satisfactory in that equilibrium pressures were not obtained over a sufficiently broad range of flow rates to give a reliable basis for establishing the correct value. Apparent pressures at intermediate flow rates (varied from 0.5 to 45 cc./min.) agreed with those obtained from effusion data, but, considered independently, no satisfactory basis for choosing the correct value was evident.

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SEATTLE, WASHINGTON

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The Lower Oxidation States of Gallium. II. The Ga_2Br_4–GaBr System

BY JOHN D. CORBETT AND ALEX HERSHAFT

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The compound Ga_2Br_4 is dimorphic, with melting points of 153 and 164.5° for the α-(metastable) and the β-forms, respectively. Reduction of this compound with gallium metal at 170° gives a liquid containing 31.4 mole % GaBr in Ga_2Br_4; the monobromide is stable in the solid state below the syntectic temperature of 164°. Complete reduction to GaBr(s) below this temperature is limited by kinetic effects to about 75% GaBr. Addition of $AlBr_3$ to the liquid Ga–Ga_2Br_4 system allows complete reduction of Ga(III) to $Ga(AlBr_4)$. Isomorphism between each of the two crystalline forms of $Ga(AlBr_4)$ and Ga_2Br_4 shows the latter compound to be $Ga(GaBr_4)$.

Introduction

Although at one time the formulation of the so-called gallium "dihalides" presented somewhat of a problem, it has been shown recently in a number of ways that the chloride is actually $Ga(GaCl_4)$.[1-3] Furthermore, the reason for the formation of such an intermediate in spite of the instability of GaCl[4] has been given.[1] Since GaI has been isolated,[5] there is no reason to believe that Ga_2I_4 is not formed by a similar acid–base interaction. The present paper deals with the Ga_2Br_4–GaBr system and the analogy between $Ga(GaBr_4)$ and $Ga(AlBr_4)$.

Results and Discussion

The compound Ga_2Br_4 exists in two crystalline forms with the transition near 90°. Due to the slowness of the transformation and a considerable tendency for the liquid to supercool, it is possible to observe melting points for both forms. These are 153 and 164.5° for the low (α) and high (β) temperature forms, respectively. The ease of the transformation depends markedly on composition. A liquid of composition $GaBr_{2.005}$ had to be quenched very rapidly from 170° in order to keep it in the higher melting configuration, while very slow cooling was necessary to put a $GaBr_{1.995}$ sample into the α-form. The transformation solid–liquid–solid was observed several times when the latter preparation was placed in the furnace at 157°. Only the β-form was observed in powder patterns of quenched Ga_2Br_4–GaBr mixtures.

Reduction of molten Ga_2Br_4 with excess gallium gives a pale yellow liquid containing 31.4 mole % GaBr in Ga_2Br_4 ($GaBr_{1.81}$) at 170°, and 30.0% ($GaBr_{1.82}$), at 290°. In comparison, reduction of the corresponding chloride and iodide at 180 and 267° gives solutions containing 7.40[4] and 89.5%[5] monohalide, respectively.[6] This trend of increasing stability of a lower halide with increasing atomic number of the halide also has been observed in a number of similar systems involving the formation of subhalides in solution or as solids.[7] Similar to other metal halide systems the trend noted here can be related primarily to a corresponding decrease in the stability of the complexes of the higher oxidation state, in this case GaX_4^-, that are being reduced.[8]

Although disproportionation of gallium monochloride results when the GaCl–Ga_2Cl_4 melt solidifies,[4] the monobromide, like the monoiodide,[5] is stable in the solid state. The liquid of composition $GaBr_{1.81}$ gives a canary yellow solid when quenched and a white one when cooled slowly. The yellow material turns white when heated above about 120°; the reverse change cannot be accomplished short of remelting and quenching. The nature of the yellow form is not understood, since the powder patterns of the yellow and white materials are identical.

The stability of solid GaBr is in accord with the phase relationships observed, Fig. 1. The eutectic is near $GaBr_{1.85}$ and 152°. As with the iodide system, where the eutectic is near Ga_2I_4 ($GaI_{1.91}$), and reduction in the liquid takes place to $GaI_{1.19}$,[5] the hypothetical melting point (or, less likely, the heat of fusion) of GaBr must be considerably greater than that of Ga_2Br_4.

As can be seen in Fig. 1, the solution of composition $GaBr_{1.81}$ is in equilibrium with solid GaBr and liquid gallium metal at 164°, the syntectic[9]

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[1] J. D. Corbett and R. K. McMullan, THIS JOURNAL, **78**, 2906 (1956).

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

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

[4] J. D. Corbett and S. von Winbush, THIS JOURNAL, **77**, 3964 (1955).

[5] J. D. Corbett and R. K. McMullan, *ibid.*, **77**, 4217 (1955).

[6] In all three systems, very small temperature coefficients for the reduction limit, corresponding to a heat of reaction of nearly zero, make the temperature variable unimportant in a qualitative comparison of the relative stabilities of the GaX products.

[7] J. D. Corbett, S. von Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

[8] The thermal history effect in melting point noted for Ga_2I_4 is probably the result of dissociation of GaI_4^- into GaI_3 and I^-; no such behavior has been observed for the bromide or chloride.

[9] An invariant system involving equilibrium between two liquids and an intermediate solid phase. F. R. Rhines, "Phase Diagrams in

temperature. Since a system containing excess metal and Ga_2Br_4 is unstable below this point, it is possible in principle to achieve complete reduction to GaBr. In practice, however, due to both the limitations of physical contact between the liquid phases once an appreciable amount of solid GaBr has been formed and the low volatility of the components, reduction to the composition $GaBr_{1.40}$ (75 mole %) at 158° is the best that has been achieved.[10] As expected from the phase relationships, the GaBr in such a mixture in excess of that required to form the liquid $GaBr_{1.31}$ was observed to disproportionate to metal and this liquid at 164–165°.

Complete separation of GaBr from this mixture has not been accomplished. In spite of the marked solubility of Ga_2Br_4 in benzene (5.35 wt. %) extraction of this from the finely powdered solid is very inefficient at room temperature. The best product that has been obtained by this technique is $GaBr_{1.3}$. More important, the stability of GaBr with respect to disproportionation is so slight that under conditions where Ga_2Br_4 dissolves, decomposition takes place at an appreciable rate at 35–40°, and slowly even at room temperature. This reaction is more pronounced with stronger bases such as mesitylene and dioxane.

Powder patterns of mixtures with Br/Ga ratios of 1.8, 1.6, 1.4 and 1.3 show no evidence of intermediate compounds in this system, and readily allow the pattern of what is presumed to be GaBr to be deduced (Experimental section).

It is possible to achieve complete reduction of Ga_2Br_4 to GaBr by the addition of the strong Lewis acid $AlBr_3$, forming $Ga(AlBr_4)$ according to the reaction $Ga_2Br_4 + 2Ga + 4AlBr_3 = 4Ga(AlBr_4)$. In view of the similar properties of aluminum and gallium tribromides considerable physical and chemical similarity between $Ga(GaBr_4)$ and $Ga(AlBr_4)$ would be expected. Such a relationship has been noted with the corresponding acid-stabilized gallium(I) chlorides.[1] That there is a marked analogy between the two gallium(I) bromide complexes is clearly shown by the fact that $Ga(AlBr_4)$ is also dimorphic, with each form being isomorphous with the respective $Ga(GaBr_4)$ phase. As indicated by the powder pattern data (Experimental section) the $AlBr_4^-$ ion is very similar in size to the corresponding gallium anion. Because of a more rapid transition in $Ga(AlBr_4)$ it was not possible to determine the metastable melting point; the β-form melts at 159°.

Experimental

Vacuum-sublimed $GaBr_3$ or distilled Br_2 (A. D. Mackay, <0.02% Cl), sealed in fragile ampoules, was handled as previously described[5] in order to obtain the weight of the material enclosed. The desired amount of solid gallium (99.95%, Alum. Co. of Amer.) was then weighed out, the $GaBr_3$ or Br_2 opened through a break-seal *in vacuo*, and the combined materials reacted at 170 to 200° for about one week. In this fashion samples of pure Ga_2Br_4 and known Ga_2Br_4–GaBr mixtures were obtained. Excess metal was used in the determinations of the limit of reduction. After equilibration such a sample was air-quenched, the metal frozen, and separated from the salt in the dry box. The metal was then washed with dry acetone in order to dissolve adhering salt. For example, 0.1582 g. of Ga was recovered from the reaction of 1.7850 g. of Br_2 with 1.0166 g. of Ga at 170° for 10 days, giving a final salt composition of $GaBr_{1.814}$. Melting the recovered metal under dil. HCl gave a weight loss of only 0.2 mg.; this change would correspond to *ca.* 0.06 mole % GaBr if this change were due entirely to the oxidation of this material. This is not considered likely. For the preparation of $GaAlBr_4$, in order to avoid the difficulty of obtaining $GaBr_3$ and $AlBr_3$ in exactly a 1:3 ratio, the reaction $4GaBr_3 + 3Al = 3Ga(AlBr_4) + Ga$ was used. The weight of metal recovered agreed with the stoichiometry of this reaction within experimental error, and the gallium contained no aluminum.

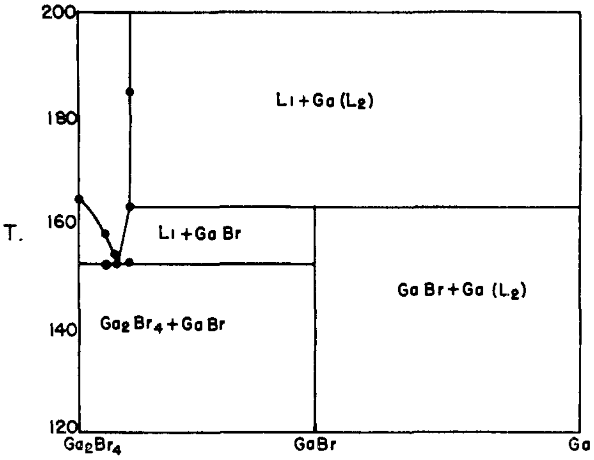

Fig. 1.—The Ga_2Br_4–GaBr–Ga system.

Melting point data were obtained as before,[5] using heating rates of about 1° $min.^{-1}$ or less. The metastable melting point of Ga_2Br_4 already described was determined by placing the α-form in the block at a temperature just below the melting point. A milkiness was observed at the α–β transformation when the low temperature form was heated slowly, although an exact determination of the temperature was not successful. β-Ga_2Br_4 melted at 164.5 ± 0.5°. The α- and β-forms of Ga_2Br_4 and $Ga(AlBr_4)$ had the form of long needles and thick plates, respectively; the former resemble the crystals of Ga_2Cl_4. For samples with Br/Ga ratios of 1.90, 1.865 and 1.81, the temperature of initial and final melting were 151.5, 158.5; 152, 154; 152, 164°, respectively (corrected). The eutectic composition was estimated graphically from these data. Since the limiting composition changes so slightly between 170 and 290°, the difference in composition of the liquid in equilibrium with metal between 170°, where it was measured, and 164°, the syntectic temperature, is considered negligible.

Since a eutectic and hence the separation of a new phase occurs in the Ga_2Br_4–Ga system, it is apparent that an amount of GaBr greater than the 31% present in $GaBr_{1.81}$ can be obtained by reaction below 164°. This was first observed by holding the salt mixture $GaBr_{1.31}$ at 156° in the presence of excess metal for a few hours; a noticeable increase in the amount of solid GaBr occurred. This reduction was facilitated by vigorously shaking excess metal with the salt at 158–160° for periods of 2 to 7 days. A 2″ × 8″ cylindrical furnace was clamped in a Burrell shaker for this purpose. The product was separated manually from the frozen metal in a dry box. The weight of metal recovered was a moderately accurate (3%) measure of the composition. This was checked by direct analysis of the salt, dissolving it in cold, dry acetone so that any free metal could be separated. The difference in weight of the filled and empty weighing bottle, corrected for the buoyancy of the former due to the presence of a helium atmosphere in the dry box, was the weight of salt taken. Analyses were carried out as previously described.[5] Determinations on pure Ga_2Br_4 showed the method to be accurate to 0.5%.

Extractions of Ga_2Br_4 from GaBr were carried out in capped flasks in a dry box, using CaH_2-dried benzene. Very anhydrous conditions were necessary to avoid the

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Metallurgy," McGraw-Hill Book Co., New York, N. Y., 1956, Chap. 10.

(10) A similar approach has allowed the isolation of BiCl from the Bi–$BiCl_3$ system, where a syntectic relationship is also found. J. D. Corbett, unpublished research.

characteristic brown color that results from the reaction of Ga(I) salts with water. Magnetic stirring was limited to short periods of time so as to avoid unnecessary heating. Extractions were carried out three or four times, each for about 24 hours duration. Nearly all of the Ga_2Br_4 that can be removed comes off in the first solution, although this solution is far short of saturation. The solubility of Ga_2Br_4 in benzene is 5.64 g./100 g. solvent at 28°; the solid phase is a benzene complex of this salt.[11,12] The complex was not detected in powder patterns of the residue remaining after extraction with benzene. The solubility of GaBr in benzene is negligible.

Powder patterns were obtained with Ni-filtered Cu Kα radiation and a 114.59 mm. Philips camera. Data for the stronger diffractions for the compounds of interest are as follows, in ångströms, with relative intensities in parentheses: α-Ga_2Br_4: 3.93(5), 3.86(10), 3.54(8), 3.33(7), 3.18(8), 3.06(5), 3.02(5), 2.92(10), 2.89(10), 2.61(6), 2.44(8), 2.25(6), 2.008(6), 1.679(6). β-Ga_2Br_4: 5.37(7), 3.68(3), 3.17(4), 3.12(10), 3.05(9), 2.98(4), 2.83(7), 2.70(4), 2.65(4), 2.35(5), 1.824(9), 1.735(7), 1.542(4). α-$GaAlBr_4$: 3.84(5), 3.54(4), 3.31(4), 3.17(10), 3.05(9), 3.00(9), 2.92(9), 2.88(10), 2.61(6), 2.42(6), 2.37(6), 2.25(6), 2.005(6), 1.676(6), 1.552(5). β-$GaAlBr_4$: 5.33(2), 3.19(10), 3.13(8), 3.04(9), 3.00(7), 2.87(10), 2.36(3), 2.25(4), 2.005(4), 1.676(4), 1.617(4). GaBr: 7.69(8), 3.84(6), 3.52(4), 3.18(6), 3.13(10), 2.96(10), 2.76(5), 2.70(5), 2.61(5), 2.57(5), 2.53(4), 2.33(5), 1.992(4), 1.925(4), 1.860(5), 1.768(6), 1.686(5). More nearly complete correspondence between the Ga_2Br_4 and $Ga(AlBr_4)$ α and β-forms is found when weaker reflections are also considered.

Acknowledgment.—The authors are indebted to Frank Albers for the measurement of the powder patterns and to Dr. Richard McMullan for some of the preliminary observations in this work.

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

[12] This has been identified as $C_6H_6 \cdot Ga_2Br_4$. Jacob Kleinberg, private communication.

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

A New Method for the Preparation of Gallium Dihalides and Some Observations on their Properties

BY RICHARD C. CARLSTON, ERNEST GRISWOLD AND JACOB KLEINBERG

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A simple, rapid method utilizing reaction between metallic gallium and mercury(I) or mercury(II) halides has been developed for the preparation of gallium dihalides. The compounds $Ga_2Cl_4 \cdot C_6H_6$ and $Ga_2Br_4 \cdot C_6H_6$ have been identified. The behavior of gallium dichloride in benzene solution toward hydrogen sulfide is consistent with the $Ga^{I}[Ga^{III}Cl_4]$ formulation.

There has been a recent revival of interest in the gallium dihalides, particularly with regard to their structure. X-Ray diffraction studies with crystalline gallium dichloride[1] have indicated it to consist of $GaCl_4^-$ tetrahedra and Ga^{+1} ions. The Raman spectrum of the fused compound[2] also points to the formulation $Ga^{I}[Ga^{III}Cl_4]$. Independent evidence for this interpretation of the structure of the dichloride has been obtained by Corbett and coworkers.[3]

The present communication describes a novel, simple method for the preparation of gallium dihalides in essentially quantitative yield and, in addition, presents some observations which are most reasonably interpreted in terms of the Ga(I)–Ga(III) nature of gallium dichloride.

Preparation of Gallium Dihalides.—The most common method heretofore employed for the preparation of the dihalidss has essentially involved reaction of the trihalide with gallium metal, followed by removal of the more volatile trihalide by distillation.[4] The diiodide has been obtained also by direct union of stoichiometric quantities of the elements.[5] The dichloride also has been made by heating gallium metal in a stream of dry hydrogen chloride.[6] The preparation of dihalide from metal and trihalide requires rather elaborate equipment and is tedious and time-consuming. On the other hand, the preparative procedure described below, in which gallium metal is heated in a sealed Pyrex tube with the stoichiometric quantity of mercury(I) or mercury(II) halide, is simple and rapid and, moreover, gives practically quantitative yields of dihalide. The same reaction also has been carried out in the presence of benzene. It should be mentioned that gallium dichloride in admixture with the trichloride has been produced by reaction between silver chloride or lead(II) chloride and gallium metal.[7]

Experimental

The halides employed were the chloride of mercury(I) and the chloride, bromide and iodide of mercury(II), all of C.P. quality. Mercury(I) iodide did not react with gallium metal even at temperatures in the neighborhood of 200°. Gallium of 99.96% purity (Aluminum Company of America) was stored under thiophene-free benzene and samples were pipetted into a weighed Pyrex reaction tube 9 × 70 mm. The tube was heated gently to remove adherent benzene and weighed. Essentially the stoichiometric quantity of mercury halide was added to the gallium, the reaction tube flushed with oxygen-free nitrogen, and sealed. The mixture was then heated to effect reaction; for mercury(I) chloride a temperature range of 100–175° was employed, for mercury(II) bromide 140–160°, and for mercury(II) iodide approximately 200°. The tubes were kept at these temperatures for 2–3 hr. to ensure complete reaction.

After the treatment described above, the tubes were cooled to room temperature, transferred to a dry box and opened. The liquid metal was poured into a weighed 25-ml. beaker, air dried and weighed. The metal was then treated with warm concentrated hydrochloric acid until the gallium had been extracted completely. The residual mercury was dried in a vacuum oven at room temperature and its weight determined.

The solids remaining in the reaction tubes were added to approximately 0.1 M aqueous perchloric acid and the mixtures warmed to effect dissolution and oxidation of the

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

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

[3] S. von Winbush, R. K. McMullan and J. D. Corbett, to be published.

[4] (a) L. S. Foster, *Inorg. Syntheses, IV*, 111 (1953); (b) J. D. Corbett, S. von Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

[5] J. D. Corbett and R. K. McMullan, *ibid.*, **77**, 4217 (1955).

[6] W. C. Johnson, P. Hammond and H. Friedman, Progress Report, "The Chemistry of Gallium," Navy Contract N6-ori-20, Univ. of Chicago, Oct. 1-Dec. 1, 1947.

[7] K. Clusius and F. Hitzig, *Helv. Chim. Acta*, **33**, 506 (1950).