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Metal-metal halide systems of gadolinium and yttrium

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METAL-METAL HALIDE SYSTEMS OF GADOLINIUM AND YTTRIUM

by

Jack Everett Mee

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. EXPERIMENTAL	15
III. EXPERIMENTAL RESULTS AND PERTINENT DISCUSSION. .	29
IV. GENERAL DISCUSSION OF RESULTS.	43
V. BIBLIOGRAPHY	48
VI. ACKNOWLEDGEMENT.	52
VII. APPENDIX	53

I. INTRODUCTION

The phenomenon of the solubility of certain metals in their molten salts is one of the most interesting areas of investigation in fused salt chemistry. Many systems have now been at least partially examined including those of the alkali, alkaline earth, transition, inner-transition, and post-transition metals. Recent reviews have been written by Ukshe and Bukun (1), Delimarskii and Markov (2), and, more critically, by Corbett (3).

In a typical system there is a depression of the melting point of the salt upon addition of the metal which terminates at an invariant, monotectic (or eutectic) point with the solution, solid salt and a liquid (or solid) metal-rich phase in equilibrium. Beyond the monotectic the concentration of the metal in the molten salt usually increases with temperature; this increase may be slight or it may be large enough to allow a consolute temperature above which the liquid salt and liquid metal are miscible in all proportions. One feature of these solutions is that they are apparently specific for the salt of the same metal; i.e. mixed metal-salt systems either show no measureable reactions or they involve oxidation-reduction reactions.

For simple salt-metal solutions there is an absence of any intermediate salt phase. Attempts to isolate new compounds, even by rapid quenching of the melts, yield just

finely-divided mixtures of the initial salt and metal. However, there are several systems which do involve separation of solid subsalts. These subsalts usually undergo peritectic or syntectic disproportionation at higher temperatures to the metal rich phase and to the normal salt rich melt. Above this peritectic (or syntectic) temperature the salt-metal phase relationship resembles that found in the simple salt-metal systems.

There are then two main points of interest in many of these studies. The first is to determine the nature of the solute in the molten solution, and the second is to determine if solid subhalides exist. Composition versus temperature phase diagram studies help clarify both points. They show the extent of the apparent solubility and, by their form, suggest conditions for other experiments in the molten state. Also they are particularly useful in showing the existence or non-existence of lower halides; several previously unknown subhalides have been discovered by these studies.

Different theories have been advanced to explain the solubility of the metal in the molten salt. Corbett (3) covers these quite extensively so this discussion will not be exhaustive. It is quite possible that no single, simple theory can fit the many varied systems. For example, the solubilities range from less than 1 mole % metal ($\text{SbCl}_3\text{-Sb}$, $\text{AlI}_3\text{-Al}$, $\text{MgCl}_2\text{-Mg}$, $\text{PbCl}_2\text{-Pb}$, $\text{PbI}_2\text{-Pb}$) to complete miscibility

between molten salt and liquid metal at the salts melting point (CsX-Cs systems, RbBr-Rb). In the latter systems then there must be complete gradation from salt-like to metallic behavior. Also, the behavior of the alkali metal systems, for instance, would very likely be expected to be quite different from the transition or post-transition metal systems. It is in fact, quite interesting to see the differences and similarities between these different groups.

At present, the two main theories are that the metal dissolves by formation of a lower oxidation state of the salt, i.e. a subhalide, or by formation of the solvent cation plus electrons. An early theory by Lorenz (4, 5) that the melts were actually colloidal suspensions has been generally disproved.

The subhalide theory has been returned to good favor in recent years. In the nineteenth century it was abused by investigators claiming many subhalides which did not actually exist. In their defense it must be noted that they did not have adequate means to differentiate between compounds and finely divided mixtures of solid salt and metal, nor did they have our present, more complete knowledge regarding trends in oxidation states. Unfortunately even some modern investigators have made unsupported claims of unusual subhalides. The current subhalide theory was put on a firm basis by work done on the post-transition metals (6, 7, 8, 9). The extent

of the metal solubility within a group of the post-transition elements increases with increasing atomic number of the metal; this is in agreement with the known trend toward increased stability of the lower oxidation state in these groups. Also, the solubility of a given metal is observed to increase with atomic number of the halide for all halide systems known except for cadmium and the alkali metals. In terms of a reaction of the type $M_{\text{soln.}}^{+2} + M_{(s,l)} = 2M_{\text{soln.}}^{+}$, this can be explained by a shift in the equilibrium toward the reduced state with the heavier halides due to a decrease in the extent the more acidic M^{+2} ion interacts with the halide ion. The inverse order for cadmium is in agreement with the known order of stability of its halide complexes in aqueous solutions. Addition of basic salts such as KCl should shift the equilibrium toward M^{+2} because of the interaction of the chloride ion with the more acidic M^{+2} ion. This is in agreement with the known facts for the solubility of Pb in PbCl (10) on addition of KCl, and for Cd in CdCl₂ on addition of KCl, CaCl₂, MgCl₂, ZnCl₂, MnCl₂, and CeCl₃ (11). Corbett pointed out that addition of a strong Lewis acid such as an aluminum trihalide should increase the amount of reduction since the halide ion would associate with the AlX₃ rather than with the M^{+2} ion thus shifting the equilibrium toward M^{+} . With CdX₂:AlX₃ equal to 1:2 the limiting compositions correspond to 67, 57, and 31% reduction of the Cd⁺² to Cd₂⁺² compared to

15.9, 16.4, and 21.6% in the respective chloride, bromide, and iodide systems (9). Furthermore, the Cd_2^{+2} ion was confirmed in the melt by Raman spectrum (12), and the solid salt $\text{Cd}_2(\text{AlCl}_4)_2$ was obtained. Actually the preparation of GaAlCl_4 and the analogous $\text{Ga}(\text{GaCl}_4)$ led to the cadmium results (13).

The "theory" that the metal goes into solution as ions plus electrons is conceived differently by different workers in the field. In 1952 Cubicciotti (11) proposed a model in which the anions were taken to be essentially close-packed so that the cations of the salt, and of any dissolved metal, occupied octahedral holes in the anion structure. Valence electrons of the dissolved metal were described as being transferred to "bands or zones of energy states belonging to the salt system as a whole." The nature of the electron zones or bands was not further defined; in certain later papers the assumption of solution as metal atoms was implied (14, 15, 16, 17). Available information on variations in solubility with size of divalent cations, with charge type of the chlorides, and from the effect of added salts on Cd in CdCl_2 was cited in defense of the model. Numerous facts have been arrayed against this specific model (3) and it simply does not hold up as a general theory.

However, a somewhat vague concept of solubility as ion plus electrons has been used to explain the solubilities and appreciable electronic conductivities observed in the alkali

halide melts and in certain of the rare earth metal halide melts (18, 19, 20, 21). Variations between systems was attributed to stability of various electron "traps" such as Na_2 molecules or Ca_2^{+2} molecule ions but the nature of the untrapped electrons was unclear except that they were conducting and cryoscopically active.

An alternate model is to consider the electrons as trapped or bound in anion vacancies; this is analogous to the solid state behavior of n-type semiconductors and of color centers in halides of the more electropositive metals. Pitzer (22) considers the formation of such solutions "may be considered in two steps: first, the conversion of the metal to a hypothetical ionic lattice of positive ions and F-centers, and second, the mixing with the metal halide." He shows that the positive energy of mixing for these systems can be accounted for reasonably well by the excess energy of this hypothetical metal. He points out that a critical factor for metallic vs. non-metallic character is the overlap of the wave functions between the F-center cavities. Intermediate states are unstable at low temperatures and one finds the continuous transition from non-metallic to metallic character only above a critical mixing temperature. For the metal halide-metal systems the non-metal to metal transitional composition may be taken to be that of the critical point for phase separation. This is of the order of 50 mole % metal whereas it is

only 4.2% metal in solutions of sodium in liquid ammonia. Apparently the electronic wave functions are much more localized in the fused salts than in ammonia. Others envision a similar picture for these systems (1, 23).

Corbett (3) compares this with the subhalide theory, which is at least better documented in certain systems, and shows that in some cases "the difference between a solvated electron and a reduced ion may be largely semantic and merely amount to a subtle difference in degree of electron localization." Bredig (24) comments that in mentioning "cryoscopically active" electrons he had in mind a

. . . more or less strong interaction with the cations which may be represented by $e(M^{z+})_x$, where z is a number essentially unknown at present, possibly varying from 1 (e.g. in hypothetical Ca^+) to perhaps 6 (F-center-like entities).

Thus the theory is in a state of flux and will undoubtedly see new developments in the near future.

Finally, brief mention should be made of a proposed conduction mechanism by Rice (25) that in those systems which display electronic conduction the electronic contribution can be considered to arise from the random walk character of a resonant charge transfer between metal atom solutes and the cations of the salt. So far the main argument against this proposal is its assumption of the metal atom solutes. It will be interesting to see how this conduction mechanism model fits in with the F-center and subhalide structural

models.

It is apparent that the battle of solution theories will rage for some time. Certainly the subhalide theory is based on the firmest ground for certain systems, but to extend it to others will require considerable sophistication in its description. Both the F-center and random walk models will undoubtedly be enlarged in scope, and either or both may attain wide acceptance.

The investigation of metal halide-metal systems has recently been extended to the rare earth metals. Phase diagram and other studies of the lighter rare earth systems have shown interesting trends in certain characteristics of these solutions but, perhaps more importantly, have shown the existence of several new lower halides. Here "lower halide" is used to describe any rare earth metal halide whose halide: metal mole ratio is less than 3:1. These lower halides are all stable with respect to disproportionation in the solid state, except for $\text{PrCl}_{2.3}$ which is stable as a solid only from ca. 594° to its incongruent melting point at 659° (26). The known lower halides are listed in Table 1; included are the previously known dihalides of samarium, europium, and ytterbium and the recently discovered TmI_2 (27, 28). A more complete tabulation of the major features of the $\text{MX}_3\text{-M}$ systems for lanthanum, cerium, praseodymium, and neodymium is given in Table 2.

Table 1. Lower halides of the rare earth metals

<u>La</u>	<u>Ce</u>	<u>Pr</u>	<u>Nd</u>	<u>Pm</u>	<u>Sm</u>	<u>Eu</u>	
					SmF_2	EuF_2	
		$\text{PrCl}_{2.3}^a$	$\text{NdCl}_{2.37}$ $\text{NdCl}_{2.27}$ NdCl_2		SmCl_2	EuCl_2	
		$\text{PrBr}_{2.4}$			SmBr_2	EuBr_2	
$\text{LaI}_{2.4}$ LaI_2	$\text{CeI}_{2.4}$ CeI_2	$\text{PrI}_{2.5}$ PrI_2	$\text{NdI}_{1.95}$		SmI_2	EuI_2	
<u>Gd</u>	<u>Tb</u>	<u>Dy</u>	<u>Ho</u>	<u>Er</u>	<u>Tm</u>	<u>Yb</u>	<u>Lu</u>
						YbF_2 YbCl_2 YbBr_2 YbI_2	
					TmI_2		

^aDisproportionates at 594° on cooling.

The diiodides of lanthanum, cerium, and praseodymium have been shown to be metallic-like rather than true ionic diiodides (29, 30). Magnetic susceptibility and electrical resistivities indicate that the metal is not present as M^{+2} ions but is still in the +3 oxidation state with an equal number of electrons in essentially metallic bonding with the cations, i.e. $\text{M}^{+3}\text{e}^-(\text{I}^-)_2$. Their lustrous colors are also suggestive of a metallic nature, essentially black with a purple luster for LaI_2 , dark bronze with a bluish luster for CeI_2 , and a golden bronze for PrI_2 . Other properties of LaI_2 , CeI_2 , and PrI_2 also distinguish them from the normal, divalent halides. Their higher melting points, relative to their triiodides, are in contrast to the lower melting neodymium and

Table 2. Major features of the MX₃-M systems for the lighter lanthanides^e

M	m.p.		Eutectic		Max. solubility ^b		Compounds			Reference
	MCl ₃	MI ₃	Temp.	Comp. %	Temp.	Comp. %	m.p.	Comp. %	Liquid % ^c	
La	860 ^o		826	9	990	11		none		31
		778-9	734	8.2	900	33.3	750	19.2±0.8 (LaI _{2.42})	14.2	29
								830	33.3 (LaI _{2.00})	33.3
Ce	812		777	9	950	9.7		none		32
		760-1	715	8.8	880	31	731	19.2±0.8 (CeI _{2.42})	16.1	29
								808	33.3 (CeI _{2.00})	30.3
Pr	786		646	17.1	780	18.7	659	24 ^d (PrCl _{2.3})	18.7	26
		738	666	11.9			676	16.7 (PrI _{2.50})	16.7	29
			669	20.9	764	28.2	758	33.3 (PrI _{2.00})	28.2	29

^aComposition as mole % metal M in MX₃, ±0.3 unless otherwise noted.

^bLargest experimentally determined solubility.

^cComposition of liquid salt phase in equilibrium at m.p.

^dDisproportionates at ca. 594^o on cooling.

Table 2. (Continued)

M	m.p.		Eutectic		Max. solubility		Compounds		Reference	
	MCl ₃	MI ₃	Temp.	Comp. %	Temp.	Comp. %	m.p.	Comp. %		Liquid %
Nd	758		640	13.8	870	30.5	680	21.0±0.7	17.5	33,34
								(NdCl ₂ .37)		
							702	24.3±0.7	20.0	33,34
								(NdCl ₂ .27)		
						841	33.3	30.3	33,34	
							(NdCl ₂)			
	787		491	26.6	800	36.5	562	35.0	35.0	33,34
							(NdI _{1.95})			

samarium diiodides. Also, contrary to normal trends of increasing stability of the dichlorides with increasing atomic number of lighter lanthanides, the metallic diiodides decrease in stability from lanthanum to praseodymium, as judged from the degree of decomposition on fusion and their melting points. Similar metallic-like behavior has been noted for the rare earth monosulfides (35) and acetylides (36) except for the normal divalent compounds of europium, ytterbium, and samarium.

Neodymium diiodide is evidently ionic with Nd^{+2} ions but its stoichiometry of $\text{NdI}_{1.95}$ and its insulating character indicate an apparent reduction below the +2 state (34). The diiodides of samarium, europium, thulium, and ytterbium are apparently stoichiometric and ionic. However, reduction below the +2 state is indicated for samarium in the iodide melt (34). The extent of reduction in the iodide melts is not known for europium, thulium, and ytterbium; thulium may also be reduced below +2 but this would not be expected for europium and ytterbium.

The intermediate iodides $\text{LaI}_{2.4}$, $\text{CeI}_{2.4}$, and $\text{PrI}_{2.5}$ have not been investigated enough to say if they are ionic or metallic-like but they would be expected to be metallic like the diiodides. Measurements on $\text{PrBr}_{2.4}$ give gross resistances in the semiconductor range indicating at least some electronic conductance (37).

The lower chlorides are evidently all ionic. As noted

above, their stability increases with the atomic number of the lighter lanthanides as evidenced by the non-existence of lower chlorides for lanthanum and cerium, the stability of solid $\text{PrCl}_{2.3}$ only over a small elevated temperature range, and finally the existence of lower chlorides of neodymium, samarium, and europium.

In conjunction with the discussion of stability of the solid halides it is interesting to note the limiting solubility of the metals in the molten salts (see Table 2). With the chlorides the metal solubility increases regularly from lanthanum to samarium but with the iodides it decreases from lanthanum to praseodymium and then increases to samarium.

Besides phase diagram studies, there have been EMF and conductivity measurements made on certain of the molten systems in an effort to determine the nature of the solute species. Actually the only EMF work was that done on the $\text{CeCl}_3\text{-Ce}$ system (38) and that was shown to be unreliable due to container attack (39). Conductivity measurements were made on the chlorides and iodides of lanthanum, cerium, praseodymium, and neodymium (20, 21, 40, 41). For both the chlorides and iodides considerable electronic conduction was found in the lanthanum and cerium systems. Praseodymium shows less electronic conduction while neodymium shows essentially ionic conduction. The question immediately arises as to the nature of the solute species and in what manner the electrons become

conducting. To date this has not been resolved. However, Corbett (3) pointed out that the electrons are not all mobile, as the positive temperature coefficient of the specific conductivity indicates that they are activated from some unknown solute specie(s). Whether these solute species are those described by the F-center or subhalide theories remains to be proven.

It is of interest to determine the trends in solubility and in solid lower halide formation for the heavy rare earth metals and for the rare earth metals yttrium and scandium. For this reason the following investigation was made of the $GdCl_3-Gd$, GdI_3-Gd , and YI_3-Y systems.

II. EXPERIMENTAL

A. Preparation of the Anhydrous Trihalides

The gadolinium and yttrium metals used for the preparation of the trihalides were readily available in the Ames Laboratory in a high state of purity. Typical impurity analyses showed 300 ppm oxygen, 130 ppm carbon, 200 ppm nitrogen and fluorine, <0.1% metallic impurities, principally as calcium, magnesium, tantalum and other rare earth metals.

The trihalides were prepared by the method developed by Druding (34) in which the metal was reacted directly with the halogen or hydrogen halide. This was considered to be superior to other procedures in avoiding the problem of oxygen contamination. Even so, it was necessary to vacuum sublime the products for ultimate purity. Varying amounts of non-volatile residue remained after the sublimations and the product trihalides were always cleaner in appearance. The purity of the trihalides were reflected in the melting points determined by thermal analysis, specifically by cooling curves. Twice-sublimed YI_3 melted at 997° compared to 989° for the unsublimed material and 965° recently given in the literature (42). Sublimed $GdCl_3$ melted at 605° compared to 603° for the unsublimed material and 602° for the literature value (43). Sublimed GdI_3 melted at 931° , the literature value is 925° (43). Typical major component analyses on sublimed salts

have halide:metal ratios of $3.00 \pm 0.01:1$ with $100.00 \pm 0.15\%$ material balance. Typical impurity analyses showed 500 ppm oxygen, trace quantities of aluminum, silicon, calcium and magnesium, with other rare earth metals, tungsten, tantalum, and molybdenum not detected.

All materials were stored in evacuated sample containers due to the hygroscopic nature of the trihalides and the reactive nature of the metals and, especially, the subhalides. All transfers were carried out in an argon-filled "dry" box. The argon was dried by passage through a -80° trap, and the box atmosphere continuously circulated through mixed Linde Molecular Sieves Types 4A and 13X.

1. Preparation of gadolinium trichloride

Gadolinium metal was placed in a molybdenum boat inside a fused silica tube which was then placed in a 12", nichrome-wound, split furnace and connected to the gas train. Incoming gases were dried by passing them through a sulfuric acid bubbler and a -80° trap. Helium and a little hydrogen were passed through the tube while it was being heated to reaction temperature (850°). When the temperature reached 850° the helium and hydrogen flow was stopped and HCl was passed through at a moderate rate until the reaction was completed. One to three hours later completion of the reaction was indicated by the appearance of white fumes of molybdenum chloride.

Hydrogen was then added at about one-half the HCl rate and the apparatus maintained at temperature another half hour. Helium was passed through the apparatus during the cooling period. The crude product was transferred to a tantalum crucible which was connected to a tantalum collector tube inside a larger tantalum tube. The entire assembly was placed in an evacuable fused silica tube and the trichloride was sublimed under vacuum at 850° . The final product was almost white with a slight yellow or green tint.

Since hydrocarbons found in commercial HCl are difficult to remove and react preferentially with the rare earth metals, the HCl was usually generated as required by dropping conc. H_2SO_4 on KCl. However, commercial HCl was used for one preparation and indeed it was necessary to sublime the crude product twice before it compared favorably in all respects to once-sublimed $GdCl_3$ made from generated HCl.

2. Preparation of gadolinium triiodide and yttrium triiodide

For the preparation of the triiodides of gadolinium and yttrium the metal was loaded into a tungsten crucible inside a large fused silica tube. The previously vacuum sublimed iodine (B&A Reagent Grade) was contained in a sidearm connected to the main tube. The section of the apparatus containing the metal was heated to a temperature $10-20^{\circ}$ above the melting point of the triiodide while the arm containing

the iodine was heated to 110° to maintain the iodine pressure at one-tenth of an atmosphere. Twelve hours were usually allowed for complete reaction.

The crude product was sublimed by the same technique as used for gadolinium trichloride. The final gadolinium triiodide was very light grey with a slight green tint. The yttrium iodide was almost white with a slight yellowish tint.

B. Analytical Methods

1. Dissolution of samples

Samples for analysis were transferred in the dry box to a weighing bottle and this was weighed in air. After transfer of the sample, the weighing bottle was again weighed in air and the necessary buoyancy correction applied. The trihalides were dissolved in water but with all reduced mixtures or subhalides sufficient acetic acid was added to dissolve the hydrolysis products. An acid solution was not added directly to reduced samples because of their extremely reactive nature. With the iodides a small amount of sodium sulfite was added to reduce any iodine to iodide.

2. Metal determination

The metal was titrated with EDTA using arsenazo indicator at pH 5.5-6.5 (44).

3. Chloride determination

The chloride was precipitated with silver nitrate, dried, and weighed as silver chloride.

4. Iodide determination

Iodide was determined by titration with standard silver nitrate using Eosin Y as the indicator.

5. Oxygen determination

Oxygen was determined by the Analytical Service Group by the inert gas fusion method (45).

6. X-ray powder pattern determination

Samples for X-ray powder patterns were loaded in the dry box into 0.1-0.3 mm. Pyrex capillaries and sealed off. Diffraction patterns were obtained using Ni-filtered, Cu K α radiation in an 11.46 cm. Debye-Scherrer camera. The camera was calibrated with sodium chloride, and no corrections were applied for adsorption. Values of θ were converted to distances using the NBS tables (46). The trihalide patterns were visually identical with those determined by Dennison.* The patterns of α -GdI₂ and GdCl_{1.6} are listed in the

*D. H. Dennison, Ames Lab. U. S. Atomic Energy Commission, Ames, Iowa, "X-ray Powder Patterns of Rare Earth Metal Trihalides", private communication (1961).

Appendix.

7. Experimental accuracy

The results of the analyses were considered reliable if the material balance totaled $100.0 \pm 0.3\%$. In the results to be quoted, the values of mole % metal are $\pm 0.3\%$ and the halide:metal ratios are ± 0.01 unless otherwise noted.

C. Measurements

1. Determination of the phase diagrams

The phase diagrams were determined by thermal analysis and equilibrations. These were supported by the analytical tools of chemical analyses and X-ray powder patterns.

a. Thermal analysis The sample containing apparatus for thermal analysis was essentially that used by Druding (34). A three section apparatus was used so that successive metal additions could be made. The bottom section was constructed of 29 mm. x 14" fused silica with a vacuum jacket of 41 mm. fused silica on the lower two-thirds. A well evacuated jacket was essential for steady cooling rates at the lower temperatures ($\leq 680^\circ$) encountered in the $\text{GdCl}_3\text{-Gd}$ system. A platinum foil radiation shield was placed around the outside of the vacuum shield; this was necessary to maintain uniform cooling rates at the higher temperatures ($\leq 1100^\circ$) encountered in the iodide systems. The middle segment of the apparatus

consisted of a Pyrex "el", while the Pyrex top had a stopcock and two tungsten-through-glass seals for the thermocouple leads. The "el" was necessary to avoid thermal gradients across the tungsten leads. When the sample temperature was being recorded it was essential to shield the tungsten leads by surrounding that portion of the apparatus with metal foil and grounding the foil. If no shield was used the temperature recording varied from slightly unsteady to violently spasmodic. A small blower was used to cool the connecting taper joints and the stopcock. The sample was contained in a tantalum crucible, $3/4$ " i.d. x 2", with a thermocouple well of $5/32$ " tantalum tubing positioned in the center and crimped so that the tip of the thermocouple was $1/4$ to $1/2$ " above the bottom of the crucible. The bottom portion of the #28 gage chromel-alumel thermocouple was encased in an alundum shield while the top end was equipped with small clips to facilitate easy replacement. A tantalum lid was placed on the crucible and three or four tantalum baffles were fastened to the alundum thermocouple insulator at one inch intervals to minimize convection currents and decrease heat loss by radiation.

The vacuum-jacketed portion of the apparatus was positioned in a Marshall tube furnace. The furnace was lined with a piece of $1/8$ " thick Inconel pipe which was grounded. The grounded pipe served to steady the temperature recording and to lower the power-off cooling rate of the furnace. The

cooling rate of the furnace could be controlled between $21^{\circ}/\text{min.}$ to its maximum cooling rate with power off, $5^{\circ}/\text{min.}$ at 600° and $10^{\circ}/\text{min.}$ at 900° . Temperature was regulated by a Weston Celestray controller or Minneapolis-Honeywell Brown Electronik Indicating Proportioning Controller with the controller thermocouple in contact with the inside wall of the furnace.

A differential thermal recording was obtained simultaneously with the sample temperature recording. The reference thermocouple was in contact with Al_2O_3 sealed in a fused silica container which was permanently positioned in the furnace just below the sample. The sample thermocouple potential and differential potential were simultaneously recorded on a Bristol Model 560 Dynamaster strip chart, two-pen recorder. This recorder is equipped with a variable, 2-10 millivolt scale with a 0-40 millivolt zero suppression for the temperature pen and fixed 0-2 millivolt range for the differential pen. A Rubicon potentiometer was subsequently used to measure the recorded thermal arrests. Positioning of the differential pen was controlled by a variable DC voltage source which in effect acted as a zero suppression. The sample thermocouple was standardized regularly against the melting points of Ag (960.8°), NaCl (800°), and NaI (660.1°). The NaCl and NaI values are those given by Bredig and Bronstein (47). The thermocouple was replaced if it did

not indicate melting points within one degree of these values. No provision was made for agitating the sample during cooling other than by shaking the entire apparatus by hand.

The procedure followed in a run was to load 25-35 millimoles of salt and the desired amount of metal in the dry box and evacuate the apparatus by mercury diffusion pump for about one hour. One-half atmosphere of argon was then introduced to keep sublimation of the trihalides to a minimum. The sample was equilibrated for 15 mins. ca. 20° above the melting point of the trihalide and then the furnace was cooled at a uniform rate. During the cooling the sample temperature and the difference between the sample and reference temperatures were continuously recorded. Thermal halts were observed whenever some event in the sample would affect the cooling rate of the sample due to the heat evolved in the event. Typically, halts were observed for liquidus, peritectic, eutectic, and phase transformations. Thermal halts were reproducible to within 1° on a given sample and, unless otherwise noted, all temperatures reported are $\pm 1^{\circ}$.

The thermal halts obtained were quite varied in nature. Melting points and eutectics showed good plateaus on the temperature (T) curve that quickly fell off beyond the break and returned to the normal cooling rate. This was accompanied by a huge hump on the differential (ΔT) curve. The only severe supercooling was observed with GdCl_3 (16°). The

liquidus halts were seen only as changes in slope on the T curve with a more dramatic displacement on the ΔT curve. The ΔT curve might or might not return to its equilibrium position depending on how soon the next halt appeared but, in either event, the separate halts were usually easily identified. The peritectic halt in the GdI_3 -Gd system was more pronounced than a liquidus halt but less than a eutectic halt. In the $GdCl_3$ -Gd system the peritectic halt was very small; the differential curve was particularly helpful here in establishing in early runs that there indeed was a peritectic halt. Halts due to phase transformations in the pure compounds were well pronounced but, of course, were smaller in mixtures.

For a melting point or eutectic the actual temperature assigned to the halt was the temperature of the plateau on the T curve. For a liquidus, peritectic, or phase transformation the assigned temperature was taken from the initial slope change on the T curve; the larger and more abrupt ΔT slope change occurred at the same time and helped with the temperature assignment. Relatively slow cooling rates ($2-3^\circ/\text{min.}$) were necessary to make this slope change abrupt and not rounded.

b. Equilibrations Equilibrations of the salts with metal were carried out in the apparatus shown in Fig. 1. The salt and metal were loaded into a $1/4$ " tantalum tube in the dry box. Best results were obtained using metal in massive

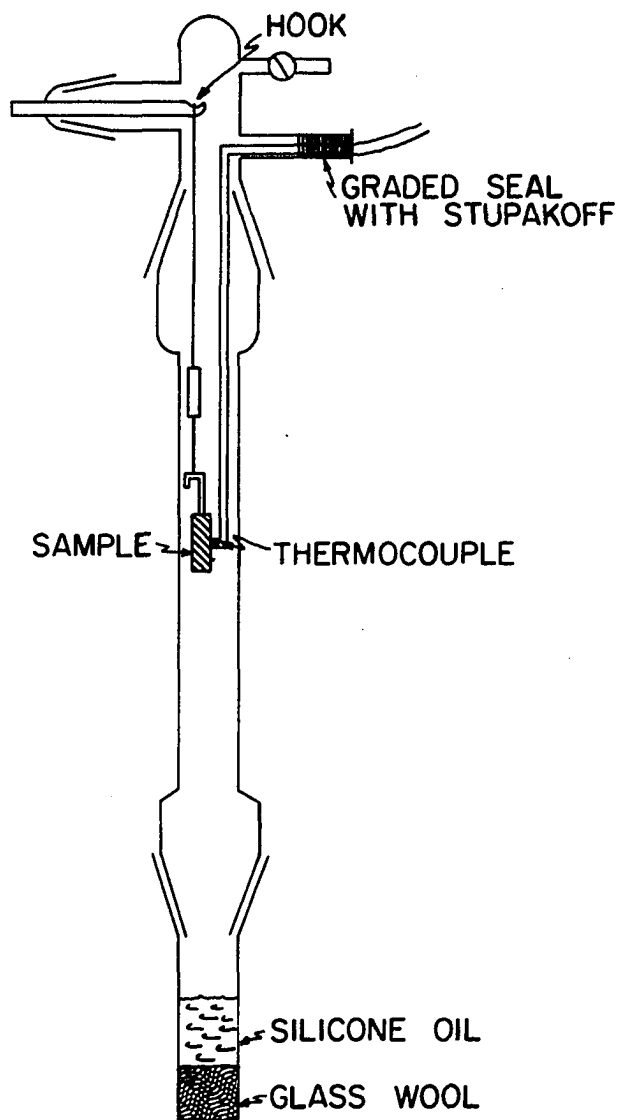


Fig. 1. Apparatus for equilibrations and quenches

chunks or buttons since metal turnings disintegrated during the reaction and the fine metal chips were difficult to separate from the salt phase after the reaction. The tube was crimped tightly and then suspended by a tantalum wire in the equilibration apparatus. The tantalum wire was in two separate lengths connected by an alumina link to prevent heat loss by heat conduction. The sample was positioned so it was in good contact with the thermocouple. The apparatus was continuously evacuated throughout the equilibration. A 12" nichrome-wound furnace was used to heat the middle (fused silica) section with the sample to the desired temperature. The top and bottom Pyrex portions of the apparatus projected out of the furnace and were cooled by small blowers. The sample was quenched by rotating the suspension hook so that the sample tube fell into the silicone diffusion pump oil.

Necessary equilibration times varied considerably. For the limiting liquidus concentrations consistent results were obtained for samples equilibrated 30-60 minutes for the iodides and 1-2 hours for the chloride system. However, to produce the lower iodide and chloride of gadolinium the trihalide and excess metal were reacted for 5-20 days between the eutectic and peritectic temperatures. In fact the lower chloride was never obtained by equilibration at constant temperature. The lowest chloride:gadolinium ratio reached by this technique was 2.04:1, subsequently found to be only ca. 70% reduced.

Best results in enriching and isolating the lower chloride were achieved by application of a temperature gradient. Two methods were used. In the first method sufficient salt and metal were loaded into a 5" length of 1/4" tantalum tubing to fill the tube to ca. 3" after the salt was melted. The tube was placed in a 5/32" i.d. evacuable fused silica container. A thermocouple was in direct contact with the sample tube. Two small 3/8" i.d. furnaces were positioned so most of the sample was held at ca. 650° but the top part of the sample was held at 600°. The sample was then raised 1/4" three times a day for four days. The second method was developed by Sallach (30) for growing peritectic-type lower halides. The sample was slowly lowered from a hotter zone into a colder zone of an adapted Marshall furnace. The furnace had a temperature profile which resulted in a uniform temperature gradient within the sample of ca. 14°/inch.

The product yield was very low but the lower chloride crystals were much larger than any grown previously and they were easily separated from the bulk salt by hand sorting in the dry box.

2. Resistance measurements

Crude gross resistance measurements were made on the solid samples in the dry box using a vacuum tube voltmeter.

3. Magnetic susceptibility measurements

Exploratory magnetic susceptibility measurements were made on samples of composition $\text{GdI}_{2.11}$ and $\text{GdCl}_{1.6}$ by members of the physics group under the direction of Dr. Sam Legvold.

III. EXPERIMENTAL RESULTS AND PERTINENT DISCUSSION

In the phase diagrams to be cited the circles, crosses, and triangles represent data obtained by equilibrations, cooling curves, and heating curves respectively.

A. Gadolinium (III) Chloride-Gadolinium System

There are two main items of interest in this simple looking phase diagram. The first item is the low solubility of metal in the molten trichloride. The eutectic composition is $1.0 \pm 0.5\%$ Gd in GdCl_3 ; the limit of solubility is 5.0% at 950° , 3.2% at 800° , and 2.0% at 670° by equilibration. This is the lowest metal solubility reported for any rare earth metal-trihalide system reported so far, even for systems where no solid lower halides exist.

The second and more exciting item of interest is the existence of a solid compound of apparent stoichiometry near $\text{GdCl}_{1.6}$. This stoichiometry below a more conventional dichloride is well documented. Trichloride and metal were carefully equilibrated below the peritectic temperature at 632° ; those samples whose salt phases subsequently analyzed near 33 mole % Gd in GdCl_3 (i.e. ca. GdCl_2) still exhibited a large eutectic halt when cooled from the equilibration temperature. In addition, powder patterns of these solids showed the presence of appreciable amounts of GdCl_3 ; in fact the characteristic trichloride lines were still of major intensity as

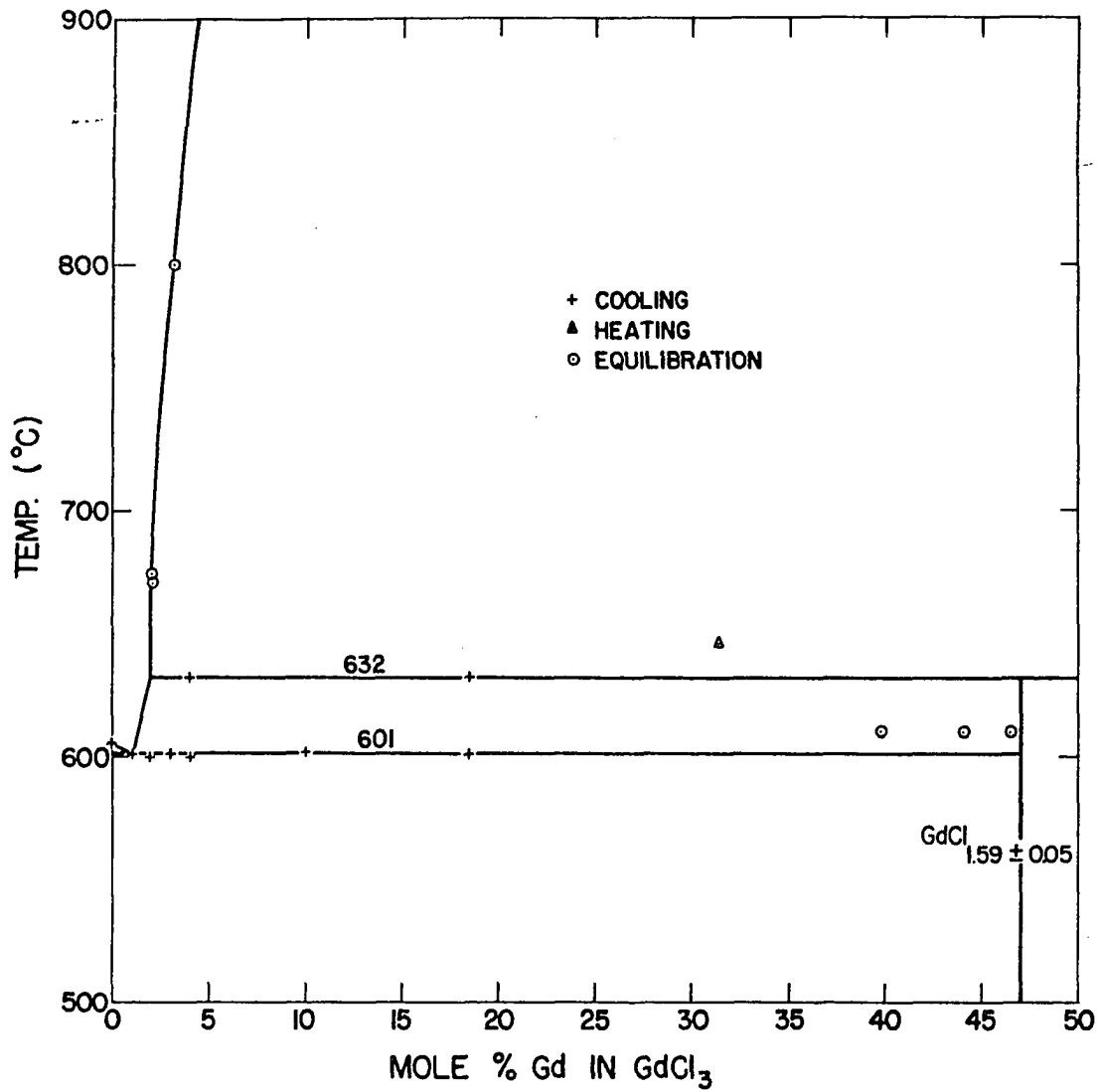


Fig. 2. Phase diagram of the gadolinium (III) chloride-gadolinium system

shown for the composition $\text{GdCl}_{2.11}$ in Fig. 3. More reduced solid samples of compositions $\text{GdCl}_{1.81 \pm 0.03}$ and $\text{GdCl}_{1.68 \pm 0.03}$ were later isolated and their patterns still showed the presence of GdCl_3 . Finally, a sample of composition $\text{GdCl}_{1.61 \pm 0.03}$ showed no powder pattern evidence of GdCl_3 .

Efforts were first made to obtain the lower chloride by reacting trichloride and excess metal between the peritectic and eutectic temperatures for 10-20 days, depending on the quantity of sample. Best reaction rates occurred at ca. 602° , as low as possible without the entire system being solid. The lowest composition attained by this constant temperature method was $\text{GdCl}_{2.04}$ but thermal analysis and powder patterns showed that there was still considerable trichloride present. Finally the best lower chloride samples were grown by means of the temperature gradient methods mentioned in the experimental section. Single crystals of the lower chloride up to $1/4$ " in length could be sorted from the bulk salt mixture; varying small amounts of bulk salt would sometimes cling to the crystals making the sorting difficult. The samples of compositions $\text{GdCl}_{1.81}$, $\text{GdCl}_{1.68}$, and $\text{GdCl}_{1.61}$ resulted from this technique.

The assignment of composition $\text{GdCl}_{1.59 \pm 0.05}$ for the lower chloride was made by the following reasoning. In the powder patterns the relative intensity of the strongest lower chloride line compared to the strongest trichloride line is 0.1 at

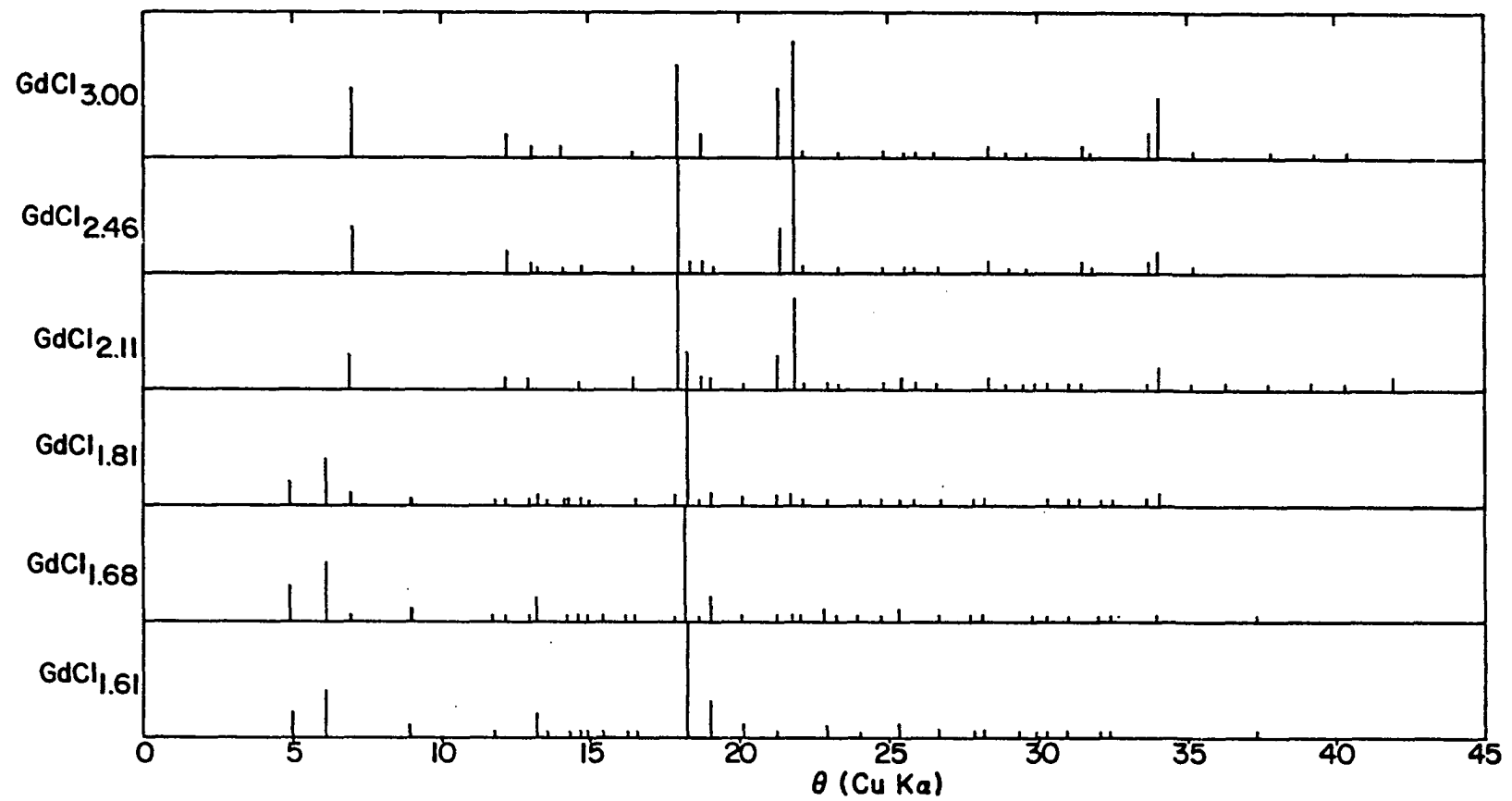


Fig. 3. X-ray diffraction data for the gadolinium chlorides

$GdCl_{2.46}$, 1 at $GdCl_{1.98-2.06}$, and 10 at $GdCl_{1.81}$. At $GdCl_{1.61}$ all trichloride lines are gone. Evidently the effective scattering power of the hkl plane(s) giving the strongest trichloride line is of the order of twice that for the strongest lower chloride line. Based on a pessimistic 10% lower limit of detection for equal scattering powers, the presence of ca. 5% trichloride in the lower chloride could probably be detected. Since trichloride was not detected at composition $GdCl_{1.61}$, the lower limit would then be $GdCl_{1.54}$. Now in the powder pattern for $GdCl_{1.68}$ seven probable trichloride lines are present. The hkl plane(s) represented by the weakest of these seven lines probably has about the same scattering power as the plane(s) represented by the strongest lower chloride line. Based on an optimistic 3% limit of detection for such a case, the weakest trichloride line would not be seen unless there were at least ca. 3% trichloride present in the $GdCl_{1.68}$ sample. This would set the upper composition limit at $GdCl_{1.64}$ and establish the assigned composition at $GdCl_{1.59 \pm 0.05}$. In this argument it is assumed that the absorption of X-rays by different mixtures of the chlorides should be similar since the linear absorption coefficient is not dependent on the chemical composition but only on the elements in the mixtures. The limits ± 0.05 are the probable limits; by assuming a liberal ± 0.03 analytical error the maximum limits of composition would be ± 0.08 . The analytical

error is large for the chloride because of the small amount of sample available at compositions $\text{GdCl}_{1.81}$, $\text{GdCl}_{1.68}$, and $\text{GdCl}_{1.61}$.

The symmetry of $\text{GdCl}_{1.6}$, as determined from the X-ray powder patterns, is orthorhombic, with lattice constants 8.99, 7.22, and 6.72 Å. The solid is isolated as brassy or brown crystals but when ground up it becomes a black fibrous material. The $\text{GdCl}_{1.6}$ is weakly attracted to a magnet; however, magnetic susceptibility measurements show only that it is paramagnetic. Resistance measurements on single crystals 1/8 to 1/4" in length using a vacuum tube volt meter gave resistances of ca. 1×10^7 ohms.

The best value of the incongruent melting point for $\text{GdCl}_{1.6}$ is 632° by cooling curves. This value is highly dependent on the cooling rate, the slowest rate giving the highest results. No phase transitions were observed down to 135° .

B. Gadolinium (III) Iodide-Gadolinium System

In this phase diagram the existence of a stable solid lower halide of apparent stoichiometry near GdI_2 is probably most noteworthy. Efforts to obtain a relatively pure diiodide were partially frustrated by the closeness of the peritectic temperature at 831° to the eutectic temperature at 825° . Despite extreme precautions the equilibrating samples

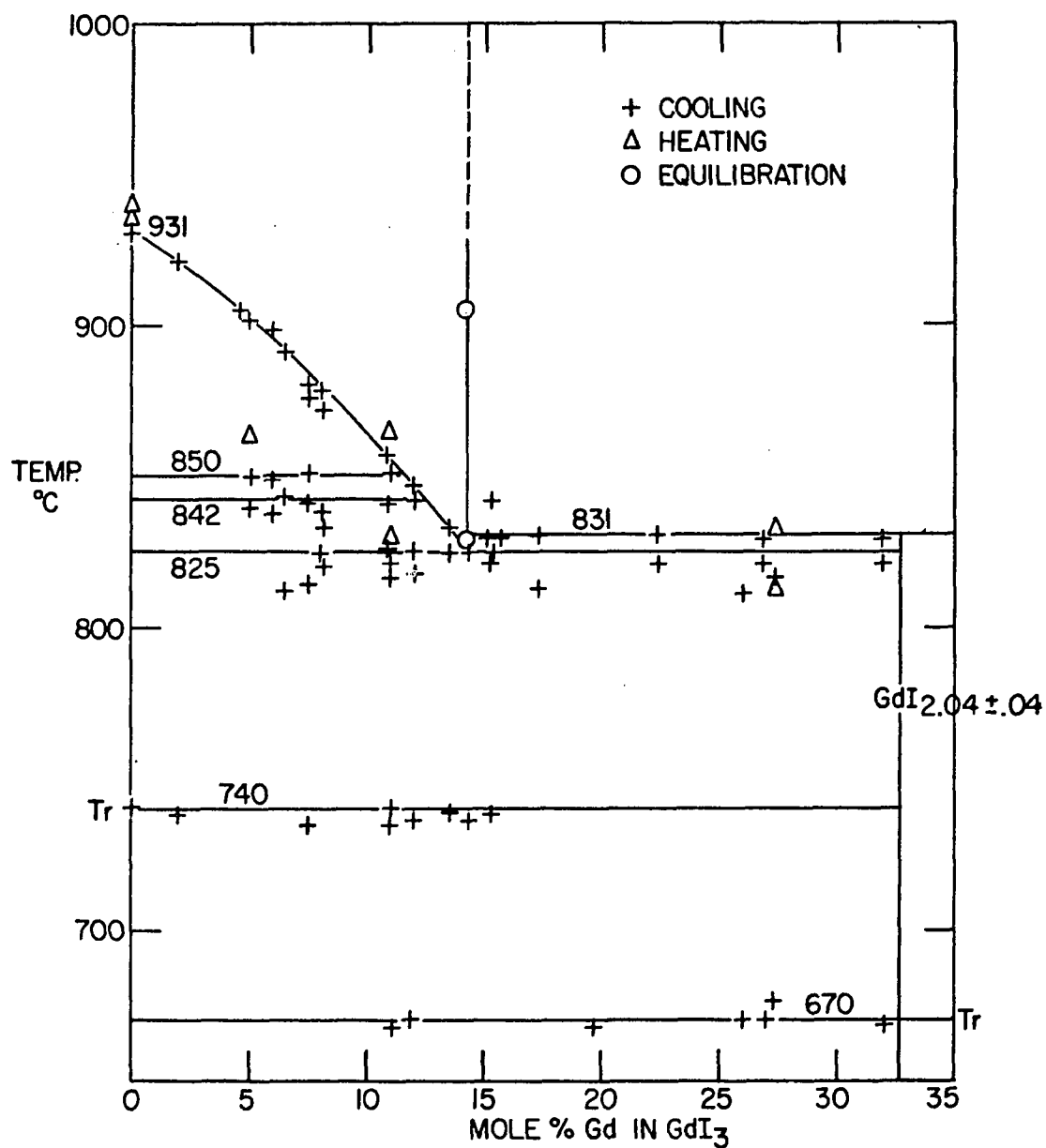


Fig. 4. Phase diagram of the gadolinium (III) iodide-gadolinium system

would evidently temperature cycle above the peritectic temperature causing any diiodide which had been formed to disproportionate to finely divided metal and melt. Finally the composition $GdI_{2.11}$ was reached by equilibrating triiodide and excess metal 5° to 10° below the apparent eutectic temperature at 825° . Strangely, the eutectic halt was then observed at temperatures as low as 808° upon cooling from the equilibration temperature. With continued equilibration this temperature halt gradually got smaller and finally practically disappeared while the diiodide transition halt at 670° grew larger.

The assignment of composition $GdI_{2.04 \pm 0.04}$ for the lower iodide was made as follows. The powder patterns showed no diiodide lines for compositions down to $GdI_{2.64}$; then the strongest diiodide and triiodide lines were of equal intensity near composition $GdI_{2.35}$; and, finally, at $GdI_{2.11}$ the triiodide lines were almost gone. A plot of I_3/I_2 versus I^-/Gd for the stronger lines roughly indicated that triiodide lines probably would not be detected at about $GdI_{2.06}$. Hence the effective scattering powers of the hkl planes represented by the strongest triiodide lines are probably almost twice that of the khl planes represented by the strongest diiodide lines. Again based on a pessimistic 10% lower limit of detection for equal scattering powers, the presence of 5-6% triiodide in the lower iodide could probably be detected. Therefore if no

triiodide is detectable at $GdI_{2.06}$ the lower limit of composition would be $GdI_{2.00}$. Then based on an optimistic 3% limit of detection for the weakest of the triiodide lines detected in $GdI_{2.11}$, the upper limit of composition would be $GdI_{2.08}$. With the ± 0.01 analytical limits the maximum limits for the assigned composition are ± 0.05 .

Qualitative supporting evidence is the fact that the eutectic halt was first seen on cooling curves at $GdI_{2.92}$, or at 19% of the eutectic composition; at $GdI_{2.11}$ the eutectic halt was practically gone, so if ca. 19% of the eutectic composition were present the lower iodide would be ca. $GdI_{2.01}$.

The diiodide is a bright brassy material which is strongly attracted to a magnet. The preliminary magnetic measurements show that there is some magnetic orientation but probably not strong enough to indicate ferromagnetism. Resistance measurements did not clearly differentiate between metallic or non-metallic character. Some polycrystalline pieces ca. 1/4" in diameter of different samples of compositions from $GdI_{2.8}$ to $GdI_{2.3}$ would typically show gross resistances as low as 30 ohms between certain points but as high as 10^5 ohms between other points. Since they were highly segregated samples, with the brassy diiodide scattered throughout the bulk grey salt, the low value may be a reasonable value for the diiodide. The most reduced sample of $GdI_{2.11}$ composition gave a relatively uniform resistance of

$1-3 \times 10^4$ ohms between all points contacted on a piece $3/4$ " in diameter. Since the resistance is well less than would be expected for an insulator it confirms at least some degree of electronic conduction. Two factors could contribute to a higher resistance than expected for a truly metallic diiodide. First, the contact resistance could be appreciable as with the light rare earth metal diiodides (29, 48). Second, the $GdI_{2.11}$ sample was very homogeneous in appearance so the ca. 11% triiodide uniformly distributed through the sample could cause the high resistance. The GdI_2 has hexagonal symmetry with lattice constants $a_0 = 8.67$ and $c_0 = 5.75 \text{ \AA}$.

The GdI_3 melts at 931° and exhibits a halt at 740° which is evidently due to a previously unreported phase transition. Efforts to quench in this β -phase failed.

There is a portion of the diagram which remains unexplained. This is the halt, or halts, in the 840° - 850° region to the left of the eutectic. With a given sample at least one halt and often two halts were observed in this region; they were not large but were about the same size as liquidus halts. If the halt (or halts) was due to the formation of a peritectic-type compound, then samples of composition to the left of the compound when equilibrated between the eutectic (825°) and peritectic (840° - 850°) temperatures should not show a eutectic halt on cooling. Also, either the powder patterns should show the presence of a new compound or a disproportion-

ation halt should be observed. However, no powder pattern evidence was found for a new compound; no disproportionation halt was observed; and, except for compositions where the eutectic halt was very small, the eutectic halt could not be "equilibrated away". Similarly, compositions to the right of the compound when equilibrated below the peritectic temperature should not show the triiodide transformation halt at 740° on cooling; if the 740° halt is observed then a disproportionation halt should be seen somewhere between 740° and 840° . In fact the 740° halt was always observed and no disproportionation halt appeared. The possibility remains that the 850° halt is a peritectic halt due to formation of an intermediate phase which then disproportionates at 840° . Attempts to isolate such a phase by quench experiments failed. A final possibility is that the halt (or halts) is due to an induced transformation in the triiodide. However, samples with 1 and 2 mole % metal in the triiodide failed to exhibit either halt.

Finally, in phase diagrams of this type the possible solute species can sometimes be inferred by calculating the cryoscopic number from the slope of the liquidus curve and the known $\Delta H_{\text{fus.}}(\text{MX}_3)$. Alternately the $\Delta H_{\text{fus.}}(\text{MX}_3)$ can be calculated if the solute specie is known. In the $\text{GdI}_3\text{-Gd}$ system a tentative value of $n = 2.1 \pm 0.1$ can be calculated if a $\Delta H_{\text{fus.}}(\text{GdI}_3)$ value of ca. 12 kcal./mole is used. This

is based on a speculative extrapolation of limited ΔS_{fus} . data for LaI_3 , CeI_3 , PrI_3 , and NdI_3 .* The most reasonable solute species Gd^{+2} and $\text{Gd}^{+3} + 3e^-$ both have $n = 3$, if the electrons are cryoscopically active. Other possible solutes are Gd^+ with $n = 1.5$ and Gd^0 with $n = 1$. Then $n = 2.1$ indicates a mixture of solute species or the formation of solid solutions. However, no other evidence of solid solutions was found.

C. Yttrium (III) Iodide-Yttrium System

The most notable feature of this system is the lack of a solid lower phase, in contrast to $\text{LaI}_3\text{-La}$. Equilibrations of metal and triiodide at temperatures just above that of the eutectic at 948° confirm the results of cooling curves that indeed there is no lower iodide. Nevertheless there is considerable solubility of the metal in the molten triiodide. The eutectic composition was 11.6 mole % Y at 948° , and the limit of solubility was 14.7% at 1150° and 12.1% at 965° by equilibration.

A phase transformation, previously unreported, was detected in the YI_3 at 978° , which is above the previously reported YI_3 melting point (42). The halt was well pro-

*A. S. Dworkin and M. A. Bredig, Oak Ridge National Laboratory, Oak Ridge, Tenn., "Entropy of Fusion Data for Certain Lanthanide Halides," private communication (1962).

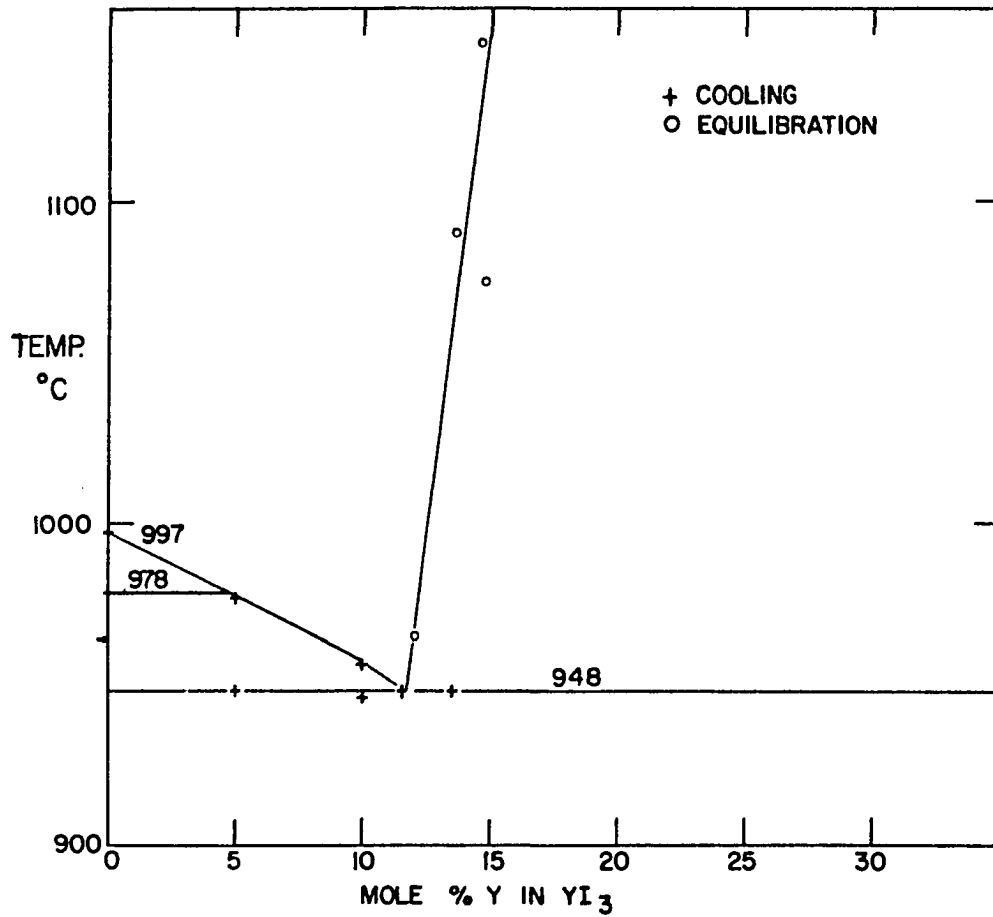


Fig. 5. Phase diagram of the yttrium (III) iodide-yttrium system

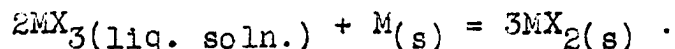
nounced on both the T and ΔT curves on cooling curves of two separate samples. Samples equilibrated between 978° and 997° and then quenched were α - YI_3 , so the $\beta \rightarrow \alpha$ transition must be relatively rapid.

By using $n = 3$, $n = 2$, and $n = 1.5$ the $\Delta H_{\text{fus.}}(\text{YI}_3)$ can be estimated as 31.9, 21.5, or 15.8 kcal./mole respectively. There is no experimental or estimated $\Delta H_{\text{fus.}}(\text{YI}_3)$ to compare with these values but certainly the 31.9 kcal./mole for $n = 3$ would not be expected.

IV. GENERAL DISCUSSION OF RESULTS

A. Discussion of the Formation of Lower Halides

The formation of a solid dihalide can be expressed by the reaction



The heat of this reaction based on a Born-Haber cycle is

$$\begin{aligned} \Delta H = & 3U_{(MX_2)} - 2(U_{(MX_3)} + \Delta H_{\text{fus.}(MX_3)}) + \Delta H_{\text{sub.}(M)} \\ & + (I_1 + I_2 - I_3) - RT \end{aligned}$$

for a truly reduced dihalide. For a metallic dihalide

$$\begin{aligned} \Delta H = & 3U_{[M+3e-(X^-)_2]} - 2(U_{(MX_3)} + \Delta H_{\text{fus.}(MX_3)}) \\ & + \Delta H_{\text{sub.}(M)} + (I_1 + I_2 + I_3) - RT . \end{aligned}$$

Salt-like dihalides are favored by high $U_{(MX_2)}$, $\Delta H_{\text{fus.}(MX_3)}$, and I_3 and by low $U_{(MX_3)}$, $\Delta H_{\text{sub.}(M)}$, I_1 , and I_2 . Metallic dihalides are favored in the same way except that I_3 should be small rather than large. The largest quantities, and thus probably the most important, are the lattice energies and the ionization potentials (e.g. $U_{\text{theoretical}}^0$ for $GdCl_3$ has been estimated as -1053 kcal./mole and the estimated sum $I_1 + I_2 + I_3 + \Delta H_{\text{sub.}(M)}$ for Gd is 987 kcal./mole (49), while the $\Delta H_{\text{vap.}}$ for Gd is 72 kcal./mole (43) and the estimated $\Delta H_{\text{fus.}}$ for $GdCl_3$ is 7 kcal./mole (50)).

Most of these quantities are unknown for the rare earth metals. The second and third ionization potentials are

especially hard to determine. The heat of vaporization of the metal and the three ionization potentials are however known for yttrium (43, 51). Since I_1 , I_2 , and I_3 are all low their effect would be to favor a metallic diiodide rather than a salt-like diiodide although neither is actually formed. The heat of vaporization for yttrium metal is high but not as high as for lanthanum and cerium (43), which both form metallic diiodides. Unfortunately, however, nothing is known about the lattice energies of the yttrium triiodide or hypothetical diiodide. If the metallic diiodide lattice energy is highly dependent on some critical cation/anion radius ratio it may well be that the heavier (and smaller) lanthanides may not form metallic diiodides either.

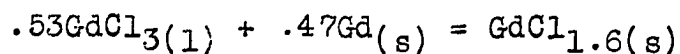
For gadolinium only the heat of vaporization of the metal (43) and the first ionization potential (51) are known. The sum of I_1 , I_2 , I_3 , and $\Delta H_{\text{sub.}}(\text{Gd})$ has been estimated (49). Therefore little can be said about the diiodide except that it exists and seems to be metallic. A careful determination of its magnetic moment would be the most direct way to determine the gadolinium oxidation state.

The existence of solid $\text{GdCl}_{1.6}$ can only be described as surprising at this stage of our knowledge. The gross resistance measurements indicate that it is a truly reduced halide and not a metallic halide. A careful determination of the magnetic susceptibility will help determine the actual oxida-

tion state(s). If it is an ionic, reduced halide then it shatters the tradition of the high stability of the f^7 configuration (e.g. for Gd^{+3}) being the only consideration for probable oxidation states for lanthanides near gadolinium. Here there are obviously other overriding thermodynamic factors. The overworked statement commonly used that certain ions are stable just because they are approaching the f^7 configuration should certainly be discarded.

The three big questions are what stabilizes the $GdCl_{1.6}$, why the unusual stoichiometry, and why is there such small solubility of the metal in the molten salt? The existence of the solid lower chloride and low solubility of metal in the melt would seem to be mutually contradictory. Evidently the $GdCl_{1.6}$ lattice energy is very high and of a special nature not possible in the liquid. Speculation regarding the nature of the forces contributing to this high lattice energy must await further experimental information. The low concentration of Gd^+ or Gd^{+2} in the molten chloride could be related to a high $\Delta H_{fus.}(GdCl_{1.6})$, e.g. the location of the eutectic near $GdCl_3$ could indicate that the inherent, hypothetical melting point for $GdCl_{1.6}$ should be much higher than that of the trichloride.

The free energy of the reaction



was calculated from the liquid composition at the peritectic

temperature at 632° to be only -42 cal., assuming unit activities for the solids and an ideal solution.

B. Proposals for Future Research

The magnetic moments of the GdI_2 and particularly the $\text{GdCl}_{1.6}$ should be determined to aid in the assignment of oxidation states. A single crystal X-ray study may be the best way to resolve oxidation state assignments, molecular weight, and reasons for the stability of the $\text{GdCl}_{1.6}$.

The nature of the magnetic coupling in the GdI_2 may be of interest to those working with magnetic phenomena but it is not of immediate interest to the study of metal halide-metal systems.

The nature of the unexplained thermal halts in the GdI_3 -Gd phase diagram might be revealed by a high temperature X-ray investigation. This technique could also be used to determine the high temperature forms of GdI_2 , GdI_3 , and YI_3 .

Electrical conductivities of the melts would be helpful to indicate the mode(s) of solution. Eventually the solution theories must explain this conductivity with regard to both structure and mechanism. The GdI_3 -Gd melt would be expected to be similar to the electron conducting LaI_3 -La and CeI_3 -Ce melts, and it would be interesting to know the extent of electronic conduction in the YI_3 -Y melt. The low metal solubility in the GdCl_3 -Gd system would make it a poor system to study

by this means.

Phase diagrams of the halides of the remaining rare earth metals should be determined. Certainly not enough is known yet to predict what they will look like. The trend for the solubility of the light rare earth metals in their molten chlorides would indicate that the solubility of the metal should increase from gadolinium to lutetium. The small solubility of gadolinium in its molten trichloride indicates that this solution behavior may go as predicted. On the other hand the formation of solid lower chlorides cannot be predicted. Since solid $\text{GdCl}_{1.6}$ exists it is not impossible that other solid lower chlorides of unusual stoichiometry may exist. The estimated lattice energy for MCl_3 increases regularly from LaCl_3 through LuCl_3 , but the same should be true for lower chlorides from gadolinium to lutetium unless a structure change causes a large change in the Madelung constant or in other ways affects the thermodynamic lattice energy. Similar lattice energy considerations would apply to the diiodides keeping in mind the differences between metallic and ionic diiodides.

Finally, even the nature of the GdBr_3 -Gd phase diagram cannot be predicted except that the metal solubility in the melt will probably be between 2 and 14%. The possible existence and nature of a lower bromide is debatable.

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VII. APPENDIX

Table 3. X-ray powder diffraction data for $\text{GdCl}_{1.6}$

d (obs.) Å	d (calc.) Å	hkl	Intensity ^a
Lattice constants: $a_0 = 8.98 \text{ \AA}$, $b_0 = 7.22 \text{ \AA}$, $c_0 = 6.72 \text{ \AA}$			
8.97	8.96	100	2
7.22	7.22	010	4
4.95	4.92	011	1
3.78	3.81	210	L 1
	3.74	201	
3.377	3.368	002	2
3.300	3.317	211	L 1
3.128	3.150	102	LL 1
3.043	3.047	012	L 1
2.996	2.998	121	LL 1
	2.997	300	
2.898	2.886	112	LL 1
2.753	2.768	310	LL 1
	2.736	301	
2.698	2.692	202	L 1
2.464	2.459	022	10
2.358	2.373	122	3
2.251	2.245	400	1
	2.242	003	

^aL 1 means less than 1 and LL 1 means much less than 1.

Table 3. (Continued)

d (obs.) Å	d (calc.) Å	hkl	Intensity
Lattice constants: $a_0 = 8.98 \text{ \AA}$, $b_0 = 7.22 \text{ \AA}$, $c_0 = 6.72 \text{ \AA}$			
2.125	2.131	401	LL 1
	2.122	230	
1.983	2.005	203	1
	1.956	032	
1.892	1.901	322	LL 1
	1.878	330	
1.799	1.805	040	1
	1.796	500	
1.716	1.711	141	L 1
1.647	1.652	104	LL 1
	1.643	430	
	1.640	033	
1.631	1.637	014	L 1
1.570	1.573	204	LL 1
	1.567	142	
1.546	1.549	512	LL 1
	1.547	340	
	1.540	233	
1.526	1.523	024	LL 1

Table 3. (Continued)

d (obs.) Å	d (calc.) Å	hkl	Intensity
Lattice constants: $a_0 = 8.98 \text{ \AA}$, $b_0 = 7.22 \text{ \AA}$, $c_0 = 6.72 \text{ \AA}$			
1.498	1.502	124	LL 1
	1.499	242	
	1.498	600	
1.450	1.451	522	LL 1
1.434	1.439	333	LL 1
	1.438	514	
	1.433	611	
1.268	1.272	630	LL 1
	1.268	215	

Table 4. X-ray powder diffraction data for GaI_2

d (obs.) Å	d (calc.) Å	hkl	Intensity ^a
Lattice constants: $a_0 = 8.67 \text{ Å}$, $c_0 = 5.75 \text{ Å}$			
7.43	7.51	100	3
3.759	3.754	200	1
2.875	2.875	002	7
2.498	2.502	300	8
2.285	2.285	202	2
2.033	2.027	221	1
1.878	1.877	400	10
1.659	1.650	321	2
1.577	1.588	213	1
	1.577	411	
1.380	1.378	421	4
1.287	1.291	332	L 1
	1.282	214	
	1.281	323	
1.274	1.272	422	5
1.217	1.223	601	LL 1
	1.221	512	

^aL 1 means less than 1 and LL 1 means much less than 1.