of six, quite different values of X_ω are obtained; in fact X_ω for pure $Al(NO_3)_3$ comes out to be about 10 if all calculations are based on anhydrous salts.

TABLE IV

OH/Al	M_ω	OH/Al	M_ω
0	138	1.75	715
0.5	256	2.0	1000
1.0	308	2.25	1430
1.5	526		

Discussion

τ-Values were obtained on freshly prepared solutions as a function of time in order to be sure that our data do represent equilibrium conditions. In the case reported, Na_2CO_3 was added to a solution of $Al(NO_3)_3$ in sufficient quantity to give an OH/Al of 1.5. Hydrous oxide precipitated immediately, but the solution cleared upon shaking for ten minutes. Following two filtrations τ was measured until no further change could be detected after waiting several hours. From the data presented in Table V, it is clear that equilibrium is established in about a week. It would appear that the dissolution of hydrous oxide to form small solute aggregates (basic salts) is much slower than the precipitation reaction.[18,19] It is considered likely that some unprecipitated aluminum species reacts with hydrous oxide, forming large but soluble aggregates. These aggregates are then hydrolytically cleaved to smaller aggregates or are attacked by more of the unprecipitated aluminum species. Such a mechanism is considered as the most likely explanation of the decrease in scattering with time. Note that the equilibrium τ-value agrees well with the value recorded for the same solution in Table III. It is believed that all values recorded in Table III are representative of true equilibrium conditions.

TABLE V

Time (hr.)	$\tau \times 10^5$ in cm.$^{-1}$ (r = 1.5, 0.4 M Al)	Time (hr.)	$\tau \times 10^5$ in cm.$^{-1}$ (r = 1.5, 0.4 M Al)
1	75.5	29	14.8
1.5	72.1	77	11.9
4	60.7	181	10.6
7	50.8	270	10.7
10	41.8	450	10.6

The interpretation of the existing data in terms of an exact hydrolysis mechanism is, of course, impossible. However, we are inclined to the view that there exists in a given solution a distribution of aluminum atoms among a number of aggregates, the average of which increases with increasing OH/Al ratio. Sillen[20] suggests that $Al_6(OH)_{15}^{+3}$ is the most important species over the entire range of basicity, although he admits that his interpretation is not final. The values of X_w and X_n for the high OH/Al ratios indicate numerous aggregates containing more than six atoms of aluminum. Furthermore if one calculates X_w and X_n for the hydrolysis of bismuth[21] based on the assumption of a continuous aggregation mechanism and compares the relative shape of the two curves to those in Fig. 2, reasonable agreement is found. Of course, the curves for bismuth are displaced toward lower values of OH/Bi.

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[18] W. D. Treadwell and M. Zurcher, *Helv. Chim. Acta*, **15**, 980 (1933).

[19] W. D. Treadwell and J. E. Boner, *ibid.*, **17**, 774 (1934).

[20] L. G. Sillen, *Acta Chem. Scand.*, **8**, 1917 (1954).

[21] L. G. Sillen and F. Graner, *ibid.*, **1**, 631 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Vapor Pressures of Aluminum Chloride, Aluminum Bromide and the Mixed Halide Phase $Al_2Br_2Cl_4$

BY THOMAS G. DUNNE AND N. W. GREGORY

RECEIVED SEPTEMBER 24, 1957

Vapor pressures of Al_2Cl_6, Al_2Br_6 and $Al_2Br_2Cl_4$ have been measured between 0 and 40° by the effusion method. The mixed halide vapor pressure is about thirty times larger than that of the chloride and one quarter of that of the bromide at room temperature. No dependence of pressures (within experimental error) on cell geometry could be detected.

At room temperature hydrogen chloride reacts with anhydrous aluminum bromide liberating hydrogen bromide; the resulting chlorine containing aluminum compounds and aluminum bromide form a solid solution until the chlorine content reaches *ca.* 18 mole %. Further reaction produces a mixed halide phase with composition near that of $Al_2Br_2Cl_4$ (65–69 mole % chloride). The characteristics of this halogen exchange reaction and of the aluminum chloride–aluminum bromide system have been discussed in some detail in an earlier paper[1]; at room temperature the mixed halide phase is quite resistant to reaction with hydrogen chloride and it has been postulated that the remaining bromine atoms are in the bridge positions of dimeric aluminum halide molecules. Structural evidence (from X-ray powder patterns) indicates that the mixed halide phase is isomorphous with aluminum chloride,[2] C2/m; the existence of molecular dimers in crystals of aluminum chloride is not as pronounced as in aluminum bromide which has a different crystal structure,[3] $P2_1/a$.

Continuing a study of the mixed halide phase we have measured its vapor pressure and that of aluminum chloride and aluminum bromide at temperatures from 0 to 40°, using the effusion technique. Vapor pressures of aluminum chloride and aluminum

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[1] J. D. Corbett and N. W. Gregory, THIS JOURNAL, **75**, 5238 (1953).

[2] J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

[3] P. A. Renes and C. H. MacGillavry, *ibid.*, **64**, 275 (1945).

bromide have not been reported previously in this temperature range; the vapor pressure of the chloride is of additional interest in view of its reported anomalous behavior at higher temperatures.[4,5]

Experimental Part

Because of the unusually vigorous hygroscopic and reactive nature of the anhydrous aluminum halides, special handling techniques were devised to introduce pure samples into effusion cells and to protect the material in the cell while removing the effusate after each run. The Pyrex apparatus consisted of an orifice, made by piercing a thin glass bubble with a tungsten needle and grinding to knife-edge thinness with carborundum and a steel ball, sealed into the cell and attached to a collecting device. The latter was made by converting a 29/42 standard taper ground-glass joint into a 15 mm. bore stopcock. The outer part was sealed closely to a two-liter round-bottom flask in which a removable collecting finger could be rotated on a ball joint near the top. On the opposite side an alternate pumping route was connected through a trap. The inner part of the stopcock was sealed across the top so that the only grease exposure was that of the single opening to one of the arms of the outer part. With the sample in place and the entire system evacuated (sample initially pumped on through the trap) a run was initiated by filling the finger with liquid oxygen, rotating the cell (inner part of the stopcock) through 180° and swinging the finger into the bore into collecting position. A collecting area of about two cm.² could easily be pushed into the space immediately above the orifice. To stop the run the procedure was reversed. After rotating the stopcock, dry air was admitted to the large bulb, the finger removed and the aluminum halide rinsed off in a solution to be analyzed. The clean finger was replaced, the bulb evacuated, and the system thus readied for the next measurement. With this arrangement the sample in the effusion cell was maintained under vacuum at all times, under continuous pumping except for the brief interval required to rotate the stopcock.

Orifice areas were measured by an optical projection method with an uncertainty of 1%. Several cells and orifices with the following dimensions were used.

Cell no.	Orifice area, cm.² × 10³	$\frac{\text{Orifice area}}{\text{Cell cross-sectional area}} = f$ $f \times 10^4$	K^a
1	6.04	10.8	0.95
2	3.05	1.44	.92
3	2.55	4.15	.92
4	12.65	45.5	.97

[a] K is the over-all cell Clausing factor.[6-8]

The simple aluminum halides were prepared by reaction of aluminum foil (in excess) with the anhydrous halogen elements. In the case of the chloride it was necessary to pretreat the metal with hydrogen chloride before reaction of the elements could be initiated easily. The products were separated from non-volatile impurities by several vacuum sublimations and collected in small glass ampoules to which were attached "break-in-skis," designed to permit transfer of the sample (after connecting the outer tube to an arm on the effusion cell) by breaking a thin glass membrane with a magnetically-lifted steel ball. Thus the anhydrous salts could be sublimed into the effusion cell (condensed there by surrounding the cell with Dry Ice) without exposure to air or to a dry-box atmosphere; this greatly reduced contamination of the sample by moisture.

The mixed halide phase was prepared by the halogen exchange reaction.[1] To minimize reaction of hydrogen chloride with the mixed halide and to reduce the latter's capacity to dissolve aluminum bromide, the preparation was carried out at 0°. Progress of the reaction and the composition of the solid phase in the equilibrium system was followed by periodic analysis of the HCl–HBr gas mixtures.[1] After formation, the mixed halide phase was sublimed in high vacuum directly into the effusion cell through a "break-in-ski." During sublimation the reactor vessel was kept at 25° and the vapor condensed in the cell at −78°. In a number of instances additional hydrogen chloride was introduced into the effusion cell after sublimation to react with traces of aluminum bromide collected during the transfer. The composition and behavior of the mixed halide phase after sublimation will be discussed after presenting results of the vapor pressure measurements.

The quantity of effusate collected (micromoles of aluminum halide in convenient time intervals) was determined by a colorimetric method of analysis, utilizing the complex formed between aluminum ion and aurin tricarboxylic acid (Aluminon). Solutions were buffered at *p*H 4.2 and the absorption of light at 520 mμ measured (in comparison with standards prepared from potassium alum) with a Beckman D.U. spectrophotometer. Concentrations in the range 1×10^{-5} to 3×10^{-5} molar could be determined within 5% uncertainty. Uncertainty was less at higher concentrations.

Temperatures were established within 0.1° with conventional water-bath thermostats.

Results and Discussion

Effusion cell pressures were calculated from the usual Knudsen equation[9] $P_{\text{mm}} = 17.14n(MT)^{1/2}/KA_0t$ where n is the number of moles of effusate of molecular weight M, assumed to be that of the dimers in each case,[10] t the time, K the over-all cell Clausing factor, and T the absolute temperature.

Aluminum Chloride.—Vapor pressures were measured between 21 and 49° using four independent samples and three effusion cells. A slow decrease of vapor pressure with time was observed, believed caused by hydration and/or hydrolysis of the sample. Very small amounts of moisture, as might be expected even in a well-functioning vacuum line containing greased stopcocks, seem sufficient to cause this effect, suggesting that it is largely a surface phenomenon. For example it was found that a sample, above which the steady-state effusion pressure had dropped to a value too low to measure conveniently, could be sublimed away by use of a hand torch without leaving any visible residue; residue would be expected if appreciable hydrolysis had occurred. If small amounts of air accidentally leaked into the effusion cell through a channel in the stopcock grease, the steady-state effusion pressure quickly dropped to an immeasurable value; in such cases a white non-volatile deposit was frequently observed around the orifice.

To minimize errors in the apparent vapor pressure caused by this effect, values of the pressure were rejected in a given series of measurements as soon as a marked decrease from initially obtained values became apparent. In most cases this resulted in selection of the first three measurements from each set (usually from a total of five or six). These pressures, with a designation of the effusion cell used, are shown in Fig. 1, where a comparison with aluminum bromide and with the extrapolated curve from the equation given by Kelley[11] can be made. Temperatures were varied randomly between measurements. The line drawn through the experimental points corresponds to the equation $\log_{10} P_{\text{mm}} = -6536/T + 17.77$ and a heat of sublimation of 29.9 kcal.

No systematic variation of pressures with cell geometry could be detected. From the relation-

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[4] A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98 (1938).

[5] L. M. Foster, THIS JOURNAL, **72**, 1902 (1950).

[6] P. Clausing, *Ann. Physik*, **12**, 961 (1932).

[7] C. I. Whitman, *J. Chem. Phys.*, **20**, 161 (1952).

[8] J. H. Stern and N. W. Gregory, *J. Phys. Chem.*, **61**, 1226 (1957).

[9] See for example, S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

[10] W. Fischer, O. Rahlfs and B. Benge, *Z. anorg. Chem.*, **205**, 1 (1932).

[11] K. K. Kelley, U. S. Bur. Mines Bull. 383, 1935.

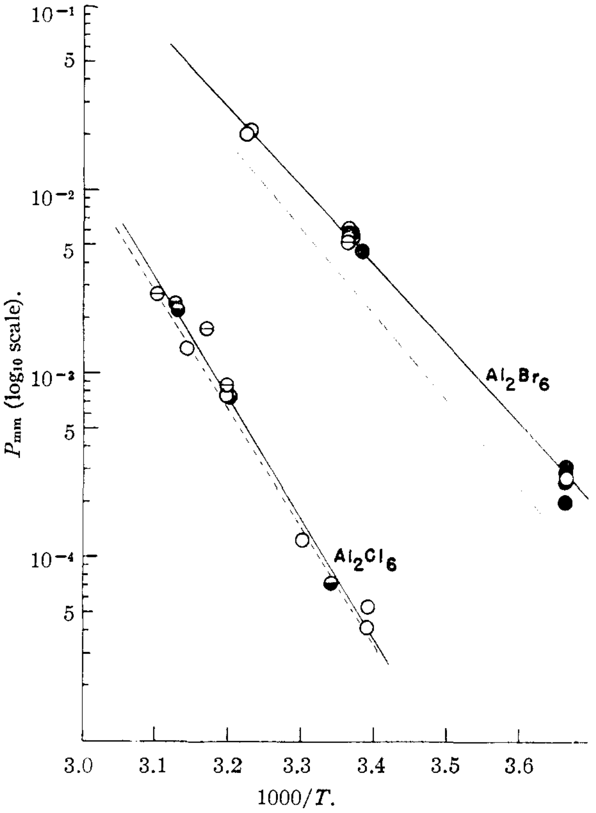

Fig. 1.—Vapor pressure–temperature behavior of Al_2Br_6 and Al_2Cl_6: ●, cell 1; ◒, cell 2; ⊖, cell 3; ○, cell 4.

ship of the condensation coefficient to steady state pressures and cell geometry,[8] the condensation coefficient must be larger than 10^{-2}; the experimental uncertainty precludes a more accurate estimate.

Aluminum Bromide.—Vapor pressures were measured between 0 and 37°. The selected values were taken from ten independent samples. A hydrolysis problem similar to that described for aluminum chloride was encountered. In some cases a fall-off was not observed throughout the entire series of measurements; however to use a consistent method of selection of values only the first two in each series are shown in Fig. 1. Two effusion experiments were conducted in a grease-free system (which could only be used for a single measurement) and results were in good accord with those from the apparatus with the stopcock.

The line shown in Fig. 1 for aluminum bromide corresponds to the equation $\log_{10}P_{mm} = -4292/T + 12.18$ and a heat of sublimation of 19.7 kcal. The dotted line is an extrapolation of an equation derived from high temperature data.[11] No systematic dependence of pressures on cell geometry could be established.

The Mixed Halide Phase, $Al_2Br_2Cl_4$.—Vapor pressures of nine independently prepared samples of mixed halide were measured. From five of these preparations a number of separate partial sublimations (removing 10–15% of the total sample) was made to transfer material into the effusion cells. Initial pressures, measured above material first sublimed from the exchange reactors, invariably were near or slightly larger than those measured above pure aluminum bromide. The second and successive measurements gave lower pressures with the majority falling in the vicinity of the line marked M, Fig. 2, after 15–20% of the sample in the effusion cell had been removed. Second and third sublimates did not give extraordinarily high initial pressures although they were usually somewhat above line M. A hydrolysis problem, similar to that discussed for the simple halides, also was encountered with the mixed halide phase; however only data where reaction with water vapor was believed insignificant have been shown in Fig. 2.

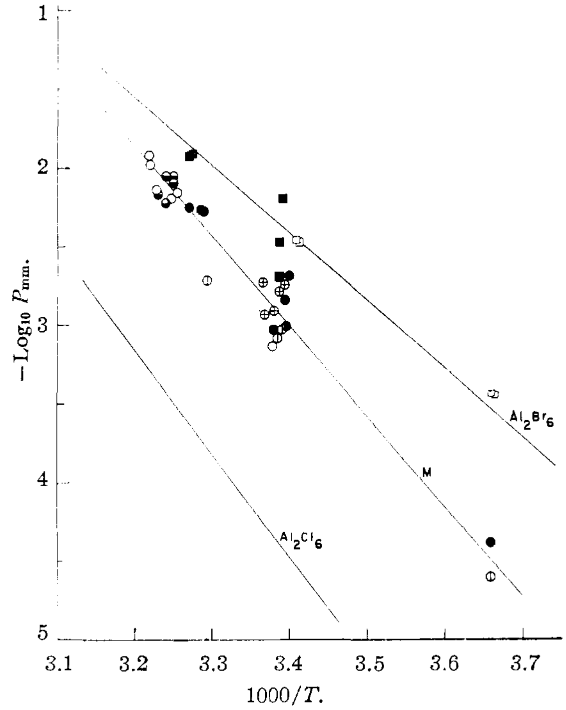

Fig. 2.—Vapor pressure–temperature behavior of the $Al_2Br_2Cl_4$ phase and the two-phase system $Al_2Br_2Cl_4$–Al_2Br_6: □, $Al_2Br_2Cl_4$–Al_2Br_6 (two-solid phases, saturated) mixture; ■, first sublimate (10–15% of the M.H. phase formed by reaction of HCl and Al_2Br_6 at 0°); ○, sublimate in cell treated with HCl before vapor pressure measured; ⦶, same as ○, independent sample; ⊕, same as ○, independent sample; point nearest Al_2Br_6 line measured before HCl treatment; ◒, entire small sample (*ca.* 10^{-3} mole) sublimed from cell in this series; first measurement made after *ca.* 1/7 sample removed; ●, same as ◒, except first measurement (highest point) made without preliminary pump-out.

With very careful handling it was found possible to make as many as seven or eight measurements without significant contamination and in two cases, described below, to sublime the sample completely from the effusion cell.

The high initial values of the pressure in these preliminary experiments lead to the conclusion that material first sublimed from the exchange reactor contained appreciable amounts of aluminum bromide, particularly when a large (1–2 g.) amount of mixed halide was prepared at one time and only a small fraction of the material transferred to the effusion cell. The aluminum bromide is believed to originate largely from incomplete reaction of hydrogen chloride; possibly some is formed by disproportion of the mixed halide during the sublimation process. However the latter source is not believed important; appreciable amounts of aluminum chloride were not observed as a residue in experiments where all of the sample in the effusion cell was removed; the degree of disproportionation has been estimated from exchange equilibrium data to be only 1.5% in the solid phase.[1]

Partial sublimation would tend to concentrate small amounts of the more volatile bromide in the sublimate. At $-78°$, the condensation temperature, the aluminum bromide vapor would likely condense as a separate phase. On warming to 0° and above, the measuring temperature, the total vapor pressure would then correspond to that of a mixture of mixed halide and aluminum bromide and would be expected to fall as solid phase solubility equilibrium is established. A two-phase system would persist until the amount of aluminum bromide becomes small enough to dissolve completely in the mixed halide phase.[1] As aluminum bromide gradually is removed from this solid solution, pressures should approach those of a pure mixed halide phase, or, if disproportionation is significant, those of a disproportionation equilibrium mixture.

A two-solid phase mixture was purposely prepared by allowing a limited amount of hydrogen chloride to react with aluminum bromide. Vapor pressures above this mixture, □, calculated on the same basis as the others in Fig. 2 (all pressures in Fig. 2 were based on the molecular weight of $Al_2Br_2Cl_4$; if the vaporizing species were all Al_2Br_6, these values should be increased by a factor of 1.22 corresponding to the use of the larger molecular weight in the Knudsen equation), are seen to lie near the curve for aluminum bromide and to correspond to the range of the initial values measured from the first sublimates described above. Only one first sublimate series of pressures is shown on Fig. 2, ■. The gradual approach of measured pressures in this series toward line M corresponds to the order in which measurements were made. The remaining data on Fig. 2 were obtained from mixed halide samples believed relatively free of aluminum bromide.

In two cases (see legend for Fig. 2) only small amounts of aluminum bromide, *ca.* 10^{-3} mole, were converted to mixed halide and the entire reaction mixtures transferred to the effusion cell. In one, ◒, the material was pumped on (through the orifice after sublimation into the cell) for 15 hours before making the initial measurement; then with continuous pumping a series of five measurements (each of *ca.* one hour duration) were made at intervals of about 12 hours until 80% of the sample had been removed. (The remaining 20% disappeared before another run could be completed.) All results are shown on Fig. 2 and group randomly around line M. In the second case, ●, the experiment was conducted similarly except that the first measurement was made immediately after bringing the sample to a constant temperature. This value is the point lying closest to the aluminum bromide line in this series; the rest (seven) fall around line M.

The other three series of measurements shown in Fig. 2, ○ ⦶ ⊕ were obtained from small samples sublimed from reactors (into the effusion cell) in the usual manner and treated further with hydrogen chloride, previously dried over phosphorus pentoxide or aluminum chloride, to convert any excess aluminum bromide to mixed halide prior to initiating vapor pressure measurements. The results agree quite well with those discussed in the preceding paragraph, though in one series, ⦶, a progressive decline of pressures was observed, suggestive of a moisture contamination effect. In the series ⊕, two measurements were made prior to hydrogen chloride treatment; these gave pressures (not shown) half-way between line M and Al_2Br_6. After treatment with HCl, the values shown on Fig. 2 were obtained. A detailed description of the history of each sample and of all measurements made may be found elsewhere.[12]

From these observations it is proposed that the major molecular species vaporizing from the mixed halide phase is $Al_2Br_2Cl_4$. Line M is given as an approximation for the vapor pressure–temperature relationship for a "pure" mixed halide phase. Measured pressures above this line are attributed to the presence of aluminum bromide; those below partially to the effect of dissolved aluminum chloride impurity, although the amount seems very small, and to the fall-off caused by reaction of the aluminum halide with small amounts of moisture in the high vacuum system. Line M may be represented by the equation $\log_{10}P_{\mathrm{mm}} = -5747/T + 16.53$ which, we suggest, gives the vapor pressure of $Al_2Br_2Cl_4$ within 30%, and a heat of sublimation of 26.3 ± 3 kcal.

The mixed halide vapor pressure is thirty times greater than that of aluminum chloride at room temperature and about one quarter that of aluminum bromide. The assumed mixed halide vapor pressure equation gives a degree of disproportionation in the vapor phase about one-tenth less than that for the solid.

No evidence of an unusually slow rate of vaporization was observed in effusion for any of the halide phases. The slow approach to equilibrium behavior observed for aluminum chloride at higher temperatures (with the vapor pressure near one atmosphere) has been attributed by Foster[1] to a heat conduction problem. This interpretation appears consistent with our observations since the energy of vaporization demanded in the effusion cells is very small and would not be expected to cause appreciable cooling of the solid.

Considerable effort was spent in an attempt to adapt the gas saturation method (as used in the study of iron(II) bromide[13]) to the measurement of vapor pressures of the aluminum halides at pressures below 10^{-2} mm. Adsorption of aluminum halides on new glass surfaces was found a serious problem in this work. After devising an apparatus to obviate this difficulty, the method was still un-

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(12) T. G. Dunne, Ph.D. Thesis, University of Washington, 1957.

(13) R. O. MacLaren and N. W. Gregory, *J. Phys. Chem.*, **59**, 184 (1955).

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.

Acknowledgment.—We wish to acknowledge with thanks financial support received from the Office of Ordnance Research, U. S. Army.

SEATTLE, WASHINGTON

[CONTRIBUTION NO. 565 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

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

BY JOHN D. CORBETT AND ALEX HERSHAFT

RECEIVED AUGUST 26, 1957

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