[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Observations on the Chlorogallates and Related Compounds[1]

BY HAROLD L. FRIEDMAN[2] AND HENRY TAUBE

In this paper observations on the chlorogallates NH_4GaCl_4, $CsGaCl_4$, $KGaCl_4$, $LiGaCl_4$ and a few analogous compounds are described. These chlorogallates are members of a larger class of compounds of the type formula $M'M'''Cl_4$ in which M' is a monovalent metal or metallic group and M''' is a trivalent metal. The analogous compounds, containing iron or aluminum instead of gallium as the trivalent metal, were studied to find the effect of this substitution on the properties.

Several methods of preparation of compounds of the type $M'M'''Cl_4$ have been tested and compared, and physical properties such as density, melting point and solubility in ether measured for some. Ammonium chlorogallate has been investigated most intensively. It vaporizes at a temperature lower than do the other chlorogallates and the system in liquid–vapor equilibrium has been studied in some detail. To aid in the interpretation of this system the liquid–vapor equilibrium for gallium trichloride monoammine was also studied.

General Experimental Techniques

Materials.—The substances investigated in the present work are sensitive to moisture, and pure products can only be prepared from carefully dried materials handled in the complete absence of moisture. Gallium trichloride was prepared from gallium metal and hydrogen chloride and was purified by vacuum distillation. Because of its great reactivity, it was handled only on the vacuum system in all glass apparatus. Reagent grade aluminum trichloride, purified by sublimation in vacuum, also was handled only on the vacuum system. Ferric chloride, prepared from chlorine and iron, was stored and handled in a dry box. Reagent grade diethyl ether was stored with lithium aluminum hydride in a vessel connected to the vacuum system. Anhydrous ether was distilled from this solution as needed. C. P. samples of the alkali metal chlorides and ammonium chloride were dried by heating them in a vacuum to as high a temperature as was practical.

Valves.—Stopcocks were used on apparatus only when a lubricant inert to the substances with which it came in contact was available. Mercury cut-offs were used in the connections to the ether reservoir. For handling the compounds $M'''Cl_3$ and $M'M'''Cl_4$ on the vacuum system, systems of "break-off" inner seals and thickened tubes were used as valves.

Temperature Measurement.—Calibrated (±0.5°) iron–constantan thermocouples were used for measurements between 200 and 500°. Calibrated thermometers were used below this range, uncalibrated chromel–alumel thermocouples at higher temperatures.

Analyses.—Gallium was determined by the gravimetric 8-hydroxyquinoline method.[3] Standard methods were used for iron, nitrogen and chlorine.

The Preparation of Some Substances of the Type $M'M'''Cl_4$

Several fairly general methods of preparation of these compounds are described below, together with some of the limitations of each method.

Method 1.—Equivalent quantities of $M'Cl$ and $M'''Cl_3$ are weighed out, and heated together in a sealed vessel. The chief disadvantage of this method is the necessity of weighing accurately the reactive component $M'''Cl_3$. The method may be presumed to work for any compound which is stable in the condensed phase up to its melting point.

Method 2.—A sample of $M'Cl$ is placed in one leg of a two-legged reaction tube, and an excess of $M'''Cl_3$ in the other. The vessel is then evacuated and sealed off. $M'''Cl_3$ is then distilled onto the $M'Cl$, and the melting point of the mixture determined after each addition. After the mixture has passed through the composition corresponding to the maximum melting point, $M'''Cl_3$ is distilled from the mixture by heating it to 400–450° while the other leg is cooled in liquid nitrogen. This distillation is also carried out stepwise, with melting point measurements after each change in composition, until the composition of maximum melting point is again reached. If it has been shown that the product is not volatile below 450°, and if its decomposition is slow at this temperature (*i. e.*, the equilibrium vapor pressure of $M'''Cl_3$ is very low), the determination of the melting point can be dispensed with, since the product can be obtained simply by heating the melt containing excess $M'''Cl_3$ above 400° in a vacuum for a period of about one hour.

Method 3.—A mixture of $M'''Cl_3$ with excess $M'Cl$ is melted, cooled and extracted with ether. The ether solution is filtered off, and evaporated to dryness in a vacuum, the residue being heated to 100° in the final stages. This method is successful if $M'Cl$ is insoluble in ether, and if the

---

[1] From the thesis submitted by Harold L. Friedman to the Graduate School of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Department of Chemistry, University of Southern California, Los Angeles 7, California.

[3] Geilman and Wrigge, *Z. anorg. Chem.*, **209**, 129 (1932).

product is soluble in ether and is stable to decomposition into M′Cl and M‴Cl_3 in the presence of ether. It is desirable to bring about reaction of the components before ether is introduced, because pure M‴Cl_3 may react so energetically with ether that decomposition of the solvent occurs. Aside from this, the preparation may as well be carried out by treating excess M′Cl with an ether solution of M‴Cl_3.

Method 4.—A solution containing equimolar amounts of M′Cl and M‴Cl_3 in aqueous hydrochloric acid is evaporated to dryness in an atmosphere of hydrogen chloride. The residue is then heated to 400–450° in an atmosphere of dry hydrogen chloride. This method works only if M′ is NH_4, and the product obtained is seldom more than 95% pure.

Method 5.—Ammonium chloride in slight excess is added to a solution containing equimolar amounts of M′Cl (when M′ is not NH_4) and M‴Cl_3 in aqueous hydrochloric acid. The solution is evaporated to dryness, and the residue is heated to 400–450° in an atmosphere of dry hydrogen chloride until all the volatile material has been distilled off. Again, the product is never very pure.

It was possible to prepare products of about 99.9% purity or better only by methods 1, 2 and 3, which do not require water, and only if water is carefully excluded at every step. A summary of the application of these methods to the preparation of a number of substances is presented in Table I.

TABLE I

METHODS OF PREPARATION OF COMPOUNDS OF THE TYPE M′M‴Cl_4

Compound	Method[a] 1	2	3	4	5
$LiGaCl_4$	—	np	np	(np)	np
$KGaCl_4$	(p)	p	—	np	p
$CsGaCl_4$	p	p	(np)	np	p
NH_4GaCl_4	(p)	np	p	p	p
NH_4FeCl_4	p	(np)	p	p	p
NH_4AlCl_4	(p)	(np)	p	np	np
$KAlCl_4$	(p)	p	—	(np)	(np)
$LiAlCl_4$	—	np	—	(np)	(np)

[a] The entries in the body of the table indicate whether the preparation of a compound by the indicated method has been found to be possible, p, not possible, np, or has not been tried but is believed to be possible, (p), or not possible (np). A dash, —, indicates that the preparation has not been tried and there is not sufficient information to predict its outcome.

Method 1 has been shown to be successful for $CsGaCl_4$ and NH_4FeCl_4, and will presumably yield any M′M‴Cl_4 which is stable at its melting point, including all compounds prepared by methods 2 or 3.

Method 2 fails for $LiGaCl_4$ and $LiAlCl_4$ because they are too unstable with respect to M′Cl and M‴Cl_3 (gas); it fails (or is expected to fail) for NH_4M‴Cl_4 because these compounds decompose to hydrogen chloride and NH_3M‴Cl_3.

Method 3 cannot be used for the preparation of $LiGaCl_4$ because material of this composition is distributed with decomposition between the solid phase and the saturated solution in ether. The ether solution is enriched in gallium chloride and the solid phase (or phases) is intermediate in composition between $LiGaCl_4$ and lithium chloride. Although method 3 as described fails for $CsGaCl_4$ because of the low solubility of this substance, a modification in which an excess of gallium chloride is heated with cesium chloride and then treated with ether might be successful.

As has already been mentioned, method 4 works only when M′ is NH_4; even with this choice of M′ it does not work for the aluminum compound. Method 5, which apparently involves method 4 as a step, will presumably fail for all aluminum compounds of the type M′$AlCl_4$.

The Physical Properties of Some Substances of the Type M′M‴Cl_4

Some physical properties of the substances which were prepared are summarized in Table II. References are given to all data from the literature and for all compounds whose preparation or existence has been reported elsewhere. Data for which no references are given have been obtained in the present study on samples which contained not more than one or two parts per thousand of impurities.

TABLE II

PHYSICAL PROPERTIES OF COMPOUNDS OF THE TYPE M′M‴Cl_4

Compound	M. p., °C.	Molar vol., ml.	Solubility in anhydrous diethyl ether at 25° wt. %
$LiGaCl_4$	. . .	. . .	Over 30
$KGaCl_4$	259	105	Over 30
$CsGaCl_4$	385	121	Less than 0.004
NH_4GaCl_4[a]	304	110	58
NH_4FeCl_4[b]	295, 297[b]	110	44
NH_4AlCl_4[c]	304[c]	108	Over 30

[a] Kraus and Toonder, *Proc. Nat. Acad. Sci. U. S. A.*, 19, 292 (1930); R. P. Hammond, Ph.D. Dissertation, University of Chicago, 1947. [b] Hachmeister, *Z. anorg. allgem. Chem.*, 109, 170 (1920). [c] Kendall, Crittenden and Miller, THIS JOURNAL, 45, 976 (1923).

NH_4GaCl_4, NH_4FeCl_4 and NH_4AlCl_4 exist as solid phases in contact with their respective saturated ether solutions, but when excess $LiGaCl_4$ or $KGaCl_4$ is treated with ether, the solid which remains contains more than one mole of M′Cl per mole of gallium chloride. No well defined etherates of any of these compounds has been isolated. NH_4FeCl_4 is soluble in benzene to the extent of less than 10^{-3} molal. Other solubilities in organic solvents have not been investigated. All of these compounds dissolve readily in water with the evolution of heat. Examination of crystals of the chlorogallates of potassium, cesium and ammonium has shown them to be anisotropic.

Volatilization of Compounds of the Type $M'M'''Cl_4$.—Some of the observations made in the preparative work imply differences in stability with respect to the reactions

$$M'M'''Cl_4\ (liq.) = M'''Cl_3(gas) + M'Cl$$

in which $M'Cl$ remains dissolved in $M'M'''Cl_4$ or separates as a solid phase. Another problem of interest is the degree of association of $M'Cl$ and $M'''Cl_3$ in the gas phase. Baud[4] reported that $KGaCl_4$ distils without decomposition, an observation which, in view of the low volatility of potassium chloride, suggests that $KAlCl_4$ is very stable in the gas phase. The following experiment was performed to study the behavior of $KGaCl_4$ on distillation. A sample of $KGaCl_4$ contained in an evacuated quartz vessel was slowly heated to 700° while a connected Pyrex vessel was cooled in liquid nitrogen. Decomposition below 500° was observed to be exceedingly slow, but at about this temperature, the distillation of $GaCl_3$ from the melt begins. At still higher temperatures, potassium chloride, whether in combination with gallium chloride or not, is also transported, and at about 650° a material presumably $KGaCl_4$ is observed to reflux in the quartz vessel. The product of the distillation consists of a mixture of $KGaCl_4$ and gallium chloride. The same behavior was found on distillation in a current of inert gas and on the distillation of $CsGaCl_4$ and $KAlCl_4$. Evidently compounds of the type $M'M'''GaCl_4$ are at least partly dissociated in the gas phase. However, these experiments give no indication of whether or not the dissociation is complete, because all of the observations are consistent with the interpretation that $M'Cl$ and $M'''Cl_3$ distil simultaneously and separately but recombine as soon as a condensed phase is formed.

The association of hydrogen chloride and $GaCl_3$ in the gas phase was also investigated. Known quantities of hydrogen chloride and $GaCl_3$ were put into a Bourdon gage and the pressure of the mixture was measured at temperatures up to 450°. It was found that within the experimental error the total pressure was the sum of the partial pressures, correcting for the dimerization of gallium chloride, and it was possible to place an upper limit of 0.1 at 400° on the equilibrium constant $K = (HGaCl_4)/(HCl)(GaCl_3)$ for a standard state of one atmosphere for each gas.

The behavior described above for compounds in which M' is an alkali metal is not expected if M' is NH_4 because ammonium chloride is itself unstable in the gas phase. A different type of decomposition takes place when a compound of the type $NH_4M'''Cl_4$ is heated and in fact sets in at temperatures as low as 200°. When heated in a vacuum, NH_4GaCl_4 loses hydrogen chloride rapidly and the residue approaches NH_3GaCl_3 in composition. A sample which was boiled for a few minutes in an evacuated vessel connected to a liquid nitrogen trap was then analyzed. Found: Cl, 58.4, 58.4. Calcd. for NH_4GaCl_4: Cl, 61.8. Calcd. for NH_3GaCl_3: Cl, 56.6. The volatilization of NH_4GaCl_4 is discussed in greater detail in the following section.

Hachmeister[5] studied the boiling points of mixtures of ammonium chloride and ferric chloride and found a sharp maximum at a composition near 50 mole %. He concluded that NH_4FeCl_4 dissociates into ammonium chloride and ferric chloride in the vapor, but his conclusion was not supported by any analysis of the vapor.

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 ammonium chlorogallate 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 liquid NH_4GaCl_4 with NH_3GaCl_3 and hydrogen chloride. The results of these experiments are also included in this section.

The symbol C_S used in this section represents the ratio of the stoichiometric amount of a given substance (NH_4GaCl_4 or NH_3GaCl_3) expressed in micromoles, to the volume of the closed gage expressed in milliliters. C_T is the concentration in micromoles per milliliter, of all gases in the system and is calculated from the observed pressure assuming the perfect gas law.

Experimental Details

The vapor pressure of ammonium chlorogallate was measured over a temperature range from 275 to 440° at three values of C_S. The Bourdon gage used for the measurements at the low values of C_S is shown in Fig. 1. It was used as a null instrument, a known pressure being applied through S to just open or close the electric switch. The variation of the pressure difference between Q and P which just opened the switch was studied as a function of temperature and of the orientation of the gage, and was taken into account in calculating the pressure in P from the known pressure applied through S. The accuracy of the pressure readings is ±0.3 mm. for a series of readings in which the gage is neither moved nor subjected to the stress of a great unbalance, and, at worst, is ±2.5 mm. Temperatures were measured by four thermocouples spaced along the Bourdon bulb. The lowest observed temperature was used in the vapor pressure data; the whole range of temperatures observed with each pressure reading is reported with the vapor density data in Table III. A similar gage was used in the experiment with

TABLE III

VAPOR DENSITY OF AMMONIUM CHLOROGALLATE

No.	Observed temp., °C. A	B	C	D	Av. temp., °K.	p, press., cm.	C_T,[a] concn., moles/ml.	$C_T{}^a/C_S$
1	428	427	428	426	700	44.0	10.10	2.055
2	433	435	434	433	707	44.7	10.16	2.068
3	464	464	462	460	736	47.4	10.34	2.104
4	474	474	470	468	745	48.5	10.45	2.128
5	476	476	473	471	747	48.8	10.49	2.137

[a] Defined in introduction to this section.

---

(4) Baud, *Ann. chim. phys.*, [8] **1**, 46 (1904).

(5) Hachmeister, *Z. anorg. Chem.*, **109**, 170 (1920).

NH_4GaCl_4 at high C_S and in the experiments with NH_3-$GaCl_3$, except that in this latter gage only the volume P was accessible to the substance being studied. The experimental procedure was similar in all respects.

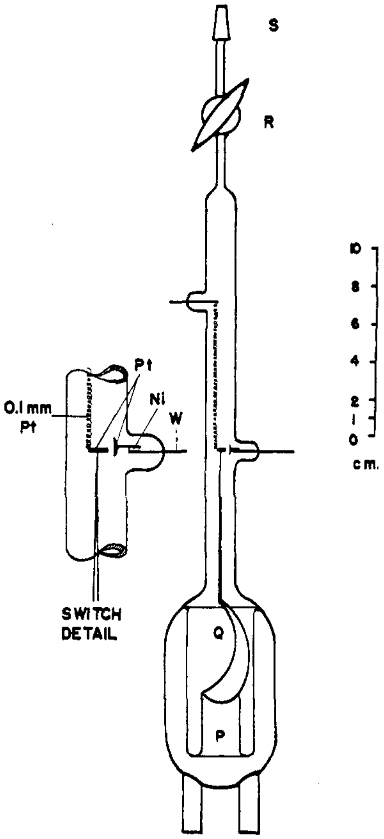

Fig. 1.—Bourdon gage.

The substance being investigated was introduced into the gage at C from a small sample tube by melting and distillation. In the case of ammonium chlorogallate, this caused some decomposition into NH_3GaCl_3 and hydrogen chloride, a pressure of several centimeters remaining after the apparatus had cooled. The sample tube was then sealed off, causing a small loss of hydrogen chloride from the system in these cases, but this loss was negligible because the ratio of the volume of the gage to that of the sample tube was large. The hydrogen chloride and NH_3-$GaCl_3$ recombined completely as soon as the gage was reheated and then cooled very slowly in a furnace.

Pressure readings were made both as the temperature of the furnace was slowly increasing and as it was decreasing in the desired range. It was found that it took as long as a day at constant temperature to get equilibrium readings of the pressure of NH_4GaCl_4 below its melting point, particularly if C_S was high. Condensation of material in the moving portion of the gage also caused difficulty, especially below the melting point. Effects due to this cause were minimized by keeping this part of the gage at a slightly higher temperature than the rest of the gage. At the end of each experiment the gage was opened and its contents analyzed to determine the amount of material which had been used.

The data for three experiments with ammonium chlorogallate at different values of C_S are presented in Fig. 2. The data for 4.9 μ moles/ml. which lie below the curve at high temperatures lead to values for the vapor density (Table IV). The data for two experiments with NH_3Ga-Cl_3 using samples of different size and from different preparations[6] are presented in Table IV and Fig. 3. Again the points below the curve at high temperatures lead to a value for the vapor density as discussed below.

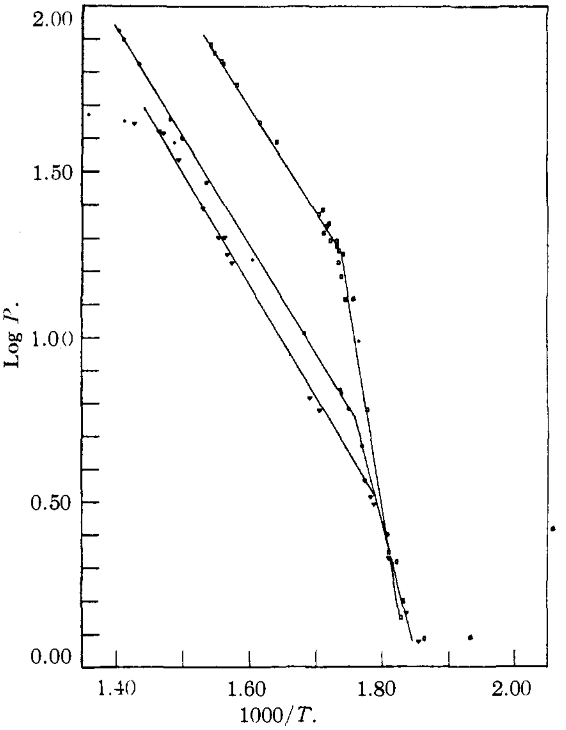

Fig. 2.—Vapor pressure of ammonium chlorogallate as a function of temperature and of the ratio of the number of moles of ammonium chlorogallate to the volume of the system: ▽, 4.9 μmole/ml.; ○, 17.5 μmole/ml.; □, 269 μmole/ml.

Experiments already described show that NH_4GaCl_3 on heating loses hydrogen chloride and that the residue becomes richer in NH_3GaCl_3. The solubility of NH_3GaCl_3 in liquid NH_4GaCl_4 was investigated by treating NH_3Ga-Cl_3 with known amounts of hydrogen chloride to convert it partially into NH_4GaCl_4 and then observing the melt visually and measuring the melting range. The mixture of 80 mole per cent. NH_3GaCl_3 has a melting range at least from 100 to 200°. The mixture of 60 mole per cent. NH_3-$GaCl_3$ likewise has a long melting range. The sample was finally converted completely to NH_4GaCl_4 by excess hydrogen chloride, after which the sample no longer absorbed hydrogen chloride at all. Under no conditions was more than one phase observed above the melting point of NH_4-$GaCl_4$ or more than one liquid phase at any temperature. The experiments show that NH_3GaCl_3 and NH_4GaCl_4 are miscible as liquids over wide ranges of composition.

Discussion of Results.—Since the information derived from the data for NH_3GaCl_3 is required in the interpretation of the more complex NH_4-$GaCl_4$ system, the data for NH_3GaCl_3 will be discussed first. The following properties of NH_3GaCl_3 are readily derived from the experimental curve presented in Fig. 3: normal boiling point, 438°; ΔH of vaporization of the liquid, 17.7 kcal./mole; ΔS of vaporization of the liquid,

---

[6] NH_3GaCl_3 was prepared by the method of Klemm, Tilk and Jacobi, *Z. anorg. allgem. Chem.*, **207**, 200 (1932). The product crystallized poorly and observation of the melting point was difficult, but it was in the range 122–123°. Klemm, *et al.*, reported a value of 124°.

TABLE IV

VAPOR DENSITY AND VAPOR PRESSURE OF NH_3GaCl_3

Data of first experiment			Data of second experiment	
Temp., °C.	Pressure, cm.	C_T/C_S	Temp., °C.	Pressure, cm.
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	292	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			

24.9 cal./mole-deg. The data for the vapor density of NH_3GaCl_3 are presented in Table IV. Evidently this compound exists largely as molecules of NH_3GaCl_3 under the conditions of this experiment, since the ratio C_T/C_S is very nearly unity. The increase of this ratio beyond unity with increasing temperature may be attributed to a slight dissociation, but further interpretation is not warranted because of the experimental errors and the uncertainty as to the deviations from ideal gas behavior.

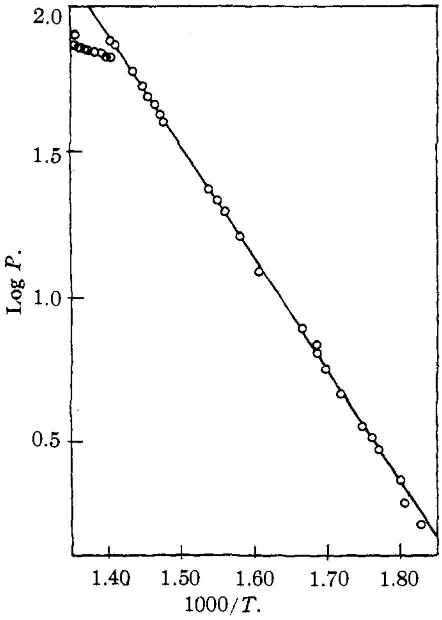

Fig. 3.—Vapor pressure of NH_3GaCl_3.

Figure 2 shows that the values of the pressure of NH_4GaCl_4 recorded at the highest temperatures for $C_S = 4.9$ lie below the extrapolated equilibrium curve and therefore correspond to the unsaturated vapor. These data are presented in some detail in Table III. The observations were made in the order 3, 2, 1, 4, 5; since there are no trends with the order of the experiments, the changes observed are not due to irreversible phenomena. The relative values of the ratios C_T/C_S are believed to be accurate to 0.2%. The ratio is observed to be nearly two, increasing as the temperature rises. A value of two indicates that the equilibrium

$$\mathrm{NH_4GaCl_4} \overset{K_1}{\rightleftharpoons} \mathrm{NH_3GaCl_3} + \mathrm{HCl} \tag{1}$$

is completely to the right in the vapor phase if further dissociation of NH_3GaCl_3 in this temperature range is excluded. The dissociation of NH_3GaCl_3, which was found to be very small below 450°, is probably responsible for the fact that the ratio of C_T/C_S in Table III exceeds two and for the trend of this ratio as the temperature increases. It is possible to calculate the heat of the gas reaction

$$\mathrm{NH_3GaCl_3} \overset{K_2}{\rightleftharpoons} \mathrm{NH_3} + \mathrm{GaCl_3} \tag{2}$$

from the data of Table III; the heat so determined is between 30 and 60 kcal./mole and is consistent with the value indirectly determined from other data (below). However, the large uncertainty in the result of the present calculation, due in part to the experimental error and in part to the assumption of perfect gas laws, make the result of little value except to indicate that the interpretation given the data is reasonable.

The vapor pressure for liquid ammonium chlorogallate may be expressed within the experimental error by the three equations

$$\log p = \frac{-14.39 \times 10^3}{4.576\,T} + 6.722 \text{ for } 269\mu \text{ mole/ml.} \tag{3}$$

$$\log p = \frac{-14.96 \times 10^3}{4.576\,T} + 6.515 \text{ for } 17.5\mu \text{ mole/ml.} \tag{4}$$

$$\log p = \frac{-15.36 \times 10^3}{4.576\,T} + 6.533 \text{ for } 4.9\mu \text{ mole/ml.} \tag{5}$$

For liquid NH_3GaCl_3 the vapor pressure is given by

$$\log p = \frac{-17.74 \times 10^3}{4.576\,T} + 7.333 \tag{6}$$

These equations give the pressure, p, in cm. as a function of the temperature, T, in degrees absolute, at temperatures above the melting points.

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 is present at least a vapor phase and one liquid phase. Direct observations 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 reaction (1) occurs. The data on the vapor densities of NH_4GaCl_4 and NH_3GaCl_3 show that the reaction (2) also takes place, but equilibrium at ordinary pressures 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 system are hydrogen chloride 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 hydrogen chloride than it is in NH_3GaCl_3. Among these are the following: NH_4GaCl_4 on heating loses hydrogen chloride and the condensed phase approaches NH_3GaCl_3 in composition; hydrogen chloride does not dissolve appreciably in molten NH_4GaCl_4, but NH_3GaCl_3 is very soluble in it. Thus the system in liquid vapor equilibrium is described by the reactions

$$NH_4GaCl_4\ (\text{soln.}) \rightleftarrows NH_3GaCl_3\ (\text{soln.}) + HCl\ (\text{gas}) \qquad (7)$$

$$NH_3GaCl_3\ (\text{soln.}) \rightleftarrows NH_3GaCl_3\ (\text{gas}) \qquad (8)$$

It is not possible to evaluate the equilibrium constants for these reactions 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 μ mole/ml. are too high (greater than 10 mole %) for this approximation to be valid.

The fact that the slopes of the three curves of Fig. 2 are constant within the experimental error and are nearly the same means that the heats of reactions (7) and (8) 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 (3) to (5) are not far different from the ΔH factor of equation (6), 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

$$NH_4GaCl_4\ (\text{crystal}) \rightleftarrows NH_3GaCl_3\ (\text{liquid}) + HCl\ (\text{gas})$$

$$NH_3GaCl_3\ (\text{liquid}) \rightleftarrows NH_3GaCl_3\ (\text{gas})$$

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

Some Reactions of Chlorogallates

Among the reactions of interest for these compounds are those in which M'Cl is displaced from $M'M'''Cl_4$ by a more basic reactant. The extraction of $GaCl_3$ from $LiGaCl_4$ by ether may be regarded as a reaction in this class.

The reaction of $KGaCl_4$ with ammonia at elevated temperatures was also examined. As the temperature is raised, the reaction begins at 200° with the formation of volatile gallium chloride ammonates, particularly $GaCl_3{\cdot}3NH_3$. At temperatures above 500° a yellow non-volatile compound of gallium and nitrogen is also formed, presumably the yellow nitride of gallium.[7] These reactions were carried out in a quartz tube under anhydrous conditions.

A reaction of NH_4GaCl_4 of preparative interest is the oxidation by chlorine

$$2NH_4GaCl_4 + 3Cl_2 \longrightarrow 2GaCl_3 + 8HCl + N_2$$

Ammonium chlorogallate may be prepared from aqueous solution as described above and then treated with chlorine to obtain gallium chloride, thus providing a relatively direct method of preparing this compound from aqueous solution. The over-all yield of purified $GaCl_3$ based on gallium is about 50%. The reaction is readily carried out by heating NH_4GaCl_4 to 330° in a current of anhydrous chlorine. The imperfectly mixed gases must be passed through plugs of Pyrex wool to mix them well, and better results are obtained if these plugs are maintained at about 450°. The gases issuing from the reaction tube may be cooled to −20° to condense the gallium chloride. The reaction requires about twenty minutes for 20 g. of NH_4GaCl_4. The trap containing the gallium chloride may then be sealed off and connected to a vacuum system to remove chlorine from the gallium chloride by distilling the product.

[7] Hahn and Juza, *Z. anorg. allgem. Chem.*, **244**, 111 (1940.)

General Discussion

Some of the 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 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 the acidity of the trihalides $M'''Cl_3$. The present research, in which some of the general properties of this class of compounds are explored, with special emphasis on the compounds of gallium, is only an introduction to such work. However, a few conclusions about stability emerge from observations made in connection with the preparative work. The comparisons of $LiGaCl_4$ with $KGaCl_4$ and of $LiAlCl_4$ with $KAlCl_4$ show that the lithium compounds are less stable than the potassium compounds. This difference may be attributed to the greater basicity of potassium chloride as compared to lithium chloride, which is expected as a consequence of the small size and greater polarizing power of Li^+. Similar trends of stability are observed in the series of lithium carbonate, sodium carbonate and potassium carbonate, and in the series Li_2SiF_6, Na_2SiF_6 and K_2SiF_6.[8] The low stability of $HGaCl_4$ in the gas phase is similarly attributed to the small size of H^+. With a larger monopositive ion such as Cs^+, it seems reasonable that the affinity of the gallium chloride for the cesium chloride might be great enough to permit a stable complex to exist in the gas phase, although attempts to prove the existence of such a gaseous complex have not been successful.

The observations on the preparation from aqueous solution of ammonium chlorogallate, chloroferrate and chloroaluminate are of interest in evaluating the relative affinities for water (or OH^- or $O^=$) of the acids Ga^{+++}, Fe^{+++} and Al^{+++}. Only with the first two was replacement of water (or ions derived from it) by Cl^- possible. This may be correlated with the ether extractibility of Ga^{+++} and Fe^{+++} from hydrochloric acid solutions as compounds of the type $HM'''Cl_4$[9] and the non-extractibility of Al^{+++} under similar conditions.

Although there are at present no observations on the relative affinities of aluminum chloride, ferric chloride and gallium chloride for a particular gaseous alkali chloride, a comparison of the affinities of aluminum chloride and of gallium chloride for ammonia may be made. All of the quantities in the following thermochemical cycle have been measured or may be estimated with sufficient precision, except ΔH_6 which is a measure of the affinity of MCl_3 for ammonia. The calculation of ΔH_6 as carried out by Klemm, *et al.*,[10] for NH_3AlCl_3 and by the present authors for NH_3GaCl_3 is summarized in Table V.

$$\begin{tikzcd}
MCl_3\,(g) + NH_3\,(g) \arrow[r, "\Delta H_6"'] & NH_3MCl_3\,(g) \arrow[d, "\Delta H_1"] \\
{}^1/_2M_2Cl_6\,(g) + NH_3\,(g) \arrow[u, "\Delta H_5"] & NH_3MCl_3\,(l) \arrow[d, "\Delta H_2"] \\
{}^1/_2M_2Cl_6\,(s) + NH_3\,(g) \arrow[u, "\Delta H_4"] & NH_3MCl_3\,(s) \arrow[l, "\Delta H_3"]
\end{tikzcd}$$

TABLE V

HEATS OF REACTION IN THE NH_3–MCl_3 COÖRDINATION CYCLE, KCAL.

	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6
NH_3GaCl_3	−17.7	−2.6	32.9	8.5	11.5	−32.6
NH_3AlCl_3	−17.4	−2.6	32	14	15	−41 ± 2

The sources of the values of ΔH for the various steps involving the gallium compounds are as follows: ΔH_1 from the present work; ΔH_2 assumed to be the same as the heat of fusion of NH_3AlCl_3[11]; ΔH_3, ΔH_4 and ΔH_5 may be calculated from data of Klemm, Tilk and Jacobi,[10] Laubengayer and Schirmer,[12] and Fischer and Juberman.[13]

Although gallium chloride is evidently a weaker acid than is aluminum chloride, at least in reaction with the base ammonia, Ga^{+++} is a stronger acid than Al^{+++}. This is shown by a comparison of the values of ΔH for the gas phase reactions[14]

$$Ga^{+++} + 3Cl \longrightarrow GaCl_3 \qquad \Delta H = -1319 \text{ kcal.}$$
$$Al^{+++} + 3Cl^- \longrightarrow AlCl_3 \qquad \Delta H = -1245 \text{ kcal.}$$

and

$$Ga^{+++} + e^- \longrightarrow Ga^{++} \qquad \Delta H = -708.3 \text{ kcal.}$$
$$Al^{+++} + e^- \longrightarrow Al^{++} \qquad \Delta H = -654.6 \text{ kcal.}$$

The relative acidities of trivalent aluminum and gallium evidently depend upon the coördination numbers of the metals and may also depend on the particular base chosen for comparison at fixed coördination number. There are at present no data with which to test this hypothesis.

The constancy of melting points in the series NH_4GaCl_4, NH_4FeCl_4, NH_4AlCl_4 is striking and suggests that the coördination number of the ion M^{+++} in each case is four in the solid. A coördination number of six in the solid is considered less likely because then $M'''Cl_3$ bonds would be affected on melting, leading to a relatively large range of melting points. Thus the melting points of gallium chloride, ferric chloride and aluminum chloride are 78, 282 and 190°, re-

---

(8) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Vol. VII, pp. 308 ff.

(9) Nachtrieb and Conway, THIS JOURNAL, **70**, 3547 (1948); Nachtrieb and Fryxell, in press (on: $HGaCl_4$).

(10) Klemm, Tilk and Jacobi, *Z. anorg. allgem. Chem.*, **207**, 194 (1932).

(11) NH_3GaCl_3 melts at 123°, NH_3AlCl_3 at 125°.

(12) Laubengayer and Schirmer, THIS JOURNAL, **62**, 1578 (1940).

(13) Fischer and Juberman, *Z. anorg. allgem. Chem.*, **227**, 227 (1936).

(14) Thermochemical data from "Selected Values of the Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949, Series I, tables 28-1, 28-2; and from Bichowsky and Rossini, "The Thermochemistry of Chemical Substances." Reinhold Publishing Corp., New York, N. Y., 1936.

spectively. The coördination number of the metal is six in ferric chloride[15] and aluminum chloride.[16] The structure of gallium chloride has not been determined. The relatively great range in melting points of the trichlorides is then explained on the basis that metal–chlorine bonds must be broken to some extent in melting, at least in the case of aluminum chloride and ferric chloride.

An interesting property of the compounds $M'M'''Cl_4$ is the high solubility of some of them in anhydrous ether. Some observations on these solutions, particularly those of NH_4GaCl_4, will be reported in a separate communication.

Acknowledgment.—This research was supported by funds from the Office of Naval Research under Contract No. N6-ori-20. Some of the experiments with NH_4AlCl_4 were performed by Mr. William Korst, and with NH_4FeCl_4, by Mr. Robert A. Plane.

Summary

Observations have been made on the chemistry of some compounds of the type $M'M'''Cl_4$ with $M' = NH_4$, Li, K, Cs and $M''' =$ Ga, Fe, Al. Five more or less general methods of preparation of this class of compounds and the applicability of these methods to the compounds studied are described. Measurements were made of the melting points, densities and solubilities in ether of these compounds.

Some differences in stability were noted. $LiGaCl_4$ and $LiAlCl_4$ undergo the reaction $M'M'''Cl_4(l) \rightarrow M'Cl(l) + M'''Cl_3(g)$ more readily on heating than do the corresponding potassium compounds. NH_4GaCl_4 is completely volatilized on heating, and the dissociation $NH_4GaCl_4(l) \rightarrow HCl(g) + NH_3GaCl_3(g)$ takes place. The system in liquid vapor equilibrium is divariant, the vapor phase being enriched in hydrogen chloride.

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 ΔH for the reaction $NH_3GaCl_3(g) \rightarrow NH_3(g) + GaCl_3(g)$. The value is +33 kcal., which may be compared with +41 reported by Klemm and coworkers for the corresponding reaction with NH_3AlCl_3.

On heating, ammonia replaces potassium chloride from $KGaCl_4$, forming gallium trichloride amines. NH_4GaCl_4 can be oxidized by chlorine at about 450°, yielding gallium chloride. Formation of NH_4GaCl_4 from aqueous solution followed by oxidation of the substance with chlorine is a convenient method for preparing gallium chloride from aqueous systems.

LOS ANGELES, CALIFORNIA RECEIVED NOVEMBER 21, 1949

(15) Klemm and Krose, *Z. anorg. allgem. Chem.*, **253**, 218 (1947).

(16) Ketelaar, *Rec. trav. chim.*, **66**, 501 (1947).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAMBRIDGE, ENGLAND]

The Diffusion Coefficients of Eight Uni-univalent Electrolytes in Aqueous Solution at 25°

BY R. H. STOKES[1]

In a previous paper[2] it was shown that the improved porous-diaphragm cell technique there described is capable of yielding accurate values for the diffusion coefficients of electrolyte solutions in the concentration-range above 0.05 normal, and some limitations of the method were examined. The present paper describes diffusion measurements on the chlorides and bromides of potassium, sodium, lithium and hydrogen at concentrations up to four normal.

Experimental

The cell and its manipulation and calibration have been described.[2] The water used in making up solutions was double-distilled and had a conductivity ~ 10^{-6} mho/cm. Potassium and sodium chlorides, hydrochloric acid and hydrobromic acid were of analytical quality, used without further purification. Potassium bromide was recrystallized once from the analytical quality salt, and sodium bromide three times from the ordinary supply. The lithium salts were prepared by dissolving the hydroxide in the appropriate pure acid until neutral, followed by three crystallizations; the hot solutions were re-neutralized before crystallizing, as some loss of acid occurred during evaporation. The 4 *N* stock solutions were filtered through sintered-glass. Times were measured on a reliable pocket-watch checked twice daily against the radio time-signals from Greenwich Observatory. The temperature was maintained within 0.01° as indicated on a Beckmann thermometer, and was known to be within 0.03° of the true 25°. Since the method is a relative one, no detectable error should arise from an uncertainty of 0.03° in the absolute temperature.

The final concentrations of the lower (more concentrated) and upper (less concentrated) cell compartments (c_3 and c_4, respectively) were determined by potentiometric titration of weighed samples against silver nitrate, using a capillary reference electrode[3] with a valve voltmeter as null indicator. Duplicate analyses were made and agreed to 0.1%. The resulting weight-concentrations were converted to volume-concentrations for 25° by means of the standard density data.

Wear of the Diaphragm.—The cell constant showed a slow increase, amounting to 0.5–1% per thousand hours

---

(1) Imperial Chemical Industries Fellow, University of Cambridge. Present address; University of W. A., Nedlands, Western Australia.

(2) R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

(3) H. Muller, *Z. physik. Chem.*, **135**, 102 (1928).