cal case of homogeneous isotopic exchange in which no gross chemical change occurs. The ordinary treatment of the exchange must be modified. If in addition to process 5 there is a reaction of the type

$$Mn^{++} + MnO_4^- \longrightarrow \text{Products} \qquad (19)$$

the familiar first-order exchange law encountered in steady-state systems does not apply and the straight line relation

$$\log (1 - f) = kt \qquad (20)$$

cannot be expected. However, it can be shown that R_0, the exchange rate for reaction 4 under the initial conditions of the experiment, is given by

$$R_0 = [d \ln (1 - f)/dt]_0(Mn^{++})_0(MnO_4^-)_0/[(Mn^{++})_0 + (MnO_4^-)_0] \qquad (21)$$

In this equation the parentheses designate concentrations.

The apparent exchange fraction amounted to nearly 40% in one of the experiments in Table III. Since the data were not sufficient for the detection of curvature in the $\ln(1 - f)$ function, a least-squares straight line through the origin, $[\ln(1 - f) = 0, t = 0]$, was used to give the slope of the $\ln(1 - f)$ curve at $t = 0$. Values of R_0 obtained by this method are included in Table III together with the predictions of Adamson's formula (6). It is seen that the observed rates were lower in each case than the prediction of formula (6); however, the agreement was to within a factor of two in each case.

It is felt that there are serious objections to the consideration of the indicated values of R_0 as the actual rate of exchange between Mn^{++} and MnO_4^- for the solutions in which gross amounts of intermediate oxidation states have formed. The same apparent exchange would appear if the tetraphenylarsonium ion precipitated, together with the permanganate, some intermediate oxidation state which had exchanged with Mn^{++}. Likewise, in Adamson's experiments, if the precipitation upon the addition of hydroxide did not completely remove intermediate species, a similar apparent exchange would be indicated. In view of these possibilities the agreement of these results with those of Adamson does seem surprisingly good. However, it is believed that the exchange Mn^{++} and MnO_4^- cannot be considered as established.

Acknowledgment.—We wish to express our appreciation of Dr. A. L. Thompson of the Radiation Laboratory of McGill University who provided the samples of radioactive manganese.

AMES, IOWA

[CONTRIBUTION NO. 383 FROM THE INSTITUTE FOR ATOMIC RESEARCH, AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Lower Oxidation States of Gallium. I. The GaI_3–GaI_2–GaI System*

BY JOHN D. CORBETT AND RICHARD K. MCMULLAN

RECEIVED APRIL 8, 1955

Gallium(II) iodide has been observed to disproportionate into gallium(III) iodide and gallium(I) iodide, instead of the trihalide and the metal that are obtained with gallium(II) chloride. A phase diagram and powder patterns confirm the existence of the two lower iodides. Gallium(II) iodide is only moderately stable at the melting point of 211°; gallium(I) iodide is sufficiently unstable that in the presence of excess gallium only a limiting composition of $GaI_{1.19}$ is obtained at a melting temperature of 265°. Gallium(I) iodide can be isolated from the limiting mixture by a solvent extraction. The demonstration of the existence of the gallium(I) oxidation state in this system may favor the formulation Ga(I)[Ga(III)I_4] for the diamagnetic gallium(II) iodide.

Introduction

The first preparations of gallium(II) chloride, bromide and iodide were reported by Boisbaudran,[1] the discoverer of the element gallium, as resulting from the incomplete halogenation of the metal. Since that time, only the dichloride has received any significant attention, and Einecke[2] has even expressed doubt as to whether the diiodide was ever isolated. Klemm and Tilk[3] found solid $GaCl_2$ to be diamagnetic; accordingly the compound has usually been formulated as either Ga(I)[Ga(III)Cl_4] or Cl_2Ga–$GaCl_2$.

The unsymmetrical structure has been somewhat unsatisfactory in that no Ga(I) halides have been isolated, although Ga_2S has been confirmed as a definite compound,[4] and Ga^+ appears to be formed by the anodic oxidation of the metal in glacial acetic acid.[5] The slight solubility of metallic gallium in liquid $GaCl_2$ first reported by Foster[6] might indicate the formation of a slightly stable GaCl. Measurements have shown that the clear solution contains about two mole per cent. gallium just above the melting point[7,8]; the metal is reprecipitated on solidification of the salt. Estimates of the stabilities of the gallium halides led Brewer[9] to predict that the monohalides would exist only in the gaseous state at higher temperatures.

(*) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[1] Lecoq de Boisbaudran and E. Jungfleisch, *Compt. rend.*, **86**, 475 (1878); Lecoq de Boisbaudran, *ibid.*, **93**, 294 (1881).

[2] E. Einecke, "Das Gallium," Voss, Leipzig, 1937; Edwards Bros., Ann Arbor, Mich., 1944, p. 82.

[3] W. Klemm and W. Tilk, *Z. anorg. allgem. Chem.*, **207**, 175 (1932).

[4] A. Brukl and G. Ortner, *Monatsh.*, **56**, 358 (1930).

[5] A. W. Davidson and F. Jirik, THIS JOURNAL, **72**, 1700 (1950).

[6] "Inorganic Syntheses," Vol. IV, J. C. Bailar, Jr., Ed., McGraw-Hill Book Co., New York, N. Y., 1953, p. 111.

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

[8] H. Taube, H. Friedman and A. Wilson, NP-636, Progress Report, "The Chemistry of Gallium," Navy Contract N6-ori-20, Univ. of Chicago, October and November, 1948.

[9] "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, p. 145.

Laubengayer and Schirmer[10] attempted to measure the vapor pressure and density of gallium(II) chloride, and, although the results were somewhat inconclusive due to disproportionation into the more volatile gallium(III) chloride and metal, the results did show that considerable amounts of $GaCl_2$ monomer must exist in the gas phase above 400°. A structure involving a metal–metal bond would be moderately unusual, and presumably similar to B_2Cl_4 and Hg_2^{++}.

During an investigation of the properties of the gallium(II) halides, directed toward a possible distinction between the suggested structures, we observed that thermal disproportionation of GaI_2 in vacuum did not produce the darkening effect of metallic gallium that is characteristic of $GaCl_2$ and $GaBr_2$, thus indicating the probable formation of a lower iodide. We have accordingly investigated the phase diagram for the gallium iodides and have confirmed the existence of gallium(I) iodide as well as gallium(II) iodide.

Experimental Procedures

Preparations.—The melting point samples were prepared by reaction of weighed quantities of the elements in evacuated 0.6 × 8 cm. tubing. Iodine (J. T. Baker Reagent) was sublimed into fragile ampoules which were sealed off and weighed; these were then broken *in vacuo*, the sublimed iodine sealed off in a second tube equipped with a break-seal, and the glass fragments weighed. Gallium (99.95%, Aluminum Company of America), which had been washed with dilute HCl and stored under vacuum, was weighed as frozen pellets, the iodine sublimed onto it in the melting point tubes, and the system sealed off. The reaction was carried out at 350 to 500° for one to three days, the longer times being necessary for complete reaction in samples of higher gallium content. A limiting composition of about $GaI_{1.2}$ can be achieved with excess gallium.

The method of preparation enabled prespecified compositions to be readily obtained, as for example, $GaI_{1.999}$. Another method for the preparation of pure GaI_3 and GaI_2 from intermediate mixtures was by vacuum sublimation of GaI_3 from the essentially non-volatile diiodide at 150°. At higher temperatures (250°) *in vacuo*, GaI_2 lost GaI_3 by disproportionation. The volatility attributed to GaI_2 by Boisbaudran[1] may instead have been this decomposition. Preparation of the triiodide by reaction of metal with excess iodine offered a distinct disadvantage in that the excess iodine was apparently bound to the salt, for a sample so prepared and slowly sublimed three times in high vacuum still had the composition $GaI_{3.64}$.

Melting Point Determinations.—When samples lower in iodine content than $GaI_{1.9}$ were rapidly solidified, glasses were formed that had little tendency to crystallize at room temperature. However, these crystallized on warming them to about 100° for a few minutes. An additional complication arose from a strong dependence of the melting point on the thermal history of some of the samples. In view of these difficulties, the phase diagram was constructed by visually observing the melting temperatures on carefully controlled samples. A 2.5 × 8 in. cylindrical aluminum block, through which a 6 mm. sample hole had been drilled longitudinally, was centered in a horizontal $2^3/_8$ in. i.d. by 12" long cylindrical furnace. A slit for viewing the sample in the cylinder was cut through the furnace and block near the center, and a light source positioned behind it. The large heat capacity of the block allowed essentially no temperature gradient along the sample. The furnace temperature was controlled by a Powerstat and a "Celectray" controller; the temperatures were read on a Leeds and Northrup Portable Potentiometer, employing a calibrated chromel-alumel thermocouple positioned in the block near the sample.

The melting points of samples in the range $GaI_{2.3}$ to $GaI_{1.2}$ depended strongly on their history, with a lower melting point being obtained when the sample was equilibrated and quenched from higher temperatures. For this reason the melting temperatures were determined by a bracketing procedure. Liquid samples were heated at a given temperature for at least four hours, quenched with an air blast, heated briefly to 100°, if necessary, to crystallize them, inserted in the furnace already heated to just below the expected melting point and heating at the rate of about 1°/min., and the temperature at which the last crystals melted noted. This procedure was repeated, heating the liquid sample at successively lower temperatures, until a maximum melting point was obtained when the sample had been quenched from one to five degrees above this temperature. At such a temperature the last crystals were essentially in true equilibrium with the liquid. The points so obtained were reproducible to within one degree, and showed no drift with time. We have also recorded approximate eutectic temperatures as the point where the first indication of premelting was observed; these are quite constant and appear in reasonable agreement with those obtained from the melting curves. However, it is recognized that where the eutectic and melting temperatures are some distance apart, the system may not have been at equilibrium. The melts are all deep red to red-brown, cooling to similarly colored glasses or yellow crystals. The diiodide appears somewhat lighter yellow than the other two compounds, and crystallizes in asbestos-like fibers upon annealing.

Analyses.—All samples for analysis (and for powder patterns) were opened and transferred in a dry box filled with nitrogen (Matheson, Prepurified, $<10^{-3}\%$ O_2) that had been dried by passage through a Dry Ice trap and a P_2O_5 column. In view of the reactivity of the compounds, and the unlikelihood of their containing elements other than gallium and iodine, the samples for analysis were not weighed. Rather the salts were directly dissolved by the admission of 0.1 *N* H_2SO_4 onto the sample in an evacuated container. The reaction with the solution was vigorous, with the evolution of hydrogen; varying amounts of a flocculent brown or orange-brown solid formed that slowly redissolved with more hydrogen evolution. (A similar behavior has also been observed upon solution of $GaCl_2$.)[8] And as with $GaCl_2$, small amounts of metallic gallium also precipitated from samples near GaI_2, presumably due to disproportionation. Compositions near $GaI_{1.2}$ can be dissolved with the temporary formation of the same colored solid, but without the precipitation of metal. The aqueous reactions of these oxidation states are being investigated further.

The aqueous solutions were heated for several hours to ensure complete oxidation. Iodide was determined by conventional silver titration using eosin as the indicator. Gallium was determined by precipitation and weighing as the 5,7-dibromo-8-hydroxyquinolate.[11] The precipitate was digested for an hour in the hot acetone solution to enable easier filtration. Average errors of less than −0.1% were obtained on analysis of solutions prepared by dissolving weighed metal in perchloric acid.

Magnetic Properties of GaI_2.—A 3-g. sample of annealed GaI_2 (sealed in a 5 mm. evacuated Pyrex tube) was suspended from a Gouy balance into an inhomogeneous field with a maximum intensity of about 12,000 gauss. A definite diamagnetism was indicated.

Isolation of GaI.—A sample of the limiting composition $GaI_{1.2}$ was powdered in the dry box and placed in a coarse grade sintered glass filtering crucible contained in a modified one-piece Soxhlet extractor. After CaH_2-dried benzene was added and frozen with a −79° bath, the apparatus was evacuated and sealed off. Extraction for 12 hours resulted in removal of most of the more soluble GaI_2, leaving a residue of composition $GaI_{1.05}$.

Powder Patterns.—Diffraction patterns were obtained for samples sealed in 0.2 to 0.3 mm. i.d. drawn Pyrex tubing, using Ni-filtered Cu $K\alpha$ radiation in a 11.46 cm. dia. camera. The following are the stronger diffractions for GaI_3, GaI_2 (annealed) and $GaI_{1.05}$ in terms of θ, with relative intensities on a scale of 0–20 indicated in parentheses:

GaI_3: 12.9(20), 14.7(9), 21.4(10), 24.9(18), 26.3(8), 34.58(7), 38.51(9).

GaI_2: 6.1(8), 7.1(8), 7.8(8), 12.1(12), 12.7(20), 13.6(14), 14.5(18), 15.4(14), 16.2(7), 17.0(8), 22.5(8), 22.96(8), 24.20(10), 25.11(10), 28.35(7).

---

[10] A. W. Laubengayer and F. B. Schirmer, THIS JOURNAL, **62**, 1578 (1940).

[11] E. Gastinger, *Z. anal. Chem.*, **126**, 373 (1941).

GaI: 11.8(12), 12.3(10), 12.8(14), 13.4(17), 14.1(20), 16.5(10), 22.83(6), 23.23(6), 23.69(6), 28.16(7), 33.46(7).

A quenched $GaI_{1.2}$ sample showed no detectable solid solution effects in the GaI_2 pattern.

Results and Discussion

The phase diagram obtained for the system is shown in Fig. 1. The approximate eutectic temperatures shown are those at which the first premelting was observed. The diagram clearly shows the existence of the slightly stable compound GaI_2 (or Ga_2I_4), as well as the higher-melting GaI. The powder patterns for the three iodides also confirm their uniqueness (Fig. 2). Although these results allow no distinction to be made between the possible formulations for the structure of the gallium(II) iodide, this demonstration of the existence of the gallium(I) oxidation state among the halides gives some weight to the unsymmetrical arrangement Ga(I)[Ga(III)I_4].

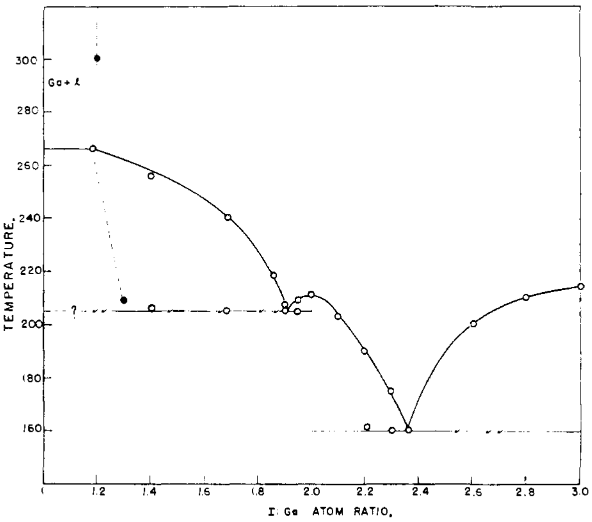

Fig. 1.—Phase diagram for gallium iodides.

The melting points of the pure Ga(III), Ga(II) and Ga(I) iodides are, respectively, 214 [literature 210°,[4] 213.5°[12]], 211 and 271° (extrapolated). The variation of the gallium(II) iodide melting point with temperature, as a result of disproportionation and the slowness with which equilibrium is attained in these moderately viscous melts, is particularly striking. The reported value is the true melting point, where the last crystals are in equilibrium with the liquid. Heating GaI_2 for a few hours at 250° caused the melting point to drop to 207°, while allowing the sample to stand for two weeks at room temperature results in a rise to 229°.

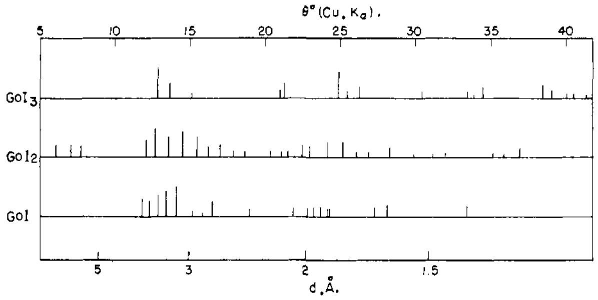

Fig. 2.—Powder pattern diffractions for gallium iodides.

The compositions obtained in the presence of excess gallium show the relative stability of the gallium(I) iodide with respect to the metal and higher iodide. As indicated on the diagram, this limiting value is $GaI_{1.19}$ at 267°, just above the melting point, and $GaI_{1.30}$ at 211° (eutectic 205°). The GaI in the mixture appears stable in the solid state with respect to disproportionation, as no gray color due to free metal has ever been observed. At 300 and 500° the compositions of the liquid in equilibrium with metal are $GaI_{1.20}$ and $GaI_{1.21}$, respectively. This constancy is somewhat surprising in view of the apparent degree of instability of the Ga(II) oxidation state at the melting point. The melting behavior may actually be misleading, with a small heat of reaction for the formation of GaI accounting for the observed liquid compositions. However, since $GaCl_2$ monomers are known to occur in the vapor state in equilibrium with liquid gallium(II) chloride,[7] the formation of appreciable amounts of a similar monomeric iodide in the liquid at the higher temperatures may be important.

We have recently noted that the gallium iodide phase diagram illustrated here bears considerable resemblance to that found for the indium iodide system by Thiel and Koelsch in 1910.[13] As might be expected, InI is more stable than the gallium analogue. However, the relative stabilities of the two diiodides, as judged from the shapes of the phase diagrams in that region, appear quite similar. Although a greater stability of InI_2 at lower temperature was recognized by Thiel and Koelsch, they did not indicate whether any tendency for slow equilibration in the melts might be responsible for their somewhat scattered freezing points.

Acknowledgment.—We are indebted to Mr. Wilford Hansen and Dr. Maurice Griffel for aid in the use of the electromagnet, and to Mr. Kenneth Herrmann and Dr. Adrian Daane for the use of the X-ray equipment.

AMES, IOWA

---

[12] W. C. Johnson and J. B. Parson, *J. Phys. Chem.*, **34**, 1210 (1930).

[13] A. Thiel and H. Koelsch, *Z. anorg. allgem. Chem.*, **66**, 288 (1910).