in Solutions

of NH₄GaCl₄ in Ether at 25°

	Upper phase	Lower phase
Density, g/ml.	0.75, 0.74	0.81, 0.83
Moles Cl/moles N	3.99	4.00
conc., molality	0.4 ₅	0.8 ₈
conc., wt. %	9.4	16.8

¹⁴⁾Axelrod and Swift, J.A.C.S., 62, 33 (1940).

¹⁵⁾Nachtrieb and Conway, J.A.C.S., 70, 3547 (1948).

¹⁶⁾Nachtrieb, private communication.

The results show that both phases are still rather dilute, the more concentrated being only 0.9 molal, and show furthermore that NH_4GaCl_4 is distributed as a compound between the two phases. Since the composition of the solute is maintained as NH_4GaCl_4 in each of the liquid phases the system is one of only two components. Since the number of phases is three, the system is therefore monovariant.

Two liquid phases have also been observed for the solutions in ether of each of the solutes: NH_4FeCl_4 , NH_4AlCl_4 and LiGaCl_4 , but these systems have not been studied in any detail.

2. Dissociation of the solute. The experiments on the distribution of NH_4GaCl_4 between the two liquid phases demonstrates that the substance does not undergo appreciable dissociation into neutral species. If considerable dissociation into HCl and NH_3GaCl_3 , for example, took place, the ratio of $\text{Cl}:\text{Ga}$ would hardly be expected to remain 4 in each of the phases.

NH_4GaCl_4 behaves as a pure substance also in its distribution between the solid phase and the solution in ether. Experiments discussed above have shown that the ratio of $\text{Cl}:\text{Ga}$ is 4 in each of these phases. NH_4FeCl_4 behaves in a similar manner. By contrast, partial dissociation does take place with the solute LiGaCl_4 . The ionic dissociation of NH_4GaCl_4 in ether is discussed in Sections H and I.

Experimental. Solid LiCl was treated with a solution of GaCl_3 in ether at 25° . After equilibration, the solution was filtered and then evaporated in vacuo. The evaporation proceeded very slowly in its final stages, and was not carried to completion. Even after being continued for 36 hours at 100° , liquid was left in the system. The solid and liquid portions of the residual mixture were separated as well as was possible, and analyzed separately for content of Cl and Ga . The results are summarized below. The calculations were made assuming that the components LiCl , GaCl_3 and ether suffice to describe the composition of the phases.

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	Solid phase	Liquid phase
$\frac{\text{moles LiCl}}{\text{moles GaCl}_3}$	1.39	.15
$\frac{\text{moles ether}}{\text{moles GaCl}_3}$	0.44	0.88

It is evident that the composition of solute in neither phase corresponds to the formula LiGaCl_4 , and that the liquid phase is enriched in GaCl_3 . When the solutions are more dilute, the composition of the solute in the liquid more nearly corresponds to LiGaCl_4 . Thus, the solid residue above, when treated with ether, yielded a solution in which the mole ratio of LiCl to GaCl_3 was 0.88.

3. Association of NH_4GaCl_4 in ether. An investigation of the vapor pressure of solvent above solutions of NH_4GaCl_4 in ether was undertaken to find the state of aggregation of the solute. The experimental information sought is the ratio of m_s , the stoichiometric molality of an ether solution to m_o , the molality as determined from the measurement of a colligative property. Each determination of m_s/m_o was made by allowing a solution of ammonium chlorogallate and one of benzil in ether to come to the same vapor pressure of ether by allowing ether to distil between the two solutions until equilibrium was reached. Solutions of benzil in ether were assumed to be ideal and the concentration of benzil at equilibrium then gave the value of m_o , while the concentration of the ammonium chlorogallate solution at equilibrium was m_s . The method is described in detail below. The data are presented in Table 7 and in Fig. 12.

Table 7
Data from Isopiestic Experiments

m_s	Density	m_s/m_o
0.009 ₉	0.70 ₉	1.1 ₀
0.024 ₅		1.3 ₇
0.025 ₁	0.71 ₄	1.3 ₅
0.043 ₂		1.5 ₀
0.047 ₄		1.6 ₇
0.059 ₆		1.7 ₇
0.062 ₀	0.71 ₈	1.6 ₇
0.087 ₅	0.72 ₀	2.0 ₄
0.18 ₆		3.1 ₂

FIG 12

ASSOCIATION OF AMMONIUM CHLOROGALLATE IN
ETHER SOLUTION AS A FUNCTION OF CONCENTRATION

FIG 13

APPROACH TO EQUILIBRIUM

The data clearly show that ammonium chlorogallate associates in ether and that the degree of association increases with the concentration. The data indicate that no definite polymer is formed but rather that clustering of the solute particles occurs at the higher concentrations. These observations will be compared in Section I of this report with data for similar systems obtained by Kraus and coworkers¹⁷⁾.

Experimental. The isopiestic method was used in determining the vapor pressure of ether above solutions of NH_4GaCl_4 . This method, applicable to non-volatile solutes, depends upon the fact that at isothermal equilibrium two solutions with the same solvent and a common vapor phase will have the same vapor pressure of solvent. Thus the vapor pressure of one of the solutions may be determined in this way if that of the other is known as a function of concentration. In this work the vapor pressures of the reference solutions, solutions of benzil in ether, were assumed to vary according to the laws of ideal solutions. The justification for this assumption is discussed below.

The apparatus used is shown in Fig. 11. The functions of the various parts will be made clear by an explanation of the way in which the apparatus was used. After the apparatus had been cleaned and dried carefully, a small glass cup, E, containing a known amount of benzil was introduced into A through D and then the end of D was sealed off. In a similar fashion a known amount of ammonium chlorogallate was introduced into A' through D', this operation being conducted in the dry box. Tube D' was then stoppered and the apparatus was removed from the dry box and attached to the vacuum line by means of the ground joint on D'. The stopper was removed just before this connection was made and the apparatus was quickly evacuated. The required amount of ether was distilled into the apparatus and the tube D' was then sealed off just behind the ground joint. Some mercury from the barometers and mercury cut-offs in the line always distilled in with the ether.

After it was filled in this way the apparatus was immersed in a thermostat and attached to a rocking mechanism. It was rocked in such a manner that the solutions ran back and forth from C and C' into A and A' respectively

¹⁷⁾ See Section I for references.

at a rate of 36 cycles/min. The solutions in A and A' were separated by a glass wall, but the vapor phases were connected through B. The volumes of the solutions, and hence their concentrations, were measured at intervals by draining the solutions into C and C'. The approach to equilibrium could be followed by observing the changes in concentrations and the attainment of equilibrium could be verified by distilling a small amount of solvent from one side to the other so as to observe the approach to equilibrium from the opposite direction. The approach to equilibrium from each direction for one system is shown in Fig. 13.

In order to calculate the weight concentrations of the solutions from the volume concentrations, the densities are needed. The densities of the benzil solutions were obtained from a curve which was constructed from the data of Tyrer¹⁸⁾. The densities of several of the ammonium chlorogallate solutions were measured at the conclusion of the experiments by weighing known volumes of these solutions and then a curve was constructed from these data and used to get densities for the remaining solutions. The density correction is not an important one because the densities of all of the solutions are within 3% of that of pure ether.

The concentration of the ammonium chlorogallate solution was checked in several cases at the conclusion of the experiment by cutting tube D' open and quickly transferring a known volume of the solution to a weighing bottle. The solution was weighed, giving an approximate value for its density which was used as described above, and then the solution was analyzed for chloride after being mixed with water. The analytical value for the concentration checked with the value obtained from the directly observed weight of the solute and volume of solution with 1% in every case in which the analysis was made. These are the solutions for which the densities are given in Table 7. The density measurements were accurate to about 1% as shown by handling ether in the same way as the solutions.

The benzil solutions were analyzed for chloride ion in each case. None was found, indicating that no ammonium chlorogallate solution had ever spilled over to the benzil side.

¹⁸⁾Tyrer, J. Chem. Soc., 97, 2629 (1910).

Some experiments were performed at lower concentrations than those described here, but equilibrium was not attained even after many weeks.

The benzil used in these experiments melted in the range 94.7 to 95.1°. The literature value is 95°.

The interpretation of these experiments evidently depends on the extent to which solutions of benzil in ether are ideal. Direct experimental observations and a calculation based on Hildebrand's equation for non-ideal solutions point to the conclusion that in the concentration range studied the solutions obey the ideal solution laws.

Beckmann¹⁹⁾ studied the boiling point elevation of solutions of benzil in ether and obtained the results shown (after recalculation to the units used in this paper) in Table 8. The values of $\Delta T/m$ in the last column of this table have been calculated from the ideal solution law using a directly determined heat of vaporization of diethyl ether¹⁹⁾. The accuracy of Beckmann's work is of the order of 10%, judging by the internal consistency of his results, and his data agree with the ideal solution law within this rather large margin.

Table 8

Boiling Point Elevation of Solutions of Benzil in Ether,
Data of Beckmann

Molality of Benzil m	Boiling Point Elevation T° C	ΔT	ΔT
		$\frac{m}{\text{Experimental}}$	$\frac{m}{\text{Calculated}}$
0.1051	0.234	2.227	2.220
0.1113	0.224	2.015	2.210
0.2130	0.458	2.127	2.207
0.3237	0.674	2.083	2.197

The magnitude of the deviations from ideality of binary systems of non-polar components may be calculated as shown by Hildebrand²⁰⁾ in terms of the differences in molal volume and internal pressures of the two components.

¹⁹⁾"International Critical Tables," The McGraw Hill Book Co., New York, 1929, V, 138.

²⁰⁾Hildebrand, Chem. Rev., 44, 37 (1949).

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Although both components in the system benzil-ether are polar, the treatment still applies because the chief effect of the relatively small and unexposed dipoles is to increase the internal pressures of the constituents in the same way the van der Waals forces do²⁰⁾. The calculation was carried out by one of us²¹⁾ for the present system with the result expressible by the equation:

$$\frac{m_c}{m_s} = 1 - 0.40 m_s$$

Thus, at 0.01 molal the colligative molality may be expected to differ from the stoichiometric molality by only 0.4%, and at 0.1 molal, by 4%.

4. Conductivity of solutions of ammonium chlorogallate in ether. The conductivity of solutions of ammonium chlorogallate in ether was measured over a concentration range to see whether these solutions exhibited the outstanding feature found by Fuoss and Kraus²²⁾ for solutions of electrolytes in solvents of low dielectric constant, namely, a minimum in the curve of equivalent conductance as a function of concentration. This minimum was found in the system studied here at a concentration of 0.0021 molar, and an equivalent conductance of 0.089. In Section I of this report, some other properties of this system will be derived from these data with the aid of data from other sources and the theory of Fuoss and Kraus. The general result is that the degree of ionization at moderate to large concentrations is too small to be important for solubility considerations.

Experimental. The conductance cell used in these experiments and shown in Fig. 14 was designed to meet the following requirements. The cell constant must be of the order of 0.005. It must require a minimum amount of solution to make a measurement. It must be possible to mix the solutions in the cell without allowing them to come in contact with stopcock lubricant. It must be possible to maintain a flow of solution over the electrodes during a conductivity measurement. The cell must be gas-tight.

²¹⁾Friedman Ph.D. Dissertation "Ammonium Chlorogallate and Some Related Compounds". Univ. of Chicago, 1949

²²⁾Fuoss and Kraus, J.A.C.S., 55, 2387 (1933).

Fig. 14.—Conductance cell

These requirements were set after a preliminary experiment using a less suitable apparatus. The data from this preliminary experiment are shown as curve I, Fig. 15, to indicate that the general character of the results is not changed by the refinements in the present apparatus. However, it is known that the apparatus in the preliminary experiment was not perfectly gas-tight because the solutions had become slightly colored by the end of the experiment, and the conductivity measurements in the preliminary experiment were much less reproducible because it was not possible to allow the solution to flow over the electrodes during a measurement.

The electrode assembly in the final apparatus consisted of four platinum sheets, 20 mm. by 10 mm. by 0.1 mm. These were spaced 0.2 mm. apart by four soft glass beads on each long side of the assembly. The alternate sheets were connected together, as shown in Fig. 14, to stout platinum wires which were sealed to the inside of the pyrox tube and which supported the electrodes. The electrical connections through the wall of the tube were made by platinum wires only 0.1 mm. in diameter. Gas-tight platinum to pyrex seals may be made with platinum wire of this size.

When the cell was completed, tube A was left open to facilitate washing and rinsing the cell. The cell was carefully cleaned with cleaning solution and then with 10% hydrofluoric acid before use and was continuously rinsed with distilled water for several hours.

This cell was then calibrated by comparing the resistance of distilled water (from the laboratory tap) in it and in a cell of cell constant 0.44 as determined with a KCl solution. This method of calibration required rinsing both cells and taking readings on them, rinsing them again, etc., until the resistance observed in each cell had increased to a steady value. This procedure is necessary because some material adsorbed on the glass or the platinum, or perhaps the glass itself, slowly goes into solution and increases the conductivity. The series of conductivity readings for the two cells and the value of the cell constant calculated from each pair of readings are presented in Table 9. The value taken as the cell constant for this cell is 0.0046. The absolute values of the conductivities of electrolytes in non-aqueous systems have no significance at present, so no attempt was made to determine the cell constant with greater precision.

Fig. 15.-- Equivalent conductance of solutions of ammonium chlorogallate in ether.

Table 9

Calibration of Conductance Cell

Resistance of cell used in present work	Resistance of comparison cell: Cell constant of this cell = 0.044_{10} ohms.	Calculated cell con- stant of cell used in present work.
1.07×10^3	25.8×10^3	0.0019
2.68	26.7	.0044
2.84	28.0	.0045
2.98	27.8	.0047
2.98	28.3	.0046
3.10	28.7	.0048
3.18	28.5	.0049
2.96	28.0	.0047
2.91	28.7	.0045

The conductivities of the ether solutions were measured in the following way. After the stopcock had been greased with Silicone high vacuum grease and the ground joint with Apiezon N grease, the cell was connected to the vacuum line and tube A was blown open, after which a steady stream of dry nitrogen was passed through the apparatus and out through tube A. A small glass cup containing a known amount of NH_4GaCl_4 was then taken from the dry box and unstoppered in the nitrogen stream from A and then quickly dropped into A. Tube A was then sealed closed and the apparatus was evacuated. Then the stopcock was closed, the grease was cleaned from the ground joint with CCl_4 and the apparatus was weighed. It was then connected to the vacuum line, some ether was distilled in, and the apparatus was disconnected from the line as before and weighed again. After the contents of the cell had been thoroughly mixed the resistance of the cell was measured on a Jones bridge at 500 c.p.s., using an oscilloscope as a detector. No attempt was made to thermostat the cell during the conductivity measurements, but the room temperature was $25 \pm 1^\circ$ during this series of measurements. It was found that the resistance was reproducible to the extent indicated in the data presented in Table 10, if the readings were taken while the solution was flowing through the electrodes, but that the resistance slowly decreased while the solution was not in motion and then increased again to the original value when the cell was tipped so that the solution flowed again.

After the completion of the first measurement, the apparatus was again connected to the vacuum line, more ether was distilled in, and the weight and resistance were determined for this new concentration. After a total of five such measurements one bulb of the apparatus was full of solution. In order to extend the range of the measurements, most of the solution was drawn out through the stopcock by means of an aspirator and the apparatus was weighed again. Then it was connected to the vacuum line, filled with nitrogen, and while the nitrogen was flowing the stopcock was quickly regreased. This was necessary because the solution dissolved part of the stopcock grease. Then the nitrogen and part of the ether of the solution were pumped off and the cell was weighed and its resistance determined. Then a series of four more measurements was made by successive dilutions. The entire experiment was completed in six hours. All of the data are presented in Table 10 and Fig. 15 (curve II).

The amount of NH_4GaCl_4 originally taken was 15.1 mg. The amount remaining after discarding part of the solution, as calculated from the fraction of the solution discarded, was 4.87 mg.

The specific conductance of the ether was measured in a separate experiment using a D.C. arrangement. A galvanometer of sensitivity 1.7×10^{-9} amp./mm. was connected in series with a switch, the cell containing ether, and a source of potential of 1.6 volts. When the switch was closed the galvanometer deflected 7 ± 1 mm. more than it did with no ether in the cell with the other parts of the circuit just the same. From this experiment the specific conductance of the ether is calculated to be 4×10^{-11} mho./cm. Values as low as 10^{-15} mho./cm. have been reported for the specific conductance of pure ether²³⁾ but since the conductance observed here is 1/100 of the smallest conductance observed for an ammonium chlorogallate solution, no attempt was made to purify the ether further.

Because volume concentrations are required for comparison with the data and theory of Fuoss and Kraus, the molarity of each solution was calculated using the density of ether at 25° , 0.708 g./ml., as the density of each of the solutions.

²³⁾Rabinowitsch, Z. Phys. Chem., 119, 70 (1926).

Table 10

Data of the Conductivity Experiment

Amount of Ether grams	Resistance ohms	Molarity	Equivalent Conductance
The solute is 15.1 mg. of NH_4GaCl_4			
9.34	8.63×10^3	49.8×10^{-4}	10.7×10^{-2}
17.32	18.8	26.9	9.10
25.46	27.8	18.3	9.02
36.09	37.3	12.9	9.54
46.48	46.0	10.0	10.0
The solute is 4.87 mg. of NH_4GaCl_4			
11.27	35.9×10^3	13.3×10^{-4}	9.62×10^{-2}
23.38	60.7	6.42	11.8
33.87	78.0	4.43	13.3
45.07	93.8	3.33	14.7
57.47	107.7	2.61	16.4
57.47*	106.7	2.61	16.5

*This measurement was made eight hours after the completion of the rest of the experiment; all other conditions were the same as for the previous entry in the table.

I. GENERAL DISCUSSION

Some implications of the experimental results which have not been considered in the foregoing sections will be discussed here.

It can be hoped that extensive quantitative data on the stability and properties of related compounds of the type $M'M''Cl_4$ will find reasonable interpretations in terms of the basicity of the monohalides $M'Cl$, and of acidity of trihalides, $M''Cl_3$. The present work, in which some of the general properties of this class of compounds are explored, with special emphasis on the compounds of gallium, is only a beginning in this field.

A few conclusions about stability emerge from observations made in connection with the preparative work. The comparison of $LiGaCl_4$ with $KGaCl_4$ and of $LiAlCl_4$ with $KAlCl_4$ shows that the lithium compounds are less stable than the potassium compounds. This difference may be attributed to a greater basicity of KCl as compared to $LiCl$ and is expected because of the small size and great polarizing power of Li^+ . Similar trends of stability are observed in the analogous series:

In view of the small size of H^+ , similar arguments can rationalize the low stability of $HGaCl_4$ in the gas phase. It seems quite possible however, that with a larger positive ion such as Cs^+ , association of $CsCl$ with $GaCl_3$ in the gas phase can take place. The large Cs^+ would polarize Cl^- much less than does H^+ , and as a result $CsCl_{(gas)}$ would be a more basic substance than $HCl_{(gas)}$.

The observations on the attempts at preparation from aqueous solution of NH_4AlCl_4 , NH_4FeCl_4 and NH_4GaCl_4 are of interest in evaluating the relative affinities for H_2O (or OH^- or $O^{=}$) and Cl^- of the acids Al^{+++} , Fe^{+++} , Ga^{+++} . Only with the latter two was replacement of water (or ions derived from it) by Cl^- possible. This observation correlates with the fact that $FeCl_3$ and $GaCl_3$ are ether-extractable as $HFeCl_4$ and $HGaCl_4$ from aqueous solution containing HCl while $AlCl_3$ does not extract under similar conditions.

Thus far no observations have been made which lead to conclusions about the relative affinities of $AlCl_3$, $FeCl_3$ and $GaCl_3$ for a particular alkali chloride. The data on the heat of vaporization of NH_3GaCl_3 considered with

24) I.C.T., VII 308 ff.

25) I.C.T., VII 308 ff.

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other thermal data do lead to a conclusion about the relative affinity of GaCl_3 and AlCl_3 for the base NH_3 . The value of ΔH for the reaction

was calculated by Klemm et al.¹⁰⁾ and for the reaction

by the present authors. The calculations were based on the cycle:

and are summarized in Table 11. The entropy changes for the two association reactions can reasonably be assumed to be nearly the same and therefore the difference in the values of ΔF would be very nearly the same as the differences in ΔH . $\text{GaCl}_3(\text{gas})$ is therefore a weaker acid than is $\text{AlCl}_3(\text{gas})$, at least with NH_3 as the reference base. This difference is consistent with the fact that GaCl_3 has a smaller tendency to dimerize than has AlCl_3 (ΔH_4 in the cycle above). The dimerization, however, is affected by differences in basicity of the chloride as well as in acidity of the central atom.

Table 11

Heats of Reaction in the $\text{NH}_3\text{-MCl}_3$ Coordination Cycle

kcal. per mole

	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6
NH_3GaCl_3	-17.7	-2.6 ^a	32.9	8.5	11.5	-32.6 kcal.
NH_3AlCl_3	-17.4	-2.6	32.	14.	15.	-41 ± 2 kcal.

^aEstimated equal to the heat of fusion of NH_3AlCl_3 .

Although GaCl_3 is a weaker acid than is AlCl_3 , at least in reaction with the base NH_3 , Ga^{+++} is a stronger acid than is Al^{+++} . This is shown by a comparison of the values of ΔH for the two reactions:

The greater affinity for electrons of Ga^{+++} compared to Al^{+++} is also shown by comparing the third ionization potential of the two elements.

The fact that Ga^{+3} , although larger than Al^{+3} , is more acidic, may be attributed to the greater polarizing power of an ion with an outer shell of eighteen electrons, as compared with one with an outer shell of eight electrons. It is consistent with this explanation that the Ga^{+3} ion is more readily saturated than the Al^{+3} ion because of the following two effects:

1. As the coordination number of an ion increases the coordinated ligands must move farther from it.
2. The electrostatic field is relatively large near an ion with an outer shell of eighteen electrons but falls off more rapidly than does the field of an ion with an outer shell of eight electrons.

In any case, the energy gained by adding the $(n + 1)$ th ligand to an ion which already has the coordination number n is partially compensated by the necessity of moving the first n ligands farther from the ion; this compensation is much more complete for Ga^{+3} than for Al^{+3} .

Comparison of melting points for a series in which M' is the same but M''' different shows that these are remarkably constant. Particularly striking is the comparison of melting points for NH_4AlCl_4 , NH_4FeCl_4 , NH_4GaCl_4 : 304° , 297° , and 304° , in order. The close agreement of the melting points suggests that the coordination number of the ion M''' in each case is four in the solid. An increase in coordination number to six would seem to be possible, but in this case, $M'''-\text{Cl}^-$ bonds would be affected on melting, and almost constant melting point would not be expected. Thus the melting points for GaCl_3 , AlCl_3 , and FeCl_3 are 78 , 190 and 282° . The coordination numbers of

Al⁺⁺⁺²⁶⁾ and Fe⁺⁺⁺²⁷⁾ in the solids have been shown to be six. M⁺⁺⁺-Cl⁻ bonds are presumably disrupted to some extent in forming the melt from the solid M⁺⁺⁺Cl₃, accounting for the relatively great range in melting points.

An interesting property of compounds of the type M⁺⁺⁺Cl₄ is the high solubility of some of them in a solvent of such low dielectric constant as ether. The investigations on the solutions of NH₄GaCl₄ show that the high solubility cannot be attributed to dissociation to HCl and NH₃GaCl₃, both of which are highly soluble in ether. The substance remains as NH₄GaCl₄, but does apparently associate appreciably at higher concentration. Appreciable dissociation of the solute to M⁺Cl and M⁺⁺⁺Cl₃ in ether is excluded when M⁺ is an alkali metal, because the alkali chlorides are only very sparingly soluble in ether.

Fuoss, Kraus and co-workers have studied the osmotic and electrical properties of a variety of polar solutes in a variety of solvents of low dielectric constant. A comparison of our results for ammonium chlorogallate with some of their systems, and a discussion of the data in terms of their theories is presented here.

The apparent degree of polymerization of the solute, and the equivalent conductance as functions of concentration are presented in Fig. 16 and Fig. 17.

Systems were selected from those studied by Fuoss, Kraus and co-workers in order to illustrate, as far as possible, the effect of changing the solute and solvent.

Fuoss and Kraus²⁸⁾ have interpreted these experiments quantitatively in terms of the following model. The solution is assumed to be a homogenous dielectric containing the ion pairs AB, which react as described by these equilibria:

26) Ketelaar, Rec. Trav. Chim. Pays Bos., 66, 501 (1947).

27) Klemm and Krose, Z. Anorg. Ch., 253, 218 (1947).

28) a Fuoss and Kraus, J. Am. Chem. Soc., 55, 476 (1933).

b Ibid., p. 2387.

c Fuoss, J. Am. Chem. Soc., 56, 1027 (1934).

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Fig. 16.--Colligative behavior of solutions of electrolytes in solvents of low dielectric constant.

- I. Silver perchlorate in benzene. Batson and Kraus, J. Am. Chem. Soc., 56, 2017 (1934).
 - II. Tributylammonium iodide in benzene. Rothrock and Kraus, J. Am. Chem. Soc., 59, 1699 (1937).
 - III. Ammonium chlorogallate in ether, Present Work.
 - IV. Tributylammonium picrate in benzene, Rothrock and Kraus, op. cit.
 - V. Triisoamylammonium picrate in benzene, Batson and Kraus, op. cit.
- m_s is the stoichiometric molality of the solute.
 m_c is the molality of the solute calculated from the measurement of a colligative property.

Fig. 17.-- Equivalent conductance of solutions of electrolytes in solvents of low dielectric constant.

- I. Ammonium chlorogallate in ether, Present work.
- II. Tetra n-butylammonium nitrate in ethelene bromide, Cox, Kraus and Fuoss, Trans. Far. Soc., 31, 749 (1935).
- III. Tetra n-butylammonium nitrate in anisole. Ibid.
- IV. Tetraisoamylammonium picrate in benzene. Fuoss and Kraus, J. Am. Chem. Soc., 55, 3614 (1933).
- V. Silver perchlorate in benzene. Ibid.

The dimerization equilibrium is the only one which is important for the colligative properties of the solutions more concentrated than 10^{-8} molar in solvents of dielectric constant less than 10. The dimerization is caused by dipole-dipole interactions between the ion pairs and the quantitative theory derived from this model agrees well with the experiments in several cases²⁹⁾³⁰⁾. However, it is not possible to apply this theory to the data for ammonium chlorogallate in ether without extending the range of measurements to lower concentrations and without obtaining a series of measurements of the dielectric constant of the solution over the same concentration range. Even without the quantitative theory, one may expect, on the basis of this model, that as the concentration increases the dipole interactions will cause the formation of higher and higher polymers of AB. This is observed both in the present work and in the systems studied by Fuoss and Kraus.

The quantitative theory of the conductivity of these solutions, based on the disociation equilibrium and the triple ion equilibrium is easier to apply to the ammonium chlorogallate solutions. The existence of a minimum in the equivalent conductance vs. concentration curve is a consequence of the simultaneous operation of the dissociation and triple ion equilibria³¹⁾. From the coordinates of this minimum, and from the limiting equivalent conductances of the single ions, Λ_o , and of the triple ions, Λ_o , one may readily calculate K and k:

$$k = \frac{\Lambda_o}{\Lambda_o} c_{\min} \quad K = \frac{(c \Lambda_o^2)_{\min}}{4 \Lambda_o^2}$$

In these equations Λ is the equivalent conductance and c the molarity of the solutions.

Λ_o has been taken as 100 and Λ_o/Λ_o has been assumed to be 3/4. These quantities are not directly measurable in solutions of low dielectric constant, but those which have been evaluated under other conditions do not show a great variation. In particular Λ_o lies between 5 and 500 for all systems at all comparable to those being studied here, and for the great majority of such systems it lies between 50 and 200.

²⁹⁾Fuoss and Kraus, J. Am. Chem. Soc., 57, 1 (1935).

³⁰⁾Rothrock and Kraus, J. Am. Chem. Soc., 59, 1699 (1937).

³¹⁾Fuoss and Kraus, J. Am. Chem. Soc., 55, 2387 (1933).

One may calculate K from the model, assuming that A^+ and B^- are uniformly charged spheres, by finding the electrical work required to separate these spheres from contact to a distance R . According to Fuoss and Kraus³²⁾ this electrical work is equal to the free energy of dissociation if R is the distance between the ions at which the electrostatic energy is equal to the average thermal energy; according to a more elementary approach the electrical work is equal to the free energy of dissociation if R is infinity. In any case, the result is that the free energy of dissociation is a function of a , the sum of the radii of the two charged spheres, and therefore a may be calculated from the experimental K . In systems of low dielectric constant it makes only a 10% difference in the value of a if one makes one or the other assumption about R .

The values of K , k , and a are presented in Table 12 for ammonium chlorogallate in ether and for some of the systems studied by Fuoss, Kraus and co-workers for comparison. a was calculated by Fuoss's method.

One may estimate a in an independent way by summing up the N-Cl distance in ammonium chloride, the covalent radius of gallium and the covalent radius of chlorine. The value so obtained is $5.6 \text{ \AA}$. The value calculated from the conductance data is uncertain by about $0.8 \text{ \AA}$ because of the uncertainty in ϵ_0 , and is certainly only a lower limit for the actual separation of the centers of the ions in the ion pair because of the fact that the dielectric constant has been assumed to be constant. Actually at small values of the separation of the ions the dielectric constant must decrease due to polarization and to "squeezing out" of the molecules of the solvent from between the ions. Mutual polarization of the ions causes an error in the same direction. Then evidently a gives no information as to the extent to which the ion pair is solvated, for solvation would increase a and an increase in a cannot be detected by this method.

The fact that systems such as AgClO_4 in benzene and NH_4GaCl_4 in ether, in which the structure of the solvent certainly is important in determining the solubility, behave in the dilute region in a manner consistent with the simple model of Fuoss and Kraus indicates that information leading to an understanding of the factors important in the determination of solubility must come from a study of the more concentrated solutions.

³²⁾ Ibid., 55, 1079 (1933).

Table 12

Summary of Quantities Calculated from Conductance Data

Solute	Solvent	Dielectric Constant of Solvent	-Log K	-Log k	<u>a</u> , Å
$\text{NH}_4\text{GaCl}_4^a$	Diethyl Ether	4.68	9.38	2.8	4.83
$(\text{nC}_4\text{H}_9)_4\text{NNO}_3^b$	Ethylene Bromide	4.76	8.320	2.588	5.34
$(\text{nC}_4\text{H}_9)_4\text{NNO}_3^b$	Anisole	4.29	10.066	3.215	4.94
$(\text{nC}_4\text{H}_9)_4\text{NClO}_4^c$	Dioxane	2.181	18.96		5.40
$(\text{nC}_4\text{H}_9)_4\text{NClO}_4^c$	Benzene	2.267	17.54		5.60
AgClO_4^c	Benzene	2.267	20.11		4.89

^aPresent work.

^bCox, Kraus, and Fuoss, Trans. Far. Soc., 31, 749 (1935).

^cFuoss and Kraus, J. Am. Chem. Soc., 58, 255 (1936).

Appendix
Thermochemical Data

"Selected Values of the Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1949, Series I, Tables 28-1, 28-2.

Ibid., Table 10-1.

Bichowsky and Rossini, "The Thermochemistry of Chemistry of Chemical Substances," Reinhold Publishing Co., New York, 1936.

Laubengayer and Shirmer, J. Am. Chem. Soc., 62, 1578 (1940).

Fischer and Juberman, Z. Anorg. Ch., 227, 227 (1936).

Klemm, Tilk and Jacobi, Z. Anorg. Ch., 207, 194 (1932).

J. SUMMARY

The compounds NH_4GaCl_4 , CsGaCl_4 , KGaCl_4 , LiGaCl_4 and some analogous aluminum and iron compounds, including NH_4AlCl_4 and NH_4FeCl_4 have been studied.

NH_4GaCl_4 was prepared in four different ways: By direct reaction of NH_4Cl and GaCl_3 , by the reaction in the presence of ether which is a solvent for NH_4GaCl_4 but not NH_4Cl , by evaporating and heating an aqueous solution containing NH_4Cl and Ga^{+++} , and by the reaction of NH_3GaCl_3 with HCl . These methods (except the last named) were also applied to the preparation of some of the other compounds. NH_4FeCl_4 , but not NH_4AlCl_4 , can be prepared from an aqueous solution by the method used for NH_4GaCl_4 . CsGaCl_4 and KGaCl_4 can, however, be prepared in this manner if NH_4Cl is also present.

The melting points and densities of some of the compounds were measured. Of particular interest is the high solubility of some of them in ether. Separation of the ether solution into two liquid phases has been observed for solutions of NH_4GaCl_4 , NH_4FeCl_4 and LiGaCl_4 .

Some differences in stability were noted. LiGaCl_4 and LiAlCl_4 undergo the reaction

more readily on heating than do the corresponding potassium compounds. NH_4GaCl_4 is completely volatilized on heating, and the dissociation

takes place. The system in liquid vapor equilibrium is divariant, the vapor phase being enriched in HCl .

NH_3GaCl_3 in the vapor is monomeric. Above about 450° at atmospheric pressure the dissociation becomes appreciable. The heat of vaporization of the liquid is 17.7 kcal. per mole. This value, together with other data, leads to a value of ΔH for the reaction

The value is -53 kcal, which may be compared with -41 reported by Klemm for the corresponding reaction with NH_3AlCl_3 .

On heating, NH_3 replaces GaCl_3 from KGaCl_4 , forming gallium trichloride amines. NH_4GaCl_4 can be oxidized by chlorine at about 450° , yielding GaCl_3 .

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Formation of NH_4GaCl_4 from aqueous solution followed by oxidation of the substance with chlorine is a convenient method for preparing GaCl_3 from aqueous systems.

NH_4GaCl_4 does not undergo disproportionation in ether. At high concentrations, association of the solute takes place. The conductance of the ether solutions at low concentrations has been measured. The behavior in all respects is analogous to that observed by Kraus, Fuoss and co-workers in their investigations of polar solutes in solvents of low dielectric constant. Some comparisons with results of their work have been made.

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