ANOMALOUS VALENCE AND PERIODICITY WITHIN THE RARE EARTH GROUP

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INTRODUCTION

Overemphasis of the fact that the rare earths are uniformly trivalent has been largely responsible for the somewhat slow development of new methods for the separation of these elements. It is indeed remarkable that, until recently, almost all separations have been carried out under conditions such that all these elements were in the trivalent state. Consequently the compounds showed such slight differences in chemical and physical behavior that a large investment of time and labor was necessary in order to attain even slight success in their separation.

Recent developments in this field have shown that, while the elements may be trivalent under most conditions, variable valence is the rule rather than the exception. The application of such variations has not yet been fully worked out in many cases. It is to be expected, however, that when such applications are perfected the rare earth separations will offer only slightly more, and in some cases even less, difficulty than the separation of certain other rare elements one from the other.

A thorough survey of the literature seems to show that some investigators had early believed that valences other than three were shown by most of the rare earths. Until recently, however, such ideas were far from popular among chemists active in the work with this group of elements. It is certain that many of the early investigations were carried out unknowingly on somewhat impure materials, and this may be in some measure responsible for many of the more startling results. Unfortunately this tendency to work with impure materials, mainly through ignorance, is still with us; the literature bears frequent testimony to numerous cases in which this has been done. Results obtained by working with such materials must be applied to pure compounds with much care and circumspection.

Recently, however, certain earths have been found to possess very well developed "anomalous" valences. A stimulus, supplied by such important discoveries, appears to have been given to the work of prediction, verifica-

121

tion, and application of other such variable valences among the members of the group.

It is firmly believed by the writer that the application of these "anomalous" valences will, in time, bring about a revolution in the standard rare earth separation methods and will, by reducing labor and increasing efficiency, make easily available reasonable amounts of pure compounds of each of these interesting elements.

<center>HISTORICAL</center>

<center>*1. Lanthanum*</center>

In 1886 Cleve (23, 24) obtained, by means of hydrogen peroxide oxidation of lanthanum hydroxide in ammoniacal solution, an oxide which when analyzed after previous drying, showed a composition very close to La_4O_9. The same product, when damp, apparently had the formula La_2O_5. To Cleve it was not clear whether the increase in weight was in reality due to an oxidation or merely to the presence of hydrogen peroxide of crystallization. Melikoff and Pissarjewski (72) obtained $La_2O_5 \cdot nH_2O$ by hydrogen peroxide oxidation in an alkaline solution in a similar manner.

The high temperature ignition of the sesquioxide in air brought about a distinct increase (7.4–12.03 per cent) in weight, which led Kolthoff and Elmquist (59) to calculate the formulas La_2O_5 and La_2O_7 for the higher oxides. The work was repeated by Jantsch and Wiesenberger (50), however, who obtained at most a 0.5 per cent change in weight on heating La_2O_3 in air to very high temperatures. Ephraim (29) and Zschiesche (127) expressed the belief that lanthanum oxide does not absorb oxygen unless cerium is present. Marc (67) and Meyer and Koss (78) also commented on the catalytic effect of cerium on the absorption of oxygen by lanthanum oxides. On the other hand, early work by Cleve (22)—probably with impure materials—tended to show that La_2O_3 absorbed oxygen at red heat.

Higher sulfides have been prepared by Biltz (5), and by Klemm, Meisel, and von Vogel (55). The first investigator prepared LaS_2 by heating the sulfate in a stream of hydrogen sulfide. At temperatures above 600°C. the compound breaks down, giving La_2S_3 and S. It yields hydrogen persulfide with acids and apparently has the structure $La_2S_3 \cdot S$ and is a "polysulfide." These results would seem to be confirmed by the magnetic susceptibility measurements of Klemm, Meisel, and von Vogel, whose data show that no increase in valence occurred during the reaction.

The work of Andrieux (1) has shown the existence of borides of lanthanum and other earths having the well-defined formulas MB_6. These were prepared by the electrolysis of fused borate and fluoride mixtures in graphite crucibles. These compounds, like the various aluminides, stan-

nides, thallides, plumbides, cuprides, etc., of Rossi and others (7, 31, 32, 53, 81, 95, 112), of such formulas as $LaAl_4$, $PrSn_3$, $LaTl_3$, $LaPb_3$, $CeCu_2$, etc., are, in all likelihood, compounds into which enter the peculiarities of the "metallic bond." Such compounds will not be considered here.

Moissan (79), Petterson (87), and Damiens (26) have prepared the carbide LaC_2, resembling MgC_2. Damiens, however, was of the opinion that the compound had the structure

$$\begin{matrix} C & & C \\ \mathop{|\!|\!|}\limits_{C}\!\!\!\diagdown\!\! La\!-\!La\!\diagup\!\!\mathop{|\!|\!|}\limits_{C} \end{matrix}$$
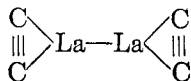
and that the metal was here tri- or tetra-valent and not divalent.

Some evidences of a valence lower than three for lanthanum have appeared. One is that of the hydrides prepared by Winkler (118), by Zhukov (126), and by Sieverts and Gotta (101). In these cases hydrides have been prepared which on analysis consistently give a ratio less than 3:1 for H:La. Sieverts and Müller-Goldegg (102) believed, however, that the volumes of hydrogen absorbed by the cerium group metals vary quite widely and depend on temperature and pressure conditions. Another line of evidence is that recently presented by Jantsch, Skalla, and Grubitsch (47). These investigators treated anhydrous lanthanum chloride with hydrogen at high temperatures. The following reactions apparently occurred:

$$2LaCl_3 + H_2 \rightarrow 2LaCl_2 + 2HCl$$
$$3LaCl_2 \rightarrow La + 2LaCl_3$$
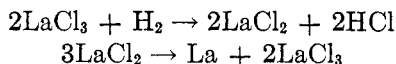
The metallic lanthanum then alloyed with the gold dish in which the reaction took place. If indeed the reactions postulated by these investigators actually represent what has taken place, then the possession of a valence of two by this element must be recognized.
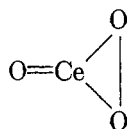
2. Cerium

Both trivalent and tetravalent cerium compounds were known early in the history of the rare earths, the higher valence compounds being particularly characteristic. Cerium was until recently assigned to a position in Group IV of the Periodic System. In this position it presented certain anomalies, and on the discovery of hafnium was definitely relegated to its more natural position among the Group III elements.

In addition to the valences of three and four, it has often been suggested that a valence of six was shown by cerium when highly oxidized in alkaline solution. De Boisbaudran (27) confirmed the opinion of Cleve (23), who had announced the formation of "perceric hydroxide" on oxidizing $Ce(OH)_3$ with hydrogen peroxide in ammoniacal solution. This compound both investigators believed to be a derivative of CeO_3. Von Knorre (114),

Job (51), Mengel (74), Pissarjewski (88), and Meloche (72) have studied similar compounds. Mengel has used such compounds, obtained by the use of sodium peroxide as a precipitating agent, for the separation of cerium from lanthanum and didymium. Meloche prepared "perceric carbonates" and investigated in particular the method of combination of the oxygen and its availability in both acid and basic solutions. Much of the available oxygen was shown to be of the peroxide type. Schwarze and Geise (97) reported a dark red precipitate, analyzed as $CeO_3 \cdot 2H_2O$, formed by the action of ammonium hydroxide and hydrogen peroxide on cerium nitrate. This compound reduced permanganate according to the reaction:

$$5CeO_3 + 13H_2SO_4 + 2KMnO_4 \rightarrow$$
$$5Ce(SO_4)_2 + 2MnSO_4 + K_2SO_4 + 13H_2O + 5O_2$$
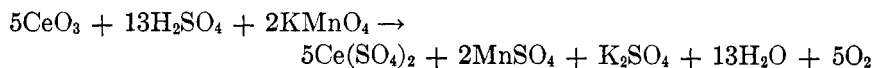
They regarded the compound, however, as a peroxide having the structure

$$O=Ce\Big\langle\!\!\begin{array}{c} O \\ | \\ O \end{array}$$

and not as a representative of hexavalent cerium. Lejeune (62) proved that the change was from Ce(III) to Ce(IV) only, but believed that Ce(VI) could exist.

Wyrouboff and Verneuil (122) have reported a white oxide, Ce_3O_4.

The unusual compound CeC_3, prepared by reduction of the oxide with sugar charcoal at a high temperature in an electric furnace was described by Damiens (25) as a red powder. Similar work had been carried out by Sterba (108) and had resulted in the formation of an oxycarbide (or a mixture of carbide and oxide) of the formula $Ce_3O_4C_2$. Damiens believed that the red crystals contained both CeC_3 and Ce_2O_3 and that they resulted from the following reactions:

$$2CeO_2 + C \rightarrow Ce_2O_3 + CO$$
$$Ce_2O_3 + 9C \rightarrow 2CeC_3 + 3CO$$
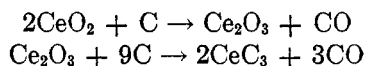
The compound reacted when treated with water or when more strongly heated:

$$2CeC_3 + H_2O \rightarrow Ce_2(OH)_6 + 3C_2H_2$$
$$CeC_3 \rightarrow CeC_2 + C$$
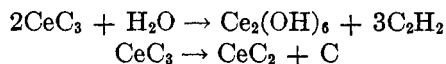
Sterba's compound reacted less readily with water. The carbide CeC_2 has been described by Hirsch (34) and by Moissan (79).

Borides similar to those described under lanthanum have been reported by Andrieux (1).

Biltz (4) subjected ceric sulfate to the action of hydrogen sulfide at elevated temperatures. The sulfide Ce_2S_4 resulted. It reacts with hydrochloric acid to give hydrogen disulfide, and decomposes at 720°C. to give the sesquisulfide and sulfur. It would appear from these results that the compound is a polysulfide. The same compound, prepared by Klemm, Meisel, and von Vogel (55), yielded magnetic susceptibility results which would tend to show it to be a polysulfide and not a true disulfide.

On dissolving the highly oxidized hydrated oxide of cerium in concentrated hydrochloric acid an intense red color is obtained. According to James and Grant (41) this solution contains $CeCl_4$, stable in concentrated acid. Koppel (60) had also prepared this compound and had studied its double salts.

The colors reported for CeO_2 and its reduction products have brought about a great deal of discussion in the literature. Sterba (107, 108) studied these oxides in some detail. His work has shown that CeO_2 is of a pale yellow color, the shade varying somewhat according to the method of preparation. On reduction of the oxide by various means certain interesting color changes resulted. By hydrogen reduction at 600°C. an indigo-blue, non-pyrophoric material—stable when completely dry but readily oxidized in moist air—was obtained. Reduction at higher temperatures gave a black, pyrophoric material, believed to contain some finely divided metal. By means of zinc reduction Sterba obtained a bluish mixture, but cadmium apparently will not reduce the ceric oxide. Meyer (40) obtained results somewhat different than those of Sterba by getting an olive-green intermediate reduction product which, on further treatment with hydrogen, became black and pyrophoric. On glowing in air the black material yielded a yellow mass of CeO_2. Similar results were reported by Bunsen (17). Rammelsburg (93) obtained a loss of 4.7 per cent on igniting CeO_2 in hydrogen. Winkler in a similar manner obtained an oxide $Ce_2O_3 \cdot 4CeO_2$, a pyrophoric compound (119); similar substances have been reported by Brauner (9). Chase (20), by decomposing the oxalate at 550°C. in atmospheres of pure hydrogen or nitrogen, obtained a bluish-black residue which he believed was a mixture of Ce_2O_3, Ce_2O_4, and C. When hydrogen was used the compound was pyrophoric. Burger (18), by reduction of ceric oxide with calcium, obtained an olive-green residue probably similar to the blue and green mixtures obtained by the other investigators. Sterba and Meyer believed that their colored oxide was to be represented by the formula Ce_4O_7. Apparently it is a mixture of Ce_2O_3 and CeO_2.

Brauner (12) outlined the controversy over the color of CeO_2. He believed the oxide was of a pale chamois color if pure, in which opinion Neish

concurred (83). Spencer, however, has prepared CeO_2 which is white if ignited at low temperature and yellowish if strongly ignited (103). It was believed by Wyrouboff and Verneuil (121) that polymers of CeO_2 were responsible for the differences in color obtainable by various treatments of the same sample. They have reported para-oxides, meta-oxides, and other polymorphic forms.

It would appear from the investigations considered that: (1) CeO_2 when pure is of a pale chamois color, but the color may vary somewhat owing to methods of precipitation and temperature of ignition. (2) Reduction of CeO_2 results in the formation of certain darker colored oxides or mixtures of oxides. (3) Pyrophoric compounds may be formed by the most drastic reduction. The formation of some finely divided metal is a possibility in these cases. (4) Compounds in which cerium is hexavalent may exist.

3. Praseodymium

Much discussion in the literature has centered around the higher oxides of praseodymium. As early as 1865 it was noticed by Herman (33) that a "super-oxide" could be prepared, and that it yielded chlorine when treated with hydrochloric acid. The oxide Di_4O_9 or Di_2O_5 was reported by Cleve (23, 24) as having been prepared by hydrogen peroxide oxidation of "didymium" hydroxide in ammoniacal solution.

When praseodymium oxalate or the sesquioxide is ignited in air a mixture of oxides is obtained. Some higher oxide is present. The formula of this product has been the subject of much controversy. Schottlander (96), Meyer and Koss (76, 78) (by reduction and reöxidation data), and more recently Brinton and Pagel (15) and Prandtl and Huttner (91) have shown that Pr_6O_{11} is the ignition product over a wide temperature range. The last investigators believe that the constitution of the oxide is to be represented by the formula $2Pr_2O_3 \cdot Pr_2O_5$ and consider it to be a praseodymium praseodymate. Jantsch and Wiesenberger (50), while concurring with the formula, believe the substance to be merely a mixture of Pr_2O_3 and PrO_2.

Brauner has conducted extensive research upon the oxides of praseodymium (10). From specific gravity and molecular volume considerations he has deduced the formula of the compound to be Pr_4O_7 or Pr_5O_9. He prefers the latter formula and believes it to be the product formed when Pr_2O_3 and Pr_2O_4 react with the latter acting as an acidic oxide. By ignition of the nitrate or by fusion of the oxide with alkali nitrates, however, he obtained an oxide of jet-black color which he believed was Pr_2O_4. His recent work substantiates his earlier claims (11). By fusing $Pr(NO_3)_3$ with sodium and potassium nitrate he was able to prepare Pr_2O_4 and, by leaching the melt with water, to separate every trace of lanthanum from

the praseodymium. Auer (2) has obtained the formula Pr_4O_7 for the ignition product of the oxalate when heated in the air.

The belief that the product may vary considerably in oxygen content, as is generally held at the present time, was put forward early in the discussion by von Scheele (115). There seems to be some evidence also that oxygen may be lost by drastic heat treatment, only to be regained on cooling.

The almost black dioxide has been prepared in a practically pure condition by Brinton and Pagel (16).

A compound Pr_2S_4 has been prepared by Biltz (5, 6) by passing hydrogen sulfide at high temperatures over the anhydrous sulfate. Higher temperatures bring about the formation of the sesquisulfide by loss of sulfur. Previously, Howe (37) commented on the oxysulfide, PrO_2S, prepared by this means. Howe believed that $Pr_2S_3 \cdot S$ resulted only in the presence of cerium, which acted as an inductor; he has suggested this as a very delicate test for the presence of cerium in praseodymium compounds. Levy (63) reports that the oxysulfide has the formula $PrSO_3$.

Moissan (79) has prepared PrC_2 similar to the analogous compounds of lanthanum and cerium.

No compounds in which praseodymium has a valence lower than three would seem to have been prepared. Matignon and Cazes (70) were unable to reduce $PrCl_3$ by heating in an atmosphere of hydrogen at 1000°C. However, Spencer (104) has called attention to the fact that the hydride, prepared by heating the metal in hydrogen, contains insufficient hydrogen to correspond to the formula PrH_3.

4. Neodymium

In the presence of cerium as an activator, neodymium oxide and oxalate on strong ignition in the air appear to be oxidized to higher-valenced compounds. Such results have been put forward by Meyer and Koss (78), and by Marc (67). These investigators have claimed that NdO_2 or Nd_2O_4 is formed under these conditions. Brauner has commented on the oxide Nd_2O_5 as well as Nd_2O_4, and apparently believes that neodymium also can show a valence of six (10, 11). More recently (13) he has proved the formula Nd_2O_4 by heating the oxide in hydrogen and collecting the water obtained. The weight of the oxide Nd_2O_3 obtained and the weight of the oxygen calculated from the weight of the water gave the ratio Nd_2O_3: $O = 1:1$. He prefers the doubled formula Nd_2O_4 rather than NdO_2 for the oxide.

Waegner (116) ignited the oxalate in oxygen and reported the formation of Nd_4O_7 which decomposed, on heating to higher temperatures, into Nd_2O_3. His results have lately been disputed by Garnier and coworkers (30, 52)

who, by means of reflection spectra, have shown the compound formed to be $2Nd_2O_3 \cdot 2H_2O$ and not Nd_4O_7; Hitchcock (35), during a rare earth study, obtained color changes of neodymium oxides which he interpreted to show the formation of Nd_4O_7.

The carbide, NdC_2, has been prepared by Moissan (80) and by Matignon (68). According to the former it is not reducible by hydrogen at red heat, reacts with chlorine to give anhydrous chlorides, and is, in general, very similar to the corresponding compounds of the other rare earths.

Several investigators have prepared and worked with the hydride. Muthmann and Beck (81) and Matignon (68, 69) obtained results showing less than three atoms of hydrogen per metal atom.

Matignon and Cazes (70) believed that the chloride should be reducible to a dichloride in a stream of hydrogen. They were unable to bring about this reaction, however, even at a temperature of 1000°C.

Jantsch, Skalla, and Grubitsch (47) have reported some evidence in favor of a valence lower than three for neodymium. The triiodide was first dehydrated and then treated with hydrogen at high temperatures. By continued heating in a silica boat some silicon was obtained. The following reactions have been proposed:

$$2NdI_3 \rightarrow 2NdI_2 + I_2$$
$$3NdI_2 \rightarrow Nd + 2NdI_3$$
$$4Nd + 3SiO_2 \rightarrow 2Nd_2O_3 + 3Si$$
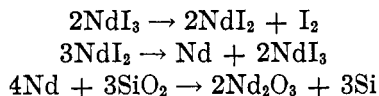
By using a gold container, neodymium–gold alloys were obtained, very clearly suggesting that the above reactions actually represent what has taken place and that neodymium can, under certain conditions, be divalent.

5. Samarium

The work of Cleve (24) has shown the possibility of samarium compounds in which the metal shows a valence higher than three. The compounds apparently indicated were Sm_2O_5 and Sm_4O_9. During a study of samarium compounds Cleve endeavored to oxidize Sm_2O_3 by heat treatment alone (23); in this, however, he was unsuccessful.

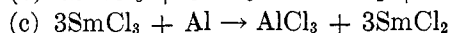The carbide SmC_2 has been prepared by Moissan (79).

While the higher valence compounds of the element are, mainly, of doubtful nature and unimportant, the samarous compounds are well defined and of extreme importance, practically and theoretically.

Matignon and Cazes (70, 71) discovered that samaric chloride could be reduced by means of hydrogen, ammonia, or aluminum to samarous chloride. Using a Jena glass apparatus they found that reduction (with hydrogen) started at a temperature below the melting point, when the chloride became dark colored. The dichloride is of a deep red-brown

hue. It is always somewhat contaminated with oxychloride owing to the reactions:

$$2SmCl_3 + O_2 \rightarrow 2SmClO + 2Cl_2$$
$$2SmCl_2 + O_2 \rightarrow 2SmClO + Cl_2$$
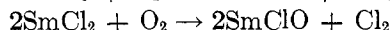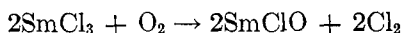
The dichloride resulted apparently from reactions such as the following:

(a) $SmCl_3 + \frac{1}{2}H_2 \rightarrow SmCl_2 + HCl$
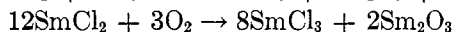
(b) $6SmCl_3 + 8NH_3 \rightarrow 6SmCl_2 + 6NH_4Cl + N_2$

(c) $3SmCl_3 + Al \rightarrow AlCl_3 + 3SmCl_2$
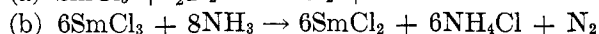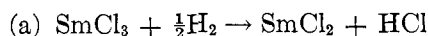
Reaction b is slower than a but, owing to the fact that it is not reversible, is preferable; reaction c must be carried out in an atmosphere of hydrogen.

The samarous chloride is insoluble and does not react with benzene, toluene, chloroform, pyridine, or absolute alcohol. In air it undergoes the following reactions:

$$2SmCl_2 + 2H_2O \rightarrow 2SmClO + 2HCl + H_2$$
$$6SmCl_2 + 3H_2O \rightarrow 4SmCl_3 + Sm_2O_3 + 3H_2$$
$$12SmCl_2 + 3O_2 \rightarrow 8SmCl_3 + 2Sm_2O_3$$

In a similar way Prandtl and Kogl (92) prepared samarous chloride and samarous bromide; the latter has a color darker than that of the chloride. When porcelain dishes were used to contain the samaric chloride being reduced (by hydrogen or ammonia), reduction of the silica took place and silicon resulted. Similarly when platinum dishes were used the higher temperatures used by these investigators caused metallic samarium to be formed, and alloys with the platinum resulted. The phenomenon is probably to be explained by the reactions:

$$3SmCl_2 \rightarrow 2SmCl_3 + Sm$$
$$4Sm + 3SiO_2 \rightarrow 2Sm_2O_3 + 3Si$$
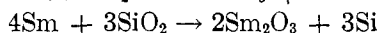
Jantsch, Ruping, and Kunze (45) obtained samaric chloride by passing chlorine with sulfur monochloride over the heated oxide. After dehydration with hydrogen chloride it was reduced to samarous chloride by heating in a stream of hydrogen and ammonia. The dark color obtained when even traces of samarium were present suggests this as a method to show the presence of small amounts of this element in other rare earths. The dichloride so obtained was soluble in water but extremely unstable, even in an atmosphere of hydrogen. Its decomposition (as formerly commented on) was rapid in the presence of acid. The investigators showed the dichloride to be insoluble in liquid ammonia, sulfur dioxide, and hydrogen cyanide as well as in stannic chloride, phosphorus trichloride, phosphoryl chloride, and sulfuryl chloride. It was insoluble in alcohols,

ketones, amines, and esters, but slightly soluble in molten lithium or sodium chloride.

Jantsch and Skalla (46) prepared samarous iodide by the thermal decomposition of samaric iodide in a high vacuum:

$$SmI_3 \rightarrow SmI_2 + I_2$$
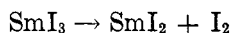
The diiodide gives a deep Bordeaux-red solution more stable than that of the dichloride; it slowly decomposes, however, yielding hydrogen and a colorless solution. By double decomposition reactions Jantsch and Skalla were able to prepare samarous chromate, phosphate, and sulfate, all of which are only slightly soluble. Samarous sulfate is a bright orange-yellow salt, soluble with decomposition in dilute acids. The diiodide decomposed on heating according to the following reaction, which commenced at 560°C:

$$3SmI_2 \rightarrow 2SmI_3 + Sm$$

The writer has been unable to reduce samarium trichloride in dilute sulfuric acid solution by the electrolytic method using a mercury cathode and high current densities.

Klemm and Rockstroh (56) obtained the molecular volumes and melting points of the dichloride and iodide and compared them with their data for the similar properties of the trihalides. The melting points of the dihalides are, as would be expected, the higher in each case.

6. Europium

In 1911 Bourion and Urbain discovered (8) the new compound europous chloride, $EuCl_2$. This was prepared by the reduction of europic chloride by hydrogen. The white amorphous material dissolved in water without noise or residue and gave a fairly stable solution. In the hot, however, the following reaction occurred:

$$12EuCl_2 + 3O_2 \rightarrow 8EuCl_3 + 2Eu_2O_3$$
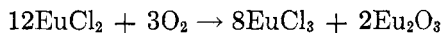
These investigators also attempted to reduce EuOCl with hydrogen at red heat. They obtained, however, only an insignificant loss of weight; EuO apparently cannot be prepared in this way.

Jantsch, Alber, and Grubitsch (42) prepared europous chloride and europous iodide, and have shown that the triiodides are easier to reduce than the trichlorides. Europous iodide is a brownish green, almost black, in color; its solutions, however, are colorless and quite stable, giving only a slight evolution of hydrogen. The solution is a great deal more stable than the solution of the corresponding samarium compound. Europic iodide has so great a tendency to decompose that these investigators

found it impossible to prepare it in the anhydrous condition by means of the action of hydrogen iodide and hydrogen on the hydrated salt. However, it was found that the best method for the preparation of europous iodide from europic iodide was to heat a mixture of the latter hydrated salt and ammonium iodide in a stream of the gases mentioned above.

Yntema (124) discovered the fact that europic chloride might be reduced electrolytically to europous chloride at the surface of a mercury cathode. In the presence of sulfate ion europous sulfate was precipitated. The colorless salt was fairly stable and could be filtered out, thus enabling an excellent separation of europium to be made from other rare earths which remained in solution.

W. E. Pearce (84) was able to reduce europic chloride in dilute sulfuric acid solution using a platinum, rather than a mercury, cathode. Attempts to prepare europous chromate by electrolytic reduction of europic chromate were unsuccessful. He was able, however, to reduce the higher chloride by means of magnesium, aluminum, and iron; in each case the powdered metal was merely slowly sifted into a solution of the chloride in water to which a small amount of sulfuric acid had been added. In attempts to obtain reduction with stannous chloride, ferrous sulfate, hydrazine sulfate, hydroxylamine sulfate, and hypophosphorous acid negative results were obtained.

7. Gadolinium

No compounds of gadolinium in which the metal shows an anomalous valence have been prepared. However, the work of Jantsch, Skalla, and Grubitsch (47) has shown that the following reactions may be brought about under sufficiently drastic treatment:

$$2GdCl_3 + H_2 \rightarrow 2GdCl_2 + 2HCl$$
$$3GdCl_2 \rightarrow Gd + 2GdCl_3$$
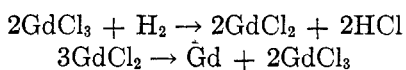
The gadolinium metal so formed then alloyed with the gold dish in which the reaction took place. These reactions, supported as they are by parallel cases in which elements known to show divalence react in an exactly similar way, show clearly that under some conditions gadolinium may have at least a transitory valence of two.

8. Terbium

Urbain and Jantsch (111) have investigated the higher oxides of terbium. According to these investigators low temperature ignition yields the dark brown to black oxide Tb_4O_7, while temperatures greater than 1600°C. break down this compound with the loss of oxygen. Urbain had earlier (110) obtained the dark brown oxide on ignition of the oxalate, and

a black oxide when the sulfate was decomposed. James and Bissel (40) prepared a black oxide, apparently Tb_4O_7, by ignition of the oxalate. Levy (64) believes that in this case, because of the remarkable presistence of the color given to a mixture of oxides by only a trace of terbium, salt formation is very probable. No experimental evidence, however, has been offered in support of this view.

Potratz (89) reported a carbide, TbC_3. This was obtained when the formate or acetate was ignited in a closed crucible. No analyses of the product were reported.

7. Dysprosium

Urbain and Jantsch (111) were unable to oxidize Dy_2O_3 by strongly heating in oxygen, nor were they able to reduce it by heating in an atmosphere of hydrogen to very high temperatures. Klemm and Schuth (58) were unable to reduce dysprosium trichloride with hydrogen at high temperatures.

Jantsch, Jawurek, Skalla, and Gawalowski (43) have investigated the halides of the terbium and erbium groups. They were able to obtain no lower-valence compounds of dysprosium, but did obtain small amounts of the metal by heating the triiodide in a high vacuum in the proximity of fresh barium metal similarly heated. The results were interpreted to mean merely that the vapor of the triiodide had reacted with the barium, and not that any lower-valence compound had been obtained.

8. Holmium

The great rarity and difficulty of separation of holmium has prevented any very thorough investigation of its compounds; no valences other than that of three have been suggested for this element.

9. Erbium

Cleve (23, 24) believed that erbium formed the oxide Er_2O_5 in addition to the normal sesquioxide Er_2O_3. He had also previously announced (23) his preparation of the oxide Er_4O_9. It is extremely likely that his materials were quite impure. No recent investigator has confirmed this discovery. Klemm and Schuth (58) were unable to reduce the trichloride, and Jantsch and coworkers (43) have obtained no evidence of an anomalous valence for this element.

10. Thulium

Jantsch, Skalla, and Grubitsch (48), while working with the halides of thulium and lutecium, could isolate no divalent compounds resulting from high temperature treatment of the trihalides with hydrogen. Metallo-

graphic and analytical examination of the gold dishes used in the experiments indicated, however, that some dihalide had been present, since its decomposition was the only tenable explanation for the presence of thulium–gold alloy within the dish.   That the gold itself had no influence on the formation of the rare earth metal was clearly proved by the fact that the same reaction took place when porcelain boats were used, except that, in these cases, some silicon dioxide was reduced by the metal.   A further evidence for the formation of some thulous chloride was believed to be the dark color of the higher salt after treatment for a certain length of time in the hydrogen stream.   The investigators believe that thulous chloride, like divalent samarium compounds, is very dark in color.   The existence of more than a very small amount of thulous chloride was, however, not shown by the analyses.   The fused salt after cooling gave only a slight evolution of hydrogen when treated with water.   They were also unable to prepare thulous iodide, although all indications seemed to show that the reactions had been similar.

While thulous sulfate would be expected to be insoluble like samarous sulfate, it would appear from experimental work by the author that Tm^{+++} is extremely difficult to reduce electrolytically in aqueous solution.
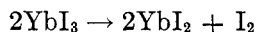
11. Ytterbium

In 1929 Klemm and Schuth (58) announced the preparation of ytterbium dichloride, by the reduction of anhydrous ytterbium trichloride with hydrogen.   The material was heated for six hours at 600–620°C. and for half an hour at 850–900°C. in the hydrogen stream.   The dichloride obtained was light grey, almost white; the water solution, however, was yellowish green.

Ball and Yntema (3) extended the method of the latter for the separation of europium (124) and were able to precipitate $YbSO_4$ from aqueous solution by reducing Yb^{+++} to Yb^{++} in dilute sulfuric acid solution.   The same method has been used by Prandtl (90) to prepare pure ytterbium, and by the author (85) for the thorough separation of ytterbium from thulium and from lutecium fractions.   These investigators have all commented on the reaction of the yellowish green $YbSO_4$ with the dilute acid as soon as the current is cut off:

$$2YbSO_4 + 2H^+ \rightarrow 2Yb^{+++} + 2SO_4^{--} + H_2$$
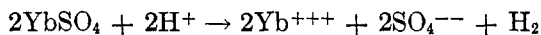
The author and coworkers (86) have shown that the form of the $YbSO_4$ precipitate may be varied from fine crystalline needles to coarse spheres by means of controlled reduction conditions.   The latter form is highly advantageous for use in the separation of ytterbium, as its reaction with dilute acid is negligible.

Jantsch, Skalla, and Jawurek (49) have shown that ytterbium triiodide if heated in vacuum above 500°C. reacts quickly according to the equation:

$$2YbI_3 \rightarrow 2YbI_2 + I_2$$

The diiodide is black by reflected light but by transmitted light is red in the central portions of the mass and almost colorless through the edges. At 250°C. ytterbium triiodide commences to split off halogen strongly; the reaction begins for the bromide at 700°C. and for the chloride at 870°C. The same investigators have prepared the dichloride; they found, however, that it was best prepared by hydrogen reduction. The dichloride dissolved in water to give the yellow-green solution and slowly evolved hydrogen. The reaction

$$3YbCl_2 \rightarrow Yb + 2YbCl_3$$
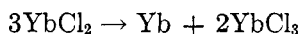
prevented the determination of the melting point of this compound. The dibromide is described as being of a golden yellow color.

12. Lutecium

Jantsch, Skalla, and Grubitsch (48) obtained the same reactions for lutecium halides as for the corresponding thulium compounds. That is, all the evidence pointed toward the intermediate formation of a dichloride which, when heated strongly, decomposed to form the metal and the trichloride. Lutecium dichloride is, however, probably white.

Klemm and Schuth (58) have commented on the effect of lutecium dichloride as an impurity on their results obtained when measuring the magnetic susceptibility of ytterbous chloride.

The recent work of Jantsch and Klemm (44) has not ascribed a definite valence of two to any of the elements lanthanum, gadolinium, or lutecium; this is, in all probability, due to the fact that while evidence points to the intermediate formation of lower-valence compounds, these have not yet been obtained in such a state as to permit their analyses and a study of their properties.

PERIODICITY IN VALENCE

It was probably R. J. Meyer who first pointed out that a periodicity in properties existed among the members of the rare earth group (77). He believed in the uniform trivalency and great similarity of lanthanum, gadolinium, and lutecium and placed them together in Group III of the Periodic Table; the remaining earths were distributed among groups following the third. More recently Brauner and Svagr have attacked the problem of the relative basicities of the rare earths (14). They considered the influence of the hydrolysis of the sulfates on the inversion of sucrose

and on the hydrolysis of methyl acetate. Gadolinium was found, by this method, to have a basicity close to that of lanthanum. Brauner has therefore placed the former element under lanthanum in his arrangement of the rare earths in the Periodic Table in order to bring out this relation. Both Meyer and Brauner believe that the rare earth group is well placed when the members are spread out across the Table. Such an arrangement certainly throws most of these elements into unnatural groupings with the common elements, and suggests relations in their chemical properties which do not appear to exist. Both investigators seem to ignore the fact that the periodicity shown by their measurements is *among the rare earths themselves*. This periodicity does not necessitate that a close relation exist between the members of the rare earth group on the one hand and the remaining elements in the system on the other, and should not then be used as a justification for the spreading out of the group which, in the opinion of the author, confuses rather than clarifies the basis for such grouping.

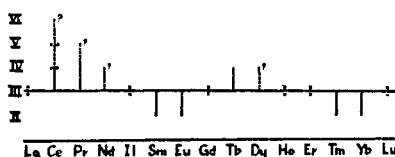Recently published work by Sherwood and Hopkins (99), who also sum-

FIG. 1. Anomalous valence within the rare earth group

marized previous measurements on the relative basicity of the rare earths, does not show this relation between gadolinium and lanthanum. Their results, however, agree in general with those previously obtained by other investigators. It would appear that the measurements of Meyer and of Brauner are complicated by the entrance of other unknown factors.

Von Hevesy (113) presented a schematic diagram which exhibited the tetravalent tendencies of cerium, praseodymium, and terbium as well as the fact that samarium and europium could show divalence. The later discovery by Klemm and Schuth (58) of the divalence of ytterbium allowed this element to be added to the diagram (54, 57). As filled out by Klemm, the diagram also shows a possible tetravalence for dysprosium and divalence for thulium. In figure 1 is shown such a schematic diagram. Here certain valences are questioned; their existence must be regarded as still not conclusively proved. If the series shown in the figure is examined it can be seen that, with respect particularly to valence, *"every eighth element resembles the first."* Thus we have the following groupings.

1. Lanthanum, gadolinium, and lutecium

None of these three shows any permanent, well developed valence other than the normal one of three. From the point of view of the electronic structure of the atom lanthanum, No. 57 (2, 8, 18, 18, 8, 3), would certainly be expected to be trivalent only. There is no tendency for an electron of the kernel to leave a completed shell and become a valence electron. Gadolinium, No. 64 (2, 8, 18, 18 + 7, 8, 3), apparently possess a comparatively stable structure, and lutecium, No. 71 (2, 8, 18, 18 + 14, 8, 3), marks the close of the fourth quantum group with its full quota of 32 electrons. Lutecium also, owing to its completed kernel, would be expected to show no tendency toward a valence other than two. If, however, the results of Jantsch and coworkers be construed to show a transitory divalence for lanthanum, gadolinium, and lutecium, the resemblances still stand, in whatever manner the existence of these extra valences be explained electronically.

The discussion by Clark (21) also brings out the similarity between these three elements, showing, as it does, the close relation of their normal spectral terms.

2. Cerium and terbium

Sidgwick (100) has reasoned that cerium, No. 58 (2, 8, 18, 18 + 1, 8, 3), shows its additional valence of four, owing to its possession in the fourth quantum group of an extra electron which may be rather easily removed. When the loss of this electron takes place a reversion to the stable inner structure of lanthanum is brought about. Thus also, it might be reasoned, does terbium, No. 65 (2, 8, 18, 18 + 8, 8, 3), show tetravalence by a reversion to the gadolinium kernel. But the extra valence in this case is not as well-marked as that of cerium, owing to the fact that the tendency to revert to the gadolinium structure is not as strong as that of cerium to revert to the structure of lanthanum. The carbides CeC_3 and TbC_3, previously described, heighten the similarity between these two elements, whatever type of valence is present in these compounds.

3. Praseodymium and dysprosium

Praseodymium, No. 59 (2, 8, 18, 18 + 2, 8, 3), which has two extra electrons over the number possessed by lanthanum, can lose one of these and show tetravalence. Here, however, the only tetravalent compound so far obtained is the oxide; this fact may be taken to show the lesser stability of praseodymic than ceric compounds. It would, of course, be expected on the above reasoning that praseodymium should show a valence of five. The compounds of Brauner and others may represent this tendency. In the case of dysprosium, related to praseodymium as ter-

bium is to cerium, a valence of four is expected.   Urbain and Jantsch (111) were unable to obtain even the oxide Dy_2O_4.   The oxide Dy_2O_5 was announced by Cleve, but criticism of the material and other interpretations of the results might be offered.

4. Neodymium and holmium

These two elements, as far as can be stated at the present time, show no similarities in valence relationships.   Brauner and others firmly believe in the tetravalence of neodymium under some conditions, but insufficient work has been done with pure holmium compounds to allow of any comparison.   No evidence we have points to any valence other than three for the latter element.

5. Illinium and erbium

The great rarity of illinium has so far precluded any detailed study of its properties.   In the case of erbium it would appear that no anomalous valences are shown.

6. Samarium and thulium

Samarium, No. 62 (2, 8, 18, 18 + 5, 8, 3), can show a valence of two, and apparently thulium, No. 69 (2, 8, 18, 18 + 12, 8, 3), can also under some conditions.   Hughes and the author (38) have expressed as their opinion, based on magnetic susceptibility measurements, that the extra electron, left behind when divalence is shown in cases such as this of samarium, is in some manner repressed and is associated more closely with the 4_4 orbital group.   This might be construed as a tendency for the samarium kernel to become as nearly as possible like that of gadolinium.   Very similar conclusions on this point have recently been published by Selwood, who clearly expresses his ideas in a valuable contribution (98).   He refers to this tendency as "a striving to reach the normal condition of lanthanum, gadolinium, or lutecium" desirable "because these three elements alone are in S states, they have no multiplet structure, the orbital component of magnetic moment in each is lacking."   Of course this reasoning again appears somewhat at a loss, since it would apparently call for thulium, No. 69 (2, 8, 18, 18 + 12, 8, 3), to show a greater tendency toward divalence than does samarium, because lutecium has a more stable electronic configuration than that of gadolinium.   But work to date would certainly show that samarium has a "stronger" valence of two than has thulium. It must be admitted, however, that existent methods of determining the "strength of the tendency" to show these anomalous valences are far from good.   They depend merely upon the apparent ease with which the anomalous compound is obtained and upon its stability.   The periodicity in

basicity shown by the results of Brauner and of Meyer is probably in some way connected with these phenomena. Electrochemical measurements conducted on such elements in anomalous valence states should supply invaluable data for the clarification of these difficulties.

7. Europium and ytterbium

Europium, No. 63 (2, 8, 18, 18+ 6, 8, 3), is very readily reduced to divalence. The tendency to retain the gadolinium kernel is strong. In a similar way ytterbium, No. 70 (2, 8, 18, 18 + 13, 8, 3), is easily reduced, and the dry ytterbous salts are fairly stable. The extra electron, not being used in valence forces, apparently becomes associated with the others in
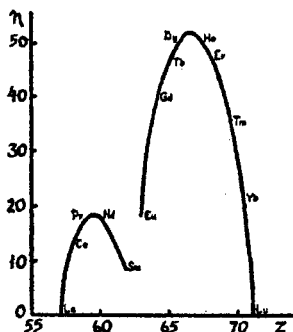

Fig. 2. Magnetic susceptibilities of the rare earths

the fourth quantum group, increasing it in effect to the completed number of 32.

MAGNETISM AND VALENCE

The great paramagnetism of the rare earth metals and their compounds is one of their outstanding properties. The use of the magnetic balance, in addition to providing a means of identification and a test of purity for these elements, has thrown considerable light on their electronic structure and the changes undergone by the various atoms on reduction and oxidation. It has enabled several problems to be solved, partially at least, which would by any other means be exceedingly difficult to attack.

Zernike and James (125) summarized previous measurements of the paramagnetism of the rare earths and compared them with their own results. These values are, in general, in good concordance with those calculated by Hund (39) on the assumption that the number of electrons in the 4_4 orbital group varies from zero in the case of lanthanum to fourteen for lutecium.

In figure 2 is shown the discontinuous curve obtained by plotting the magnetic susceptibility against the atomic number (109).

The results of St. Meyer (106) and of Cabrera (19) show that the sus-

ceptibility values of ceric and praseodymic compounds fall in close proximity to those of the corresponding lanthanum and cerous compounds, respectively. In a similar way the work of Klemm and Rockstroh (56) brings out the fact that the susceptibility of a samarous compound is near that of the corresponding europic compound. Klemm and Schuth (57, 58) have determined the susceptibility of a sample of somewhat impure ytterbous chloride. They believe that the divalent ytterbium ion is diamagnetic.

Hughes and the author measured the susceptibilities of certain europous, europic, ytterbous, ytterbic, and gadolinium compounds (38). The results, when considered along with those of previous investigators, are seen to bear out the law that *the susceptibility of a rare earth ion in a valence of four approaches that of the ion of atomic number one less in the valence of three; also the susceptibility of a rare earth ion in a valence of two approaches that of the ion of one greater atomic number in the valence of three.* The recent work of Selwood (98) adds confirmation to this view. These facts can only be interpreted to mean that on reduction for instance, the third electron—that one not in use for valence forces—is suppressed and becomes closely associated with the 4_4 orbital group. Obviously it is that same inner group which is affected on oxidation and is forced to give up an electron for valence uses. We thus arrive at electronic structures for certain of the rare earth ions as shown in table 1.

The usefulness of magnetic susceptibility measurements has already been mentioned. Klemm, Meisel, and von Vogel (55) actually used this principle when they proved that the compound Ce_2S_4 was a polysulfide of trivalent cerium rather than a simple sulfide of tetravalent cerium. This was shown to be the case as the susceptibility was the same as that of Ce_2S_3. According to the principle stated in the last paragraph, if there had been a valence change there would have been a large change in the magnetic susceptibility, since the sulfide of quadrivalent cerium should have the same susceptibility as La_2S_3. These considerations indicate that Ce_2S_4 is a cerous compound with a possible structure

$$S{=}Ce{-}S{-}Ce\diagup\begin{matrix} S \\ | \\ | \\ S \end{matrix}$$
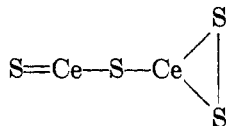
whereas if it were a ceric compound it might have a structure

$$S{=}Ce\diagup\begin{matrix} S \\ \diagdown \end{matrix}Ce{=}S$$
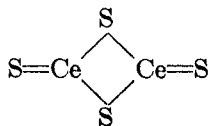
COLOR AND VALENCE

Since the rare earth atoms differ, as far as orbital electrons are concerned, apparently only in the fourth quantum group, it would be expected that the colors are mainly due to the degree of incompleteness of this shell. Color relations, then, might be expected to be periodic just as are anomal-

TABLE 1

Electronic structures of certain rare earths in various valence states

ATOMIC NUMBER	ELECTRONS IN KERNEL	ION	K	L	M	N	O	P VALENCE ELECTRONS
57	54	La $^{+++}$	2	8	18	18	8	3
58	54	Ce $^{++++}$						4
58	55	Ce $^{+++}$	2	8	18	18 + 1	8	3
59	55	Pr $^{++++}$						4
59	56	Pr $^{+++}$	2	8	18	18 + 2	8	3
62	59	Sm $^{+++}$	2	8	18	18 + 5	8	3
62	60	Sm $^{++}$	2	8	18	18 + 6	8	2
63	60	Eu $^{+++}$						3
63	61	Eu $^{++}$	2	8	18	18 + 7	8	2
64	61	Gd $^{+++}$						3
65	61	Tb $^{++++}$						4
65	62	Tb $^{+++}$	2	8	18	18 + 8	8	3
66	62	Dy $^{++++}$						4
66	63	Dy $^{+++}$	2	8	18	18 + 9	8	3
69	66	Tm $^{+++}$	2	8	18	18 + 12	8	3
69	67	Tm $^{++}$	2	8	18	18 + 13	8	2
70	67	Yb $^{+++}$						3
70	68	Yb $^{++}$	2	8	18	18 + 14	8	2
71	68	Lu $^{+++}$						3

ous valence relations, the latter so evidently owing to this shell and its gradual increase from 18 to 32 electrons. Lanthanum and gadolinium, cerium and terbium, praseodymium and dysprosium, etc., should be similarly colored. That this is not the case is shown by the last pair and many succeeding pairs in which the elements are first and eighth.

The origin of the colors of the rare earth ions is obscure. They have, however, generally been assumed to be due to the incompleteness of this 4_4 orbital group, where also the highly variable and large paramagnetic forces presumably arise (61, 105). Also Yntema (123) has put forward his opinion that the colors originate in this level. He was led to this conclusion by a study of the absorption bands of the various ions and their apparently regular shift toward higher frequency with increase in atomic weight.

Again, reasoning from the kernel structures as derived from magnetic susceptibility measurements, we might expect the ceric ion to be the same color, or very nearly the same color, as the lanthanum ion, praseodymic as cerous, samarous as europic, europous as gadolinium, and ytterbous as lutecium. These colors are certainly not similar in any instance. But in

TABLE 2

Colors of certain rare earth ions in normal valence states

La^{+++} 57	(Colorless).................................(Colorless)	71 Lu^{+++}
Ce^{+++} 58	(Colorless) ....(Colorless)	70 Yb^{+++}
Pr^{+++} 59	(Irish green) ....(Apple green)	69 Tm^{+++}
Nd^{+++} 60	(Red to violet) ....(Rose-red)	68 Er^{+++}
Il^{+++} 61	(Probably yellow) ....(Yellow)	67 Ho^{+++}
Sm^{+++} 62	(Pale yellow)................................(Yellow)	66 Dy^{+++}
Eu^{+++} 63	(Pale pink)................................(Colorless)	65 Tb^{+++}

Gd^{+++} 64 (Colorless)

each case except that of europium, the element when in the anomalous valence state is more highly colored than when in the normal valence condition. In the words of G. N. Lewis (65), "we may still say that a colorless substance is converted into a colored substance by a loosening of the electronic structure." The compounds of the rare earths in anomalous valence are more unstable electronically than are the compounds of these elements in the normal valence state, and one outward expression of this instability is increased color. This view is quite in keeping with all our experimental evidence bearing on this problem.

Other facts, however, enter to complicate the question of color and its origin. These facts consist of two relationships which can be pointed out.

1. Let us compare the color, first of the extreme members of the group, then of the second with the second from the last, and so on. We arrive at the data shown in table 2.

This color sequence was discussed by Main Smith (66). He believed that the relation was due to the fact that, after deducting 54 (the number of planetary electrons in the normal xenon atom) from the number of planetary electrons in the rare earth ion, one of two similarly colored ions has as many electrons more than zero as the other has less than fourteen. Thus Nd^{+++}, for example, has 57 electrons, less 54 gives 3; for Er^{+++}, $14 - (65 - 54) = 3$. The full significance of this relation is still not apparent but, on the face of it, it means that in the N shell the number of electrons increases from $18 + 0$ in lanthanum to $18 + 14$ in lutecium, and that two subgroups of the rare earths may be considered to exist, the one from lanthanum to gadolinium inclusive, the other from gadolinium to lutecium inclusive. Gadolinium is therefore common to both subgroups. The color sequence, however, can still not be considered as explained.

2. The colors of bivalent rare earth ions show an interesting resemblance to the colors of the trivalent ions of the elements which immediately

TABLE 3

Colors of bivalent rare earth ions

ATOMIC NUMBER	ION	COLOR	COLOR	ION	ATOMIC NUMBER
61	Il^{+++}	Yellow?	Orange-yellow	Sm^{++}	62
62	Sm^{+++}	Pale yellow	Colorless	Eu^{++}	63
68	Er^{+++}	Rose-red	Brick-red?	Tm^{++}	69
69	Tm^{+++}	Green	Green	Yb^{++}	70

precedes. This relationship is shown in table 3. The evidence for the brick-red color of Tm^{++} was obtained by the author in one experiment during attempts to reduce Tm^{+++} by means of high current densities on a mercury cathode. Attempts to obtain this color in other experiments by the same method were unsuccessful, but no explanation other than that mentioned above seems adequate.

VALENCE AND SEPARATIONS

It was pointed out in the introduction that rare earth separations were tedious, time-consuming, and wasteful because, in general, the methods employed were of such a type that they perforce dealt with elements which were in the same valence state and hence were chemically similar in the extreme. This difficulty of separation and purification is, without doubt, itself the chief reason why better methods have not been developed! Recently the pure compounds have become more available; materials which it has taken years to prepare offer opportunities of research which often

result in the discovery of new properties and new and better separation methods. In the case of only a very few of the fifteen elements need it now be said that their rarity is the biggest factor in the difficulty of preparing them. An examination of the "intermediate fractions" in any rare earth laboratory would reveal that it is the inefficient separation methods and not the rarity of the elements that causes the trouble in most cases.

Rolla and Fernandez (94), from a study of the solubilities of the double magnesium and double manganese nitrates of the earths of the cerium group, evolved an exceedingly ingenious separation method. The solubility of the pure double manganese and double magnesium nitrates in water increases with increasing atomic number; however, the solubility, in the solid state, of a double manganese nitrate in the corresponding double magnesium salt was found to decrease with increasing atomic number. Therefore crystallization of a mixture of these double salts of the cerium group rapidly concentrated the earths of higher atomic number in the liquor and soluble end of the series, and the earths of lower atomic number in the crystals and insoluble end. This, however, is still but a fractional method.

It was discovered quite early in the history of the group that cerium could be removed most easily from the other elements by oxidizing it to tetravalence and precipitating it in that state. Various oxidizing agents such as potassium bromate, potassium permanganate, chlorine, etc., have been used. The most efficient method, however, is probably that of electrolytic oxidation, perfected by Neckers and Kremers (82). The sulfate or nitrate solutions are electrolyzed and a soluble phosphate is added after anodic oxidation has taken place, whereupon ceric phosphate is precipitated. The rare earths may be rendered cerium-free in one operation, but the gelatinous phosphate occludes much of the mother liquor and the precipitate must be treated several times to prepare pure cerium compounds.

Electrolytic reduction methods for the separation of highly pure europous and ytterbous sulfates have already been mentioned. It would be a valuable addition to rare earth methods if samarium could be separated in a like manner. It seems probable that the use of solvents other than water might bring about the desired result.

Brauner (13) has introduced the method of fusion with potassium nitrate, often used for the removal of traces of cerium, to the separation of praseodymium and neodymium. He has claimed that, under temperature control, oxidation of the praseodymium to tetravalence takes place and that a good separation of the resulting Pr_2O_4 from the $Nd(NO_3)_3$ may be obtained by extracting the melt with water.

Willard and Fowler (117) undertook the separation of mixtures of cer-

tain rare earths by a partial thermal decomposition of the sulfates followed by leaching with water. They first determined the products formed in such decompositions and the dissociation pressures of the pure anhydrous sulfates at definite temperatures. The attempt was then made to maintain the partial pressure of the sulfur trioxide above the heated, mixed isomorphous sulfates at a value intermediate between those of the constituents and thus cause a complete decomposition to the insoluble oxide of the one compound without affecting the other, remaining as the soluble sulfate. Following these principles a separation of cerium from the other earths was obtained, owing to the fact that the cerous sulfate ignited easily to ceric oxide, while the other rare earths remained as the trivalent sulfates. A partial separation only of praseodymium from lanthanum was possible, as the sulfate of the former ignited only partially to the higher-valence oxide and as only that which was oxidized was separable. In attempting to separate rare earths which when ignited did not tend to oxidize no success was obtained, owing to the fact that the salts, being isomorphous, gave solid solutions the dissociation pressures of which were intermediate between those of the pure constituents. Thus the decomposition products themselves formed solid solutions and no great solubility differences between the constituents existed. Very similar work has recently been carried out by Wohler and Flick (120).

The separation of terbium has always been accomplished only with very great difficulty. This is due not so much to its great rarity, although it is one of the least abundant of the rare earths, but largely to its position in the group and its proximity to the abundant gadolinium on the one side and to the rare dysprosium on the other. If indeed the peculiar compound TbC_3 can be prepared, it is very likely that a better method for the separation of terbium is at hand. Thus the oxide will in all probability be extractable from the carbide, or vice versa. Certainly the method would be only fractional, and its application to the preparation of cerium by taking advantage of the compound CeC_3 would be no improvement over the present efficient methods, but there may be here at hand a welcome method for the separation of terbium.

Kalischer and the author, in unpublished work, have determined the temperatures at which certain rare earth nitrates lose some and all of their molecules of water of crystallization. When some mixtures of such carefully heated, partially dehydrated nitrates are extracted with anhydrous ether at low temperatures, separations are obtained. Some of these have been reported by Hopkins and Quill (36). It seems probable that the ease of dehydration depends in some way upon the ability of the element in question to exhibit anomalous valence, probably because there is a variation in the strength of coördination valences holding the water molecules.

It is also extremely likely that the degree of dehydration affects the solubility in ether.   The full meaning of the experimental data at hand has not yet been worked out.

In the newer chemistry of the rare earths—the chemistry of the "anomalous valences"—much still remains to be done, in spite of the great contributions of Jantsch, Klemm, and others, both abroad and in this country. The study of this group is not exhausted; indeed it still presents many problems that are fresh and new, and that challenge the ingenious mind to devise methods of attack.

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