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STUDIES ON THE GALLIUM-IODINE  
AND SCANDIUM-IODINE SYSTEMS

BY

HSU-YUAN LI

A thesis submitted  
in partial fulfillment of the requirements for the  
degree Master of Science, Major in  
Chemistry, South Dakota  
State University

1969

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STUDIES ON THE GALLIUM-IODINE

AND SCANDIUM-IODINE SYSTEMS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

\_\_\_\_\_  
Thesis Adviser

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Date

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HYL

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## INTRODUCTION

The mass transfer from a hot zone to a cooler zone by means of a gaseous carrier has been observed to take place for many metals and compounds. Lee (19) studied the transport of many metals by their chloride and dissimilar gaseous chlorides. The subhalides, which form at higher temperatures, on cooling disproportionate to metal and normal halide. This technique has been applied to purify many metals and compounds for which a sublimation or distillation method is not practical due to the very high temperatures required. Aluminum has been purified using aluminum trichloride as a carrier (29). Pizzarello (25) has studied the epitaxial growth of GaAs in a system containing hydrogen and iodine gases.

The gallium-iodine system has been studied by several methods. Vapor pressure measurements show that ideal gas behavior of a GaI species exists above 650°C (30). Phase diagram studies (3,4) indicate the presence of GaI, GaI<sub>2</sub>, GaI<sub>3</sub>, Ga<sub>2</sub>I<sub>3</sub>, and dimeric iodides. Absorption spectroscopy was used by Richman (27). The stable species of gaseous iodides is dependent on the amount of the starting materials used in a system. The spectra of GaI species were observed at 3050 and 3900 Å, and those of GaI<sub>3</sub> species at 2450 and 2650 Å. The

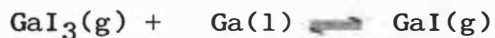
results of thermodynamic calculations made by Fergusson and Gabor (7) in the GaAs system are in agreement with experimental values.

Only a little work has been done on Sc-ScX<sub>3</sub> systems. The phase diagram of the Sc-ScCl<sub>3</sub> system has been studied (5,26), but the results are not consistent with each other. The Sc-ScI<sub>3</sub> system, in which the composition of ScI<sub>2.17</sub> melts at 892°C to give metal and the liquid of composition ScI<sub>2.26</sub>, also has been studied.

The relative stability of scandium dihalides with respect to metal and trihalides has been inferred from the calculated heats of reaction at 25°C. This shows that the dihalides, which are on the borderline of stability, should be obtainable (1).

In the present work, gallium and scandium iodides in the gaseous state were investigated using absorption spectroscopy. The reactions were carried out in evacuated quartz cells and heated in a nichrome wound furnace. The hypothesis was that the metals would react with iodine to form triiodides at low temperatures, followed by decomposition or reaction with excess metal to form lower oxidation states of the iodides at elevated temperatures. The lower iodides would disproportionate to metal and triiodide on cooling.

The heats of reaction, entropy changes, and free energy changes of the reaction



were calculated as a function of temperature.

The species in the solid state of the Sc-I<sub>2</sub> system were identified with x-ray powder patterns. From the x-ray results and the thermodynamic interpretations the possible reactions in the system were evaluated.

## HISTORICAL

## Gallium-iodine system

Several reports have described the reaction of aluminum and aluminum trihalides at high temperature to form aluminum monohalides which on cooling disproportionate to metallic aluminum and aluminum trihalides. In 1943, Klemm and Voss (15) reported that a black sublimate was formed when a mixture of aluminum and aluminum trifluoride was heated in vacuum at  $650 - 670^{\circ}\text{C}$ . The black sublimate was identified as metallic aluminum by x-ray diffraction. They also concluded that aluminum monofluoride exists in the gaseous state, which on cooling disproportionates to form aluminum and aluminum trifluoride.

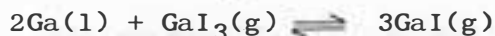
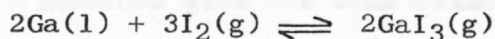
In 1950, Foster, Russell and Cochran (8) reported that aluminum trichloride reacts with metallic aluminum at high temperatures. Aluminum monochloride was found in the gaseous state at  $1000^{\circ}\text{C}$  by absorption spectroscopy. The intensity of the absorption lines increased with increasing temperature indicating that the concentration of the  $\text{AlCl}$  increases with temperature.

The equilibrium and rate of aluminum monochloride formation from aluminum trichloride and aluminum have been measured by determining the amount of aluminum transported by aluminum trichloride

in an alumina-lined quartz tube at about 1000°C (29). This method has been applied to extract or refine aluminum from aluminum-silicon, aluminum-iron and other aluminum alloys (10,21).

Corbett and McMullan (4) have studied the GaI<sub>3</sub>-GaI<sub>2</sub>-GaI system. The gallium iodides were prepared by reaction of the weighed elements in an evacuated tube at 350 to 500°C. A composition of GaI<sub>1.2</sub> was obtained by using an excess of gallium. After it was treated with benzene to extract the more soluble GaI<sub>2</sub>, a residue of GaI<sub>1.06</sub> was obtained. Pure GaI<sub>3</sub> and GaI<sub>2</sub> were also prepared from the intermediate mixtures by vacuum sublimation of GaI<sub>3</sub> from the non-volatile diiodide at 150°C. By the study of the phase diagram, gravimetric analyses, and the x-ray powder patterns, they confirmed the existence of gallium monoiodide and gallium diiodide. The diamagnetism of the diiodide was explained by the formulation [Ga(I)][Ga(III)I<sub>4</sub>]. Gallium diiodide was observed to disproportionate into gallium triiodide and gallium monoiodide, instead of trihalide and gallium metal which were observed with gallium dichloride (18). Some discrepancies were observed in the gallium-iodine system. The melting points of the samples were not congruent. Some premelting at temperatures several degrees below the melting point was observed. The melted compounds were all deep red to red brown, which on cooling turned to yellow crystals.

In 1962, Silvestri and Lyons (30) studied the vapor phase equilibria in the systems, GaAs-GaI<sub>x</sub>-As<sub>y</sub>, and GaI<sub>x</sub>-Ga, by means of pressure measurements. In the GaI<sub>x</sub>-Ga system, they found the pressures correspond to the reactions:



Gallium triiodide formed at about 80°C. Then it reacted with excess metal to form gallium monoiodide at temperatures in the range of 420 to 650°C. Above 650°C the temperature-pressure curves showed the ideal gas behavior for GaI species. On cooling gallium monoiodide disproportionated to gallium metal and gallium triiodide. This result conflicts with Corbett and McMullans' work which was discussed previously.

In the GaAs-I<sub>2</sub> system, gallium triiodide was formed at about 100°C, but at higher temperatures, 560 to 890°C, the reaction is:



The tetrameric arsenic also dissociates to dimeric molecules. In this experiment, both systems showed that GaI species is more stable at high temperature.

Fergusson and Gabor (7) studied the transport of gallium arsenide by iodine or chlorine gas in the presence of hydrogen

between 500 and 1000°C. Gallium arsenide at the hotter end of the tube was transported to the cooler end. The possible species involved were GaAs(s), Ga(l), GaI<sub>3</sub>(g), GaI(g), HI(g), H<sub>2</sub>(g), As<sub>4</sub>(g) and As<sub>2</sub>(g). The reactions predicted to describe the equilibria between the species involved give the same result reported by Silvestri and Lyons (30).

The systems of GaAs(excess)-I<sub>2</sub>, Ga(excess)-I<sub>2</sub>, and GaI<sub>2</sub>(excess) in the gaseous state were studied spectroscopically by Richman in 1963 (27). The investigation covered the spectral region from 2500 to 12000 Å. In the Ga-I<sub>2</sub>(excess) system, the stable compound is gallium triiodide. Absorption bands at 2450 and 2650 Å were obtained above 135°C, with the intensity increasing with increasing temperature. Also two other bands at 3050 and 3900 Å appeared after the iodine disappeared at high temperature. In the Ga(excess)-I<sub>2</sub> system, both GaI<sub>3</sub> and GaI species are stable in the gaseous state, but the intensity of the two bands of gallium monoiodide at 3050 and 3900 Å increases with increasing temperature. In the GaAs(excess)-I<sub>2</sub> system, the spectra of gallium triiodide, gallium monoiodide and arsenic are all present. These results again are in agreement with those of Silvestri and Lyons, and Fergusson and Gabor.

Recently the molecular species in the vapor phase of the GaAs-I<sub>2</sub> system at 400°C were investigated using electron diffraction (34). The results showed that gallium triiodide was the predominant species at this stage, while the product, As<sub>4</sub>, remained mainly in the solid state and did not affect the diffraction pattern.

The phase diagram of the Ga-I<sub>2</sub> system was re-examined by Chadwick, Atkinson and Huckstepp in 1966 (3). The samples for investigation were prepared in vacuum from the elements at 320 to 350°C. The existence of the compounds Ga<sub>2</sub>I<sub>3</sub> and Ga<sub>3</sub>I<sub>5</sub>, which are diamagnetic, was confirmed. The structures suggested are [Ga(I)]<sub>3</sub>[Ga(III)I<sub>6</sub>] and [Ga(I)]<sub>2</sub>[Ga(III)I<sub>5</sub>] respectively. The compound, Ga<sub>2</sub>I<sub>3</sub>, which has an orthorhombic unit cell, was interpreted from x-ray powder patterns. Even so, the conclusion is doubtful since the samples in the phase range GaI<sub>1-2</sub> were intensely colored which made the freezing point measurements difficult. For example, the freezing point of one of the samples (Ga:I = 1:1.65) was entirely random between 212 to 230°C. The accumulated data were not complete enough to clearly demonstrate the presence of the Ga<sub>2</sub>I<sub>3</sub> and Ga<sub>3</sub>I<sub>5</sub> species.



## Scandium-iodine system

Not much work has been done in studying the lower oxidation states of scandium halides. A few reports have recently appeared in this field, but no consistent results have been presented.

In 1963, the existence of scandium dichloride was first reported by the studies of the fusion diagram and the isotherm of the vapor pressure of Sc-ScCl<sub>3</sub> system at 960°C, in a molybdenum coated quartz ampoule (26). The result showed that ScCl<sub>2</sub> and 2ScCl<sub>3</sub>·ScCl<sub>2</sub> were present. The observed ScCl<sub>2</sub> melted incongruently at 878°C, and 2ScCl<sub>3</sub>·ScCl<sub>2</sub> melted with decomposition at 855°C. The observed eutectic point at 805°C had a composition 29 mole per cent of scandium in liquid trichloride.

The above results were not confirmed by Corbett and Ramsey in 1965 (5). The phase diagram of the same system was studied in a tantalum tube. The scandium metal and scandium trichloride used were purified by sublimation. The equilibrium diagram showed that the composition ScCl<sub>2.45</sub> had the eutectic point at 803°C, and scandium had the solubility of 22.2 mole per cent in scandium trichloride at 960°C. They pointed out that the error in the previous work might be accounted for by an impurity in the unsublimed trichloride and by the failure of the molybdenum coating which loosened on cooling.

In 1968, McCollum and Corbett (20) reported the synthesis of reduced scandium chloride, bromide, and iodide by the study of the phase diagram of the  $\text{ScX}_3\text{-Sc}$  systems. But none of the simple dihalide stoichiometries were obtained. The experiments were carried out in a sealed tantalum container. The observed  $\text{ScI}_{2.17\pm 0.01}$  species melts incongruently at  $892^\circ\text{C}$  to give metal and the liquid of composition  $\text{ScI}_{2.26}$ . In  $\text{ScBr}_3\text{-Sc}$  system, an eutectic near  $816^\circ\text{C}$  and the liquid of composition  $\text{ScBr}_{2.40}$  were found. Also the solid compound  $\text{ScBr}_{1.50\pm 0.01}$  was found to be in equilibrium with metal and the liquid  $\text{ScBr}_{2.30}$  at the peritectic point  $880^\circ\text{C}$ . In the chloride system, the compound  $\text{ScCl}_{1.5}$  was found to be in equilibrium with metal and the salt at  $850^\circ\text{C}$ .

From a study of the x-ray powder patterns (22), a rhombohedral unit cell is suggested for scandium triiodide. The anhydrous sample was made by reaction of excess scandium powder with iodine in an evacuated quartz ampoule at  $600^\circ\text{C}$ . The product was yellow and exceedingly hygroscopic.

The theoretical treatment of the relative stabilities of the mono-, di-, and trihalides of the first transition elements of the periodic table, was reported by Barber, Linnett and Taylor (1). The relative stabilities were interpreted from the calculated heats of reaction at room temperature. They found that the expected

behavior of the compounds agreed well with those which are known.

The heats of formation,  $\Delta H_f^0$ , at room temperature, are calculated using the Born-Haber cycle. The general formula is

$$\Delta H_f^0 = \Sigma I + L - n(A - \frac{1}{2}D) - U$$

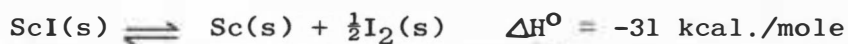
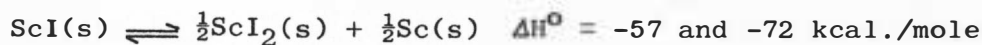
where  $\Sigma I$  is the sum of the ionization potentials of the metals,  $L$  is the latent heat of vaporization of the metal at room temperature,  $A$  is the electron affinity,  $D$  is the dissociation energy of the diatomic molecule,  $n$  is the number of halogen atoms in a compound, and  $U$  is the lattice energy which is calculated from Kapustinskii's simple formula (13)

$$U = 256.1(\Sigma n)Z_+Z_-/(r_+ + r_-)$$

where  $n$  is the number of ions in a molecule,  $Z_+$  and  $Z_-$  are the ionic charges, and  $r_+$  and  $r_-$  are the ionic radii. The values used for the radii of the scandium ions were  $\text{Sc}^+$ : 1.06 Å,  $\text{Sc}^{++}$ : 0.82 Å and 1.00 Å,  $\text{Sc}^{+++}$ : 0.81 Å. Since the radius of the  $\text{Sc}^{++}$  is not known, the two extreme values were used. The radius of iodide ion is 2.16 Å.

The calculated heats of formation of scandium iodides are  $\text{ScI}$ : +31,  $\text{ScI}_2$ : -52 and -81, and  $\text{ScI}_3$ : -84 kilocalories per mole. Therefore it was predicted from the calculated heat of reaction

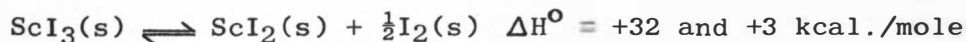
that the scandium monoiodide should be unstable relative to scandium diiodide and scandium metal, and also unstable with respect to decomposition to metal and iodine, i.e.,



Scandium diiodide should be just stable relative to scandium metal and scandium triiodide, i.e.,

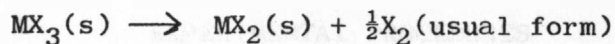


Scandium triiodide was predicted to be stable with respect to scandium diiodide and iodine, i.e.,



This agrees with the observed behavior of scandium triiodide. So they suggested that it might be possible to make scandium diiodide as well as scandium dibromide.

Also in 1966, the thermal stabilities of the trihalides of the metals of the first transition series at 25°C were interpreted by Nelson and Sharpe (23). The heats of reaction of the decompositions of trihalides:



were calculated from Hess's law by the equation:

$$\Delta H^\circ = -U_3 - I_3 + U_2 - A$$

where  $U_3$  and  $U_2$  are the lattice energies of  $\text{MX}_3$  and  $\text{MX}_2$ , and  $I_3$  and  $A$  are the third ionization potential of the metal and the electron affinity of halogen respectively. The results show that the feasibility of the above decompositions increases across the series. A value of  $46 \pm 5$  kcal. per mole was used as the standard heat of reaction for scandium iodides. Also the standard entropy and the standard free energy changes of  $3 \pm 7$  e.u. and  $45 \pm 7$  kcal. per mole were calculated respectively. The positive quantity of free energy change indicates that scandium triiodide does not decompose at  $25^\circ\text{C}$ .

## EXPERIMENTAL PROCEDURES

The purpose of this work was to investigate the presence of lower oxidation states of gallium and scandium halides using spectroscopic methods. For experimental convenience, the vapor phase of the gallium-iodide and scandium-iodine systems were chosen for this work. It was postulated that the metals would react with iodine to form triiodides at low temperatures followed by decomposition or by reaction with excess metal to a lower oxidation state at elevated temperatures. Since the temperatures were not to be very high, emission lines should not be excited. Therefore absorption techniques were used in these experiments. The reactions were carried out in evacuated quartz cells.

## Vacuum system

The arrangement of the vacuum system is shown in Figure 1. The system was evacuated using a Kinney Model KC-2 High Vacuum Pump, and a NRC Type 0149 Vacuum Diffusion Pump. The pressures were measured with a NRC Type 721 thermocouple gauge in the pressure range from 1 to  $10^{-6}$  atmosphere, and a NRC Type 724 cold cathode ionization gauge in the pressure range from  $4 \times 10^{-3}$  to  $2 \times 10^{-7}$  torr. Iodine crystals were contained in a modified 50-ml. Pyrex round-bottom flask which was connected to the vacuum system with a stopcock.

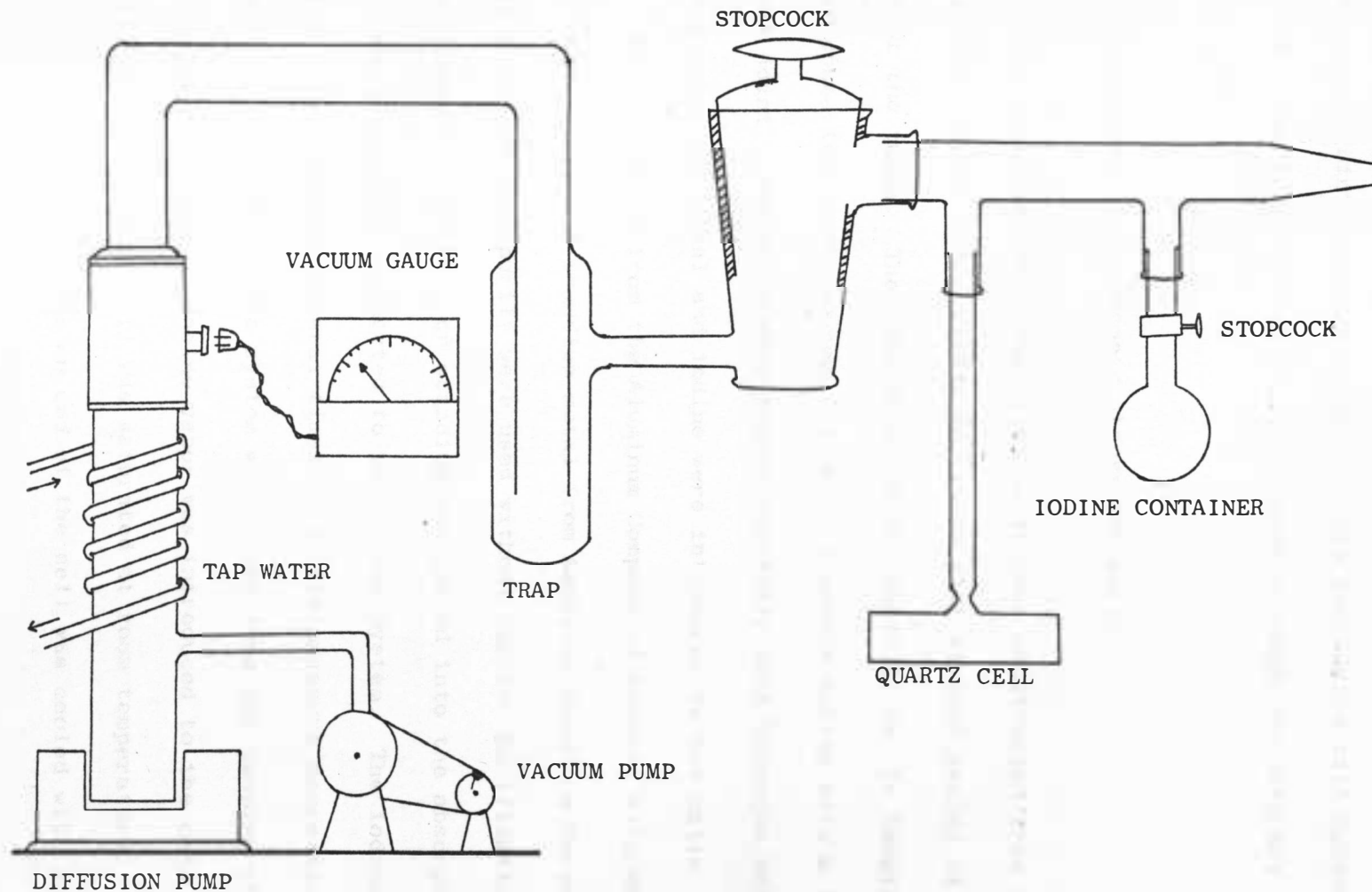


Figure 1. Vacuum System

The ground joints and the stopcocks were lubricated with Apiezon H grease. The trap was cooled with liquid nitrogen or with dry ice in acetone.

#### Preparation of spectroscopic absorption cells

The spectroscopic absorption cells were constructed from 20-mm. diameter quartz tubing with 2 mm. thick flat windows sealed at each end of the tubes. The absorption cells, about 13 cm. in length, were connected to the vacuum system by a quartz tubing with a 10/30 Vycor joint. The cells were sealed carefully with hydrogen and oxygen torch after the metal and iodine were introduced to the cells.

Gallium metal from the Aluminum Company of America with 99.99 per cent purity and scandium metal from American Scandium Corporation with 99.9 per cent purity were used without further purification. A small amount of gallium or scandium was placed into the absorption cell which was then connected to the vacuum system. The iodine container was evacuated several times until the pressure decreased to about  $1 \times 10^{-6}$  torr. The system was closed from the pumping stage by use of a stopcock. Iodine vapor was introduced to the cell by sublimation until the cell was saturated at room temperature. If more iodine was required, an end of the cell was cooled with ice.



## Spectrographic system

The spectra were obtained using a Bausch and Lomb Model 11 grating spectrograph and light source. The arrangement of the equipment is shown in Figure 2. This instrument is a 1.5 meter stigmatic grating spectrograph which covers a spectrum range of 3700 to 7400 Å in the first order and 1850 to 3700 Å in the second order. The dispersions approximate 15 and 7.5 Å per millimeter in the first and second orders respectively. Due to film shrinkage the measured dispersions were 14.8 and 7.4 Å per millimeter respectively.

The film holder takes 25 cm. of 35-mm. film. The exposures were made using Kodak High Speed Infrared film in the visible and infrared regions, and Kodak Spectrum Analysis No. 3 film in the ultraviolet region. Also Du Pont SR 106 film was used for the visible region. Films were developed in D-19 developer for 3 minutes and fixed in F-5 fixing bath for 10 minutes (14).

A G.E. reflector type photoflood lamp was used as the light source of the visible and infrared regions, and a high pressure hydrogen discharge lamp for the ultraviolet region. This hydrogen lamp, which is the light source for the Beckman Model DU spectrophotometer, has a continuous emission spectrum from 1850 to 3750 Å. Low pressure mercury spectra were taken as the reference lines.

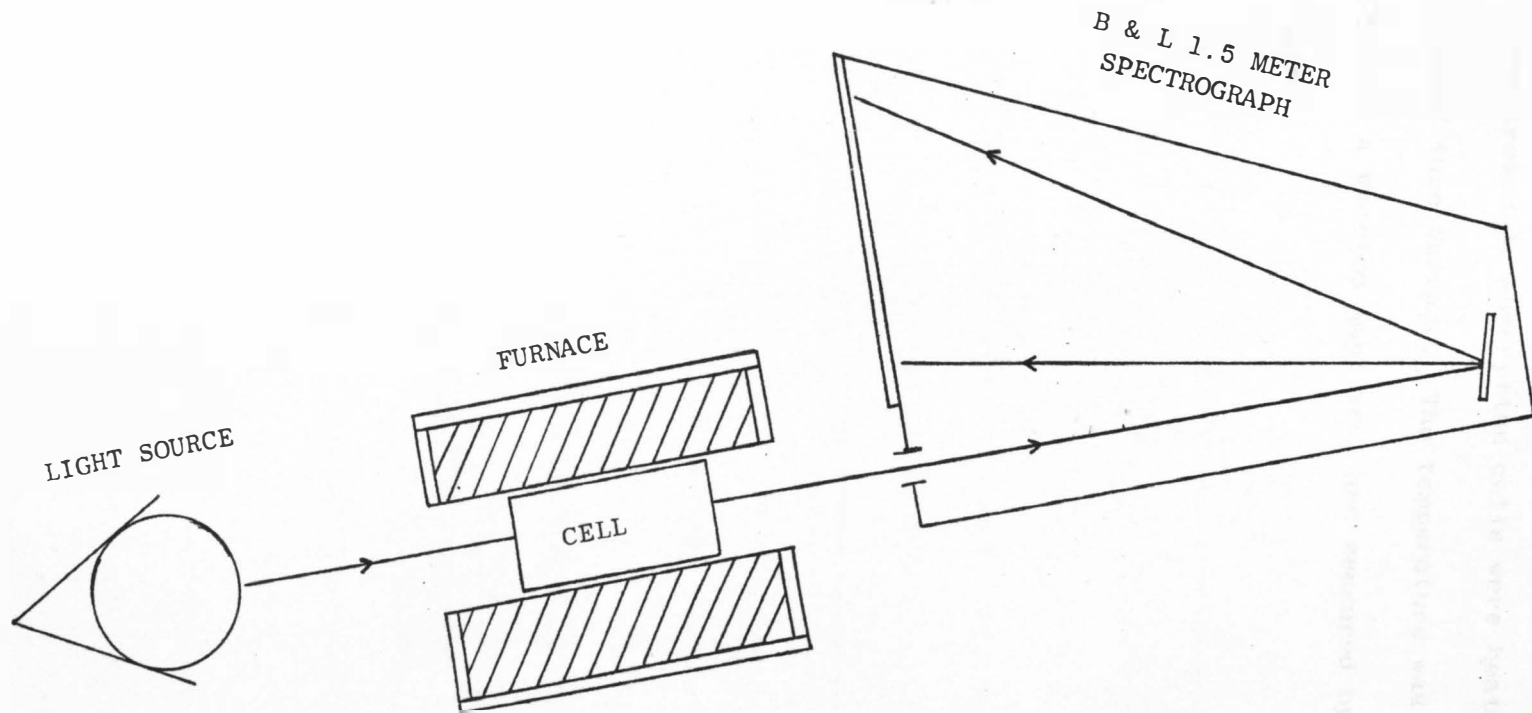


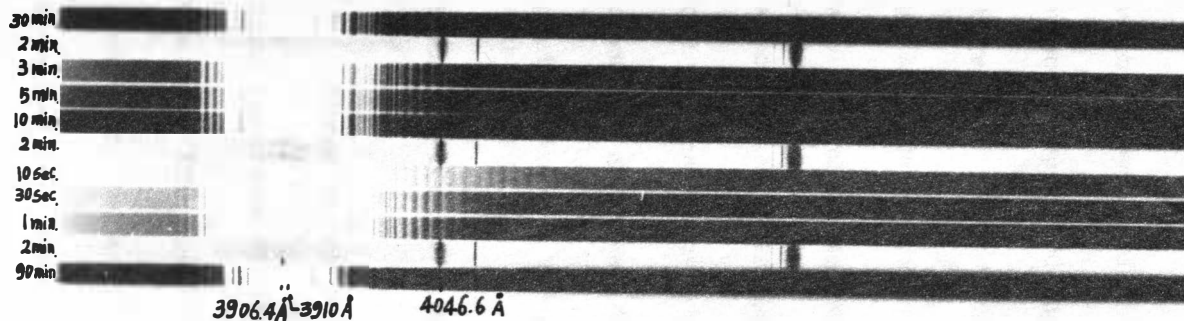
Figure 2. Spectrographic System

The spectroscopic absorption cells were heated in an one-inch nichrome-wound tube furnace. The temperature was controlled automatically with a Wheelco Amplitrol and measured by a chromel-alumel thermocouple.

## RESULTS

## Gallium-iodine system

In this experiment the quartz cell contained only iodine vapor and excess gallium metal. The spectra of the species in the gaseous state were detected at one hundred degree intervals from room temperature to 1000°C. No spectra were obtained under 200°C. The spectrum of iodine was not observed due to its low concentration. A few absorption bands which extended from 3850 to 3940 Å were observed at 300°C. The strongest absorption band appeared at 3910 Å. With increasing temperature the absorption bands extended toward the longer wavelengths, and also slightly toward the short wavelength side. The shortest absorption band appeared at 3790 Å at 500°C and above. Also the intensity increased and the band broadened as the temperature increased. At 1000°C, the bands extended from 3790 to 4220 Å, and overlapped to give a broad absorption from 3870 through 3960 Å. The spectra at 500 and 700°C at various exposure times are shown in Figure 3. The strongest band at 3910 Å corresponds to the band reported at 3900 Å by Richman (27) in the absorption spectra of GaI. This is taken as proof of the formation of GaI species in this system. The emission lines in Figure 3, are those of mercury spectra used as reference lines.

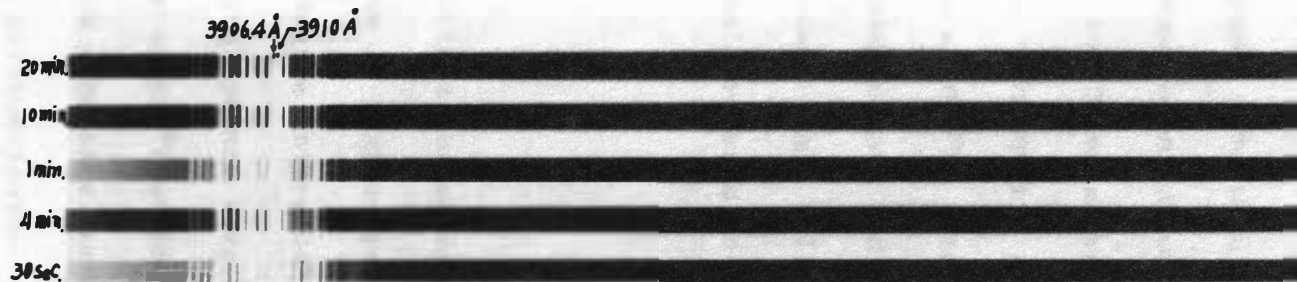


A

Figure 3. Absorption Spectrum of GaI vapor; A. at 700°C. B. at 500°C.

The strongest band at 3910 Å. Emission lines are Hg spectra using as reference.

B



The following characteristics were observed during the reaction. Both windows were coated by a dark red liquid and gallium metal when the cell was heated at 300 and 400°C. The dark red compound was removed by heating the windows with a Bunsen burner. The metal was removed by swirling the cell so the gallium particles could combine together. The dark red compound disappeared at 500°C and above but gallium metal deposited on the windows as before. The quartz cell was corroded and became foggy when it was heated at 900°C. The species was colorless in the gaseous state, turned to dark red liquid as the temperature decreased, and finally became lemon yellow crystals at lower temperatures. The reaction was performed repeatedly using the same cell.

#### Scandium-iodine system

Three types of reaction were performed to detect the absorption spectrum of the species in the gaseous state at high temperatures. The spectra were taken at one hundred degree intervals from room temperature to 500°C, but no interesting spectra were obtained. A black deposit formed on the windows at 600°C which could not be removed by heating. After the black substance formed in this system, the reverse changes seen in the gallium-iodine system could not be accomplished.

### Type A system

Two quartz cells which contained iodine vapor and excess scandium metal, were subjected to the same procedures. The same results were observed. No reaction occurred under 200°C since the metallic lustre of scandium metal and violet iodine vapor remained unchanged. After the cells were heated at 300°C for 12 hours, scandium metal was coated with a layer of black substance. Also the iodine vapor disappeared. No other changes were observed after heating at 400 and 500°C for 18 hours. The cells were coated with a thin layer of black substance after they were heated at 600°C. One of the cells was heated up to 800°C, but no further changes were observed.

### Type B system

A reaction tube 47 cm. in length was constructed. A small amount of iodine crystals and a piece of scandium metal were placed in the tube. Both ends of the tube extended about 7 cm. out of the furnace. The purpose of this experiment was to determine whether the black substance which formed in the type A system would deposit on the quartz wall and not block the windows. The tube was heated at 400°C for 16 hours; no spectrum except that of iodine was obtained. It was then heated at 500°C for 10 hours.

Yellow crystals, probably scandium triiodide, deposited at both sides of the tube, which were about 350°C. It was heated at 550, 600 and 700°C for 10, 24 and 8 hours respectively, but no further change was observed. The yellow crystals turned to pale yellow at room temperature. No black substance was formed on the quartz wall, which was different from the type A system.

#### Type C system

Since no spectrum other than iodine was found in the previous types of reactions, a third system type was used in an attempt to increase the concentration of the product in the cell and possibly obtain the spectrum before the windows were blocked. An iodine container and the spectroscopic cell (11 cm. in length) were connected by a stopcock so that the amount of iodine required could be adjusted while the cell was heated to 550°C. Any required amount of product could be made. The cell, which had an amount of yellow crystals, was sealed after 24 hours of heating. The observations were made at the temperature of 360, 400, 500, 550, and 600°C, but no spectrum was found. When the cell was heated at 400°C and above, the yellow crystals evaporated and deposited on the windows, which could be removed by heating the windows with a Bunsen burner. The



black substance formed again after the tube was heated at 600°C. Also some yellow crystals remained.

### Analyses

The products of the scandium-iodine system were treated with 52 per cent of hydrofluoric acid and with dilute hydrochloric and nitric acids to evolve a gas. The black substance disappeared slowly and a brown residue was obtained after the material was placed in acids for about a week. It was noticed that the brown residue was not the product from the reaction with acids. The brown substance dissolved in hydrofluoric acid in ten days. The brown substance dissolved readily in warm sodium hydroxide and in a mixture of nitric and hydrofluoric acids, and it did not react with hydrochloric, nitric or sulfuric acids nor did it dissolve in many organic solvents: carbon tetrachloride, carbon disulfide, ethyl alcohol, diethyl ether, and toluene.

The brown substance was also heated but it did not melt or decompose up to 300°C.

X-Ray powder diffraction patterns were taken with the G. E. XRD-1, x-ray spectrograph by Dr. E. H. Shaw, Jr., University of South Dakota. The camera has a diameter of 143.2 mm. Kodak No-Screen Medical X-Ray Film was used (16). The powder patterns were

obtained with  $\text{CuK}\alpha$  radiation at 28.5 kilovolts and 15 milliamperes. The samples were sealed in glass capillaries. The black and the brown samples were exposed for 17 and 16 hours respectively. The diagrams were measured in this laboratory with a comparator with an accuracy of 0.05 mm. The powder diagrams of the black and brown samples are shown in Figure 4. The numbers refer to the line number in Table 1.

The x-ray powder pattern shows that the black substance obtained from the type A system is a mixture of scandium oxide and an unknown substance. The x-ray pattern of scandium oxide (32) is compared with the observed pattern in Table 1. The intensities of the experimental lines are classified visually into six scales, with 1 being the most intense value. After the mixture was treated with 6 N HCl for 8 days, a brown residue was obtained which was washed with water and ethyl alcohol, and dried at  $120^{\circ}\text{C}$  for 10 hours. From the x-ray powder pattern, it was confirmed that the brown substance is a mixture of silicon and an unknown material. The x-ray pattern of silicon (33) and the observed patterns are given in Table 1.

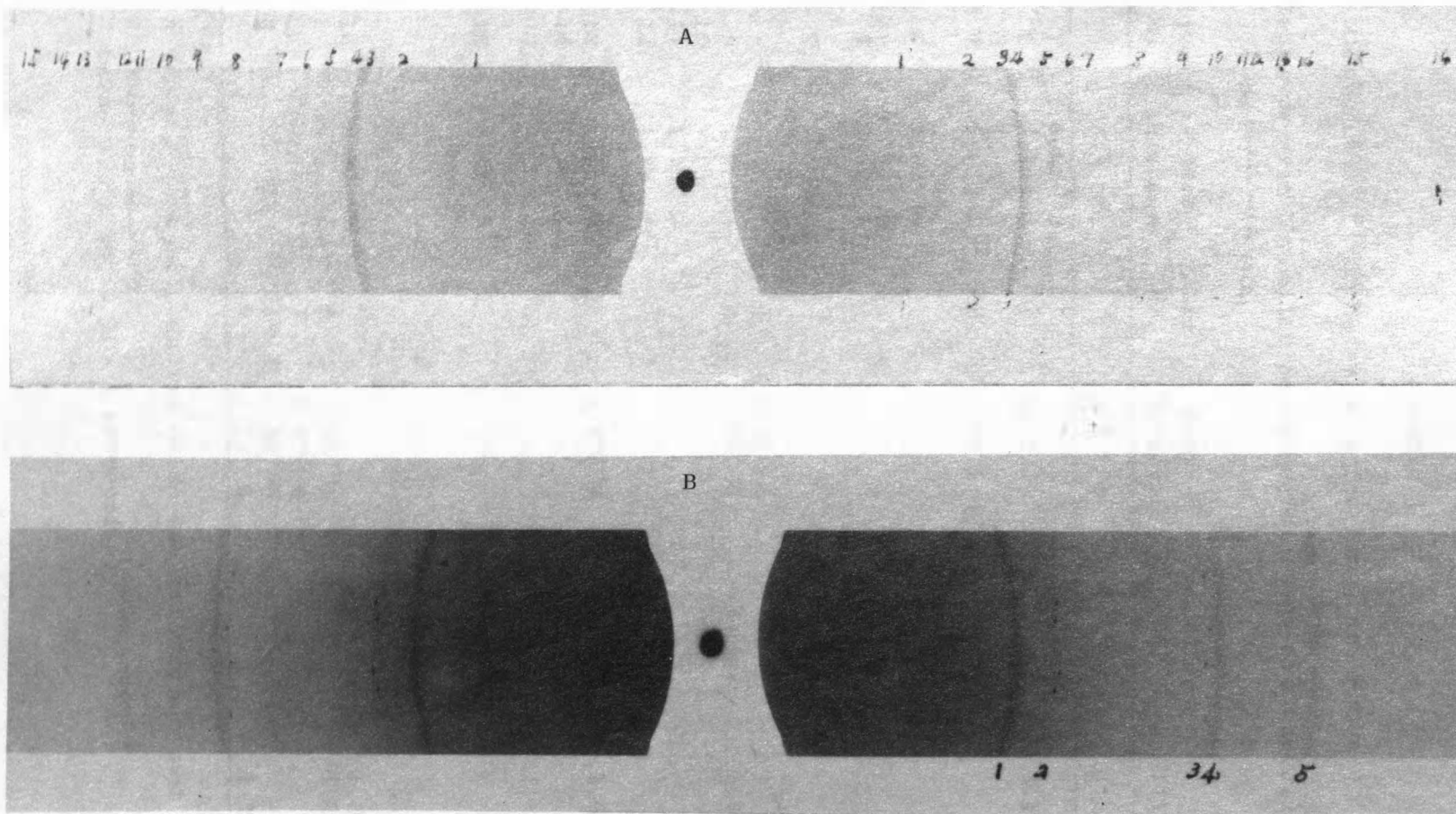


Figure 4. X-ray Powder Patterns;  $\text{CuK}\alpha$  Radiation. A. Black Sample, B. Brown Sample. The numbers refer to the line number in Table 1.

Table 1

Comparison of the X-Ray Data for Black and Brown

Residues with Those for Scandium Oxide and Silicon(33).

Line No.	Black Residue		Line No.	Brown Residue		Scandium Oxide*		Silicon*	
	d Å	I		d Å	I	d Å	I/I <sup>o</sup>	d Å	I/I <sup>o</sup>
1	4.02	3				4.021	30		
2	3.12	5	1	3.12	1			3.138	100
3	2.85	1				2.841	100		
4	2.80	6	2	2.79	6				
						2.631	4		
5	2.59	3							
6	2.46	4				2.461	15		
7	2.32	6				2.321	8		
						2.202	3		
8	2.08	3				2.099	26		
						2.009	4		
			3	1.95	6				
9	1.92	4	4	1.91	2	1.930	20	1.920	60
10	1.82	5				1.798	9		
11	1.74	2				1.741	78		
12	1.72	6							
						1.689	5		
13	1.64	6	5	1.63	3	1.641	2	1.638	35
14	1.58	6				1.597	10		
						1.557	4		
						1.519	9		
15	1.48	3				1.484	33		
						1.452	12		
						1.421	4		
						1.392	4		
						1.365	3		
16	1.33	6				1.340	8	1.357	8
			6	1.25	5			1.246	13
			7	1.23	4				
			8	1.16	5				
			9	1.11	5			1.108	17

\* The d values of scandium oxide and silicon are not shown

below 1.340 and 1.108 Å respectively.

## DISCUSSION AND CONCLUSION

## Gallium-Iodine System

The thermal disproportionation of gallium iodides at high temperatures has been studied by the phase diagrams, vapor pressure measurements, thermodynamic calculations and spectroscopic determinations. After a considerable number of investigations, certain results are in agreement with one another.

## Spectroscopic studies

GaI in the gaseous state was directly proved with absorption spectroscopy by Richman (27). From the absorption intensity he found that either decreasing iodine concentration or increasing temperature of the system favored the GaI species. Also  $\text{GaI}_3$  species was stable if the system contained excess iodine. Two bands of gallium monoiodide at 3050 and 3900 Å were obtained.

In the present work, a strong absorption band of gallium monoiodide at 3910 Å was obtained, which appeared starting at 300°C. Plates A and B of Figure 3 show the spectra of the gaseous species obtained by heating gallium iodides in the presence of metallic gallium at 700 and 500°C. An increase in gallium monoiodide concentration resulting from increasing temperature is apparent by

comparing Plate A with Plate B of Figure 3, in that the number and intensity of GaI bands increase with increasing temperature. Since a limited amount of iodine vapor was introduced to the cell, only a limited amount of triiodide could form at lower temperature. Thus the monoiodide concentration could only increase by a decrease in the triiodide concentration at elevated temperatures.

It is concluded from the phase diagram studies of the Ga-I<sub>2</sub> system (3,4) that the pure compounds cannot be readily obtained by melting or freezing point measurements because of peritectic decomposition or incongruent melting.

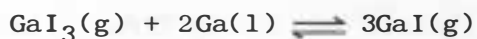
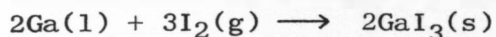
In the present work, the dark red liquid observed at 300 and 400°C, is probably due to the presence of a small amount of free iodine (3,4,12). The vapor is colorless, since the observed spectra around 3900 Å are in the near-ultraviolet region.

The deposition of metallic gallium on the quartz windows occurred either by evaporation or disproportionation of gallium monoiodide to the triiodide and gallium metal when the vapors came in contact with the cooler windows. Since gallium has a very low vapor pressure at the experimental temperatures, the disproportionation is the only process that can account for the above result.

Some previous works show that gallium tri-, di-, and monoiodides are all yellow crystalline compounds (2,3,4) with the triiodide the

most stable species at room temperature. Corbett and McMullan pointed out that gallium monoiodide might be relatively stable with respect to the metal and the higher iodides in the presence of excess gallium metal. Therefore, the yellow crystalline material observed at lower temperatures in this work may be a mixture of the iodides with the triiodide species predominating.

From the spectroscopic results and the observations of the reactions at various temperatures, it is concluded that gallium metal first reacts with iodine to form gallium triiodide at about 100°C. This is followed by a reaction with excess gallium metal to form gallium monoiodide at 300°C. More monoiodide species forms in the vapor phase at higher temperatures which shows the monoiodide is more stable than triiodide as temperature increases. But on cooling gallium monoiodide disproportionates to metal and triiodide. The reactions are

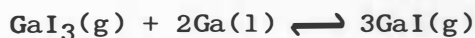


Also not to be overlooked in liquid state is the presence of species more complicated than GaI and GaI<sub>3</sub>. These include the dimeric iodides, Ga<sub>2</sub>I<sub>4</sub> and Ga<sub>2</sub>I<sub>6</sub> (6) which have the formulation [Ga(I)] [Ga(I)I<sub>4</sub>]

$[\text{Ga(I)}] [\text{Ga(III)}\text{I}_6]$  respectively. Since most of the inorganic compounds in which the same metal is present in two different oxidation states are usually intensely colored (9), the observed dark red color of the liquid substance may also account for the presence of the above dimeric species.

#### Thermodynamic calculations

From vapor pressure measurements, Silvestri and Lyons (30) concluded that GaI is a predominant species above 650°C. The equilibrium constant for the reaction:



is given as

$$\ln K_p = -\frac{25300}{T} + 28.5$$

The heats of formation and entropy changes of the species involved in the reaction as a function of temperature are listed as

Species	$\Delta H_f^\circ$ (cal./mole)	$S^\circ$ (e. u./mole)
GaI <sub>3</sub> (g)	20.0T - 34100	19.50 ln T - 22.6
GaI(g)	8.9T + 7800	8.94 ln T + 10.0
Ga(l)	6.65T - 650	6.65 ln T - 23.8



These are given by Fergusson and Gabor (7), except that of gallium at liquid state. The enthalpy and entropy of gallium metal are obtained from data given by Stull and Sinke (31), and Kelley (14). The entropy of gallium in the liquid state at 298°K, 14.2 e. u., is estimated as the sum of the entropy of the solid state at 298°K (9.8 e.u.), and the entropy of fusion at 303°K (4.4 e.u.). The very small entropy change from 298 to 303°K is ignored. The entropy of gallium in the liquid state as a function of temperature is then calculated to be:

$$S_T^O = 6.65 \ln T - 23.8$$

The heat of reaction and the free energy changes of the above reaction are calculated from the above data to be:

$$\Delta H_T^O = -6.6T + 58800$$

$$\Delta G_T^O = 5.98T \ln T - 106.8T + 58800$$

The calculated values of enthalpy and free changes at 1000° K agree with those of Fergusson and Gabor (7).

## Scandium-Iodine System

As described before, very little work has been done in the study of scandium-halogen systems in an attempt to find the lower oxidation states of scandium halides. Only in the phase diagram has this system been studied. The observed results are not consistent with each other. Due to the discrepancies in the phase diagram in scandium-scandium halide systems, a spectroscopic investigation of the vapor species in the scandium-iodine system was attempted. Unfortunately, no absorption spectra were obtained since the windows were blocked by a deposited black substance. Although it was not possible to directly observe the species in the vapor phase, some information can be inferred from the identification of the solid products. The possible reactions may be predicted from the study of x-ray powder patterns and thermodynamic calculations.

### Species present

In the type A system, iodine vapor reacted with scandium at 300°C to form a dark layer on the surface of the metal. A black substance formed on the quartz wall at 600°C. Several reactions might possibly account for the observed products.

The possibility of a reaction between scandium and quartz or between iodine and quartz was investigated using two other reaction

cells. One of the cells contained only iodine and the other contained scandium. Both cells were sealed at a pressure of  $4 \times 10^{-6}$  torr. The cell containing scandium was heated at 600 and 700°C for 23 and 7 hours respectively. The surface of the metal turned slightly grey after it was heated. From this result it is concluded that scandium does not react with quartz at the above temperatures to give the black substance found in the scandium-iodine system. The cell containing iodine was heated at 200, 300, 400, 500, 600, and 700°C for 7, 5, 12, 5, 12, and 4 hours respectively. The violet color of iodine vapor turned lighter as the temperature increased, and finally turned almost colorless at 700°C. The violet vapor appeared again as the cell cooled. From these observations, it is concluded that a reaction does not occur between iodine and quartz to give the black substance at the above temperatures. The iodine absorption spectrum was obtained at all temperatures except 700°C. The intensity decreased with increasing temperature due to the dissociation of the iodine molecule into atomic iodine. A continuous absorption spectrum was found near 5000 Å (24).

Since neither iodine nor scandium reacted with quartz up to 700°C, apparently the reaction in this system might occur between the iodide and quartz. The observed dark coating at 300°C might be a thin film of scandium triiodide.

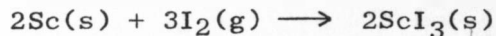
In the type B system the sublimate was a yellow crystalline material which deposited at the cooler ends at about 350°C. This yellow material might be scandium triiodide which has been prepared using this technique. The crystals are a pale yellow at room temperature. These become more intensely yellow at elevated temperatures. This might result from the greater polarizability of iodide ions since intense color occurs when an electron is transferred from iodide ion to the metal ion (9). Since no black material formed on the cell in this system, the triiodide does not react with quartz at the temperatures below 350°C.

In the type C system the results were similar to that of type A system, a black material deposited on the cell while the cell was heating at 600°C. Two reactions might account for the observed products — scandium triiodide reacting directly with quartz or scandium triiodide reacting with excess scandium metal forming an intermediate which then reacts with quartz. The former reaction is not consistent with the formation of silicon which was found in the black deposit. Thus the reaction took place through the latter route.

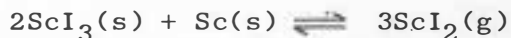
The x-ray powder patterns show that the black substance is a mixture of scandium oxide, silicon, and some other material. The brown residue is a mixture of silicon and the unknown impurity. A

comparison of the d values of black and brown samples in Table 1 shows that scandium oxide disappears when the black product is treated with acid. Except for a fairly strong line (2.59 Å) in the black sample, the remaining lines appear in the brown sample. This indicates that the brown residue is a part of the black product, not the product of a reaction with acid. The line at 2.59 Å and a few lines in the brown residue were not identified. These may represent a trace of a complex silicate.

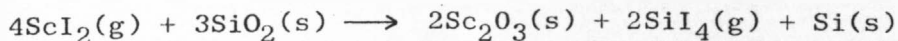
From the above observations, it is concluded that scandium metal reacts with iodine to form scandium triiodide at about 300°C,



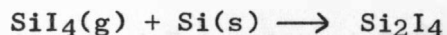
Scandium triiodide then reacts with excess scandium metal at 600°C forming an iodide of a lower oxidation state,



The dihalide is postulated from the thermodynamic calculations discussed later. Scandium diiodide then reacts with quartz to form the black product at 600°C.



The brown residue is not  $\text{SiI}_4$  or  $\text{Si}_2\text{I}_6$  since it does not melt or decompose up to  $300^\circ\text{C}$ , nor does it dissolve in carbon disulfide. The few residual lines might be due to a trace of a complex silicate or  $\text{Si}_2\text{I}_4$  formed as a result of the reaction (28),



Some amorphous iodides,  $(\text{SiI}_2)_x$  and  $(\text{SiI})_x$  might be present also (11), but no attempt was made to identify them.

#### Thermodynamic calculations

Since the lower oxidation states of scandium halides are not well known, the thermodynamic data for these species are not known. Thus the direct comparison of theoretical results with experimental is not possible. But both previous thermodynamic calculations for the halides of the first row transition elements of the periodic table correspond well with those for known compounds (1,23). This leads to confidence in the calculations and the postulated reactions. The calculation procedures are the same as those described previously for the Ga-I<sub>2</sub> system. The thermodynamic data are calculated for  $25^\circ\text{C}$ . The standard heats of formation and standard entropies of iodides at  $25^\circ\text{C}$  based on Barber, Linnett and Taylor (BLT) (1),

and Nelson and Sharpe (NS) (23) are listed in Table 2, while the other species are from Kubaschewski, Evans and Alcock (17).

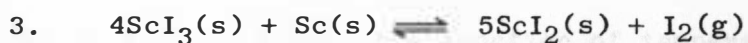
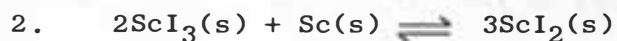
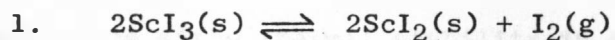
Table 2

The Standard Heats of Formation and  
Standard Entropies at 25°C

Species	BLT	NS	NS
	$\Delta H_f^\circ$ (kcal./mole)	$\Delta H_f^\circ$ (kcal./mole)	$S^\circ$ (e.u.)
ScI <sub>3</sub> (s)	-84	-125±3	46±5
ScI <sub>2</sub> (s)	-52, -81	-79±3	35±5
ScI(s)	+31	-	-
Sc(s)	0	0	8.2
I <sub>2</sub> (g)	+14.9	+14.9	62.3
I <sub>2</sub> (s)	0	0	27.9

Since scandium monoiodide has been shown to be relatively unstable with respect to diiodide and triiodide (1), only scandium diiodide is considered in the following study.

Scandium diiodide is possibly formed from triiodide by one of the following reactions:



The heats of reaction and free energy changes of the above reactions at 25°C calculated from the data in Table 2 are listed in Table 3.

Table 3

The Heats of Reaction, Entropy Changes,  
and Free Energy Changes at 25°C

Reactions	BLT	NS	NS	NS
	$\Delta H^\circ$ (kcal.)	$\Delta H^\circ$ (kcal.)	$\Delta S^\circ$ (e.u.)	$\Delta G^\circ$ (kcal.)
1.	+79, +21	107±12	40±20	95±18
2.	+12, -75	13±15	5±25	11±23
3.	+91, -54	120±27	45±45	106±41

Iodine is considered to be in the gaseous state rather than the solid state used in previous calculations (1,23). The present calculations refer to heats of reaction and free energy changes at room temperature. The heats of reaction calculated from either set of data show that reaction 2 is the one most likely



to take place since thermal stability is determined by the sign of free energy changes,  $\Delta G^{\circ}$ . The heat of reaction, entropy and free energy vary with temperature. Since heat capacities of the species involved in the reactions as a function of temperature are not all known, further thermodynamic interpretation at elevated temperatures are not feasible.

According to the above thermodynamic treatments, reaction 2 is postulated as one of the reactions in the system. Therefore it is indirect evidence of the reaction of scandium triiodide with scandium metal at  $600^{\circ}\text{C}$  to form a lower iodide,  $\text{ScI}_2$ , which reduces silicon dioxide to silicon at these temperatures.

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