STUDIES ON THE RARE EARTHS

by

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A Thesis submitted in Partial Fulfillment of
The Requirements for the Degree of

MASTER OF ARTS

in the Department
of

CHEMISTRY

The University of British Columbia

SEPTEMBER, 1942

Accepted on behalf of the
Department of Chemistry.

Head of the Dept. of Chemistry.
FOREWORD

This investigation was undertaken originally with the intention of attempting to synthesize organometallic rare earth derivatives, i.e., compounds of those elements with alkyl or aryl radicals, involving a direct metal-carbon linkage. For further detail, the reader is referred to the author's 1940 thesis submitted to the U.B.C. Dept. of Chemistry, in partial fulfillment of the requirements for the Bachelor of Arts degree.

A preliminary survey of relevant literature, together with early experiments, brought to light several problems which the author considered could only confuse subsequent inexperienced investigators, and hence deemed expedient to eliminate before proceeding with the main investigation. Experimental study was made of the following:

1. Elimination of cerium from rare earth mixtures.
2. Preparation of anhydrous rare earth bromides.
3. Quantitative determination of mixtures of rare earth elements in their salts.

Suggested methods of synthesizing rare earth organometallic compounds, with a discussion of the unsuccessful attempts made at the University of Illinois have also been included.

The author gratefully acknowledges the generous advice of Dr. J. Allen Harris rendered in the supervision of this research. I am also indebted to Dr. L.F. Audrieth for his many helpful suggestions, and for his account of parallel investigations at the University of Illinois. Thanks are due to the University of Illinois Dept. of Chemistry for supplying the rare earth oxides used in this investigation.
Following are the three mixtures used:

X : mainly La₂O₃, with small amounts of Nd₂O₃ and PrO₂.

Y : Nd₂O₃, with traces of PrO₂ and Sm₂O₃.

Z : 60% La₂O₃ + 40% PrO₂, with traces of Nd₂O₃ and Sm₂O₃.

Subscript _₁ denotes presence of varying amounts of Ce, as in X₁, Y₁, Z₁.

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Sept., 1942.

University of B.C.
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STUDIES ON THE RARE EARTHS

I. SEPARATION OF CERIUM.

Rare earth materials used in the research laboratory generally consist of oxide mixtures, the first step in the resolution of which is the removal of cerium. The great majority of current methods employed for the separation of cerium involve oxidation to the tetravalent state, wherein the element manifests properties sharply distinguishing it from other rare earth elements. Some of the more important methods are mentioned by Neckers and Kremers, others by Mellor, and by Levy. In the following, two such processes have been examined with a view to increasing their efficiency.

A. Bromination.

The method of treating a suspension of rare earth oxides in KOH solution with Cl₂ was first employed by Mosander. Subsequent workers have described parallel use of Br₂ and I₂. Several repetitions of the process were found necessary to completely remove cerium.

Experimental

1. 5g. oxide X₁ was simmered with 3ml. Br₂ + 100 ml. H₂O till Br₂ fumes ceased to evolve. The hot mixture was filtered, the residue washed with a little cold H₂O and the washings united with the filtrate. This treatment was repeated 6x.

The filtrates were united and concentrated to 25 ml. Spectrum examination revealed the same heavy absorption bands characteristic of the original oxide in both the concentrate and in HNO₃ solution of the residue. However, on treatment with H₂O₂ + dilute NH₄OH, the concentrated filtrate gave a negative test for Ce, whilst the HNO₃
solution of the residue showed a higher concentration of Ce than did the original oxide.

A sample of oxide $X_1$ subjected to the same treatment reacted in a like fashion.

2. 5g. oxide $X_1$ were refluxed 12 hours with 10 ml. $Br_2$ + 300 ml. $H_2O$ in a pyrex apparatus equipped with ground joints (500 cc. flask, surmounted by 5 - 30 cm. condensers). After cooling, the mixture was filtered and 25 ml. of the filtrate set aside for spectroscopic examination. The filtrate and residue were returned to the flask with 5 ml. more $Br_2$ and refluxed for an additional 12 hour period. Considerable amounts of $Br_2$ remained at the end of the period. The cold mixture was filtered and 25-ml. of the filtrate set aside for spectroscopic examination.

The absorption spectrum lines of both filtrates were of the same approximate density indicating that no appreciable solvation had occurred during the second refluxing. An $HNO_3$ solution of the residue showed the same absorption spectrum, indicating solvation to be incomplete. The filtrates gave negative tests for Ce whilst the $HNO_3$ solution of the residue gave a stronger Ce test than the original oxide mixture.

A sample of oxide $X_1$ subjected to the same treatment reacted in a like fashion.

3. 5g. oxide $X_1$ were refluxed 2 hours with 5 ml. $Br_2$ and 300 ml. $H_2O$. After cooling, concentrated $NH_4OH$ was added dropwise until the brown color of $Br_2$ just disappeared. Refluxing was continued 1½ hour more, then the mixture was cooled, filtered, and the filtrate evaporated to 25 ml.
As before, the filtrate showed the absorption spectrum lines of the original oxide, but in this instance also gave a positive Ce test. The HNO₃ solution of the residue behaved in the same manner.

4. 5g. oxide \( X_1 \) was refluxed 2 hours with 5 ml. Br₂ and 300 ml. \( H_2O \). 25 ml. 49% aqueous HBr were then slowly added and refluxing continued 1/2 hour longer. The mixture was cooled, filtered, and the filtrate evaporated to 25 ml.

The filtrate showed the usual absorption spectrum, and also gave a positive Ce test. An HNO₃ solution of the residue gave a positive Ce test but showed no absorption spectrum.

5. 7.5g. oxide \( X_1 \) were placed in an alundum thimble which was seated atop a 1'' length of 1'' diameter glass rod in a pyrex Soxhlet extractor, equipped with \( F \) joints and surmounted by 3 - 30 cm. condensers. 6 ml. Br₂ were carefully poured into the thimble and 300 ml. \( H_2O \) into the flask and heating commenced with an electric hotplate.

The author found that if the Br₂ were initially mixed with the \( H_2O \) in the flask, it tended to condense in the extractor body, falling to the bottom and entering the siphon tube, where by virtue of its higher density, the \( H_2O \) subsequently distilling over flooded above the thimble and ran down the vapor inlet tube.

Unless heating was carefully regulated, too rapid condensation of water occurred, with ensuing overflow of the thimble. Further, excessive ebullition of Br₂ therein tended to eject the solid into the extraction liquor; therefore, the optimum quantity of Br₂ must be experimentally found. Due to the fine porosity of the alundum
thimble, extraction proceeded at a very slow rate, siphoning occurring once every hour with the above precautions. It was necessary to add a little Br₂ from time to time to offset losses sustained through volatilization.

After 12 hours, extraction was discontinued. The walls of the extraction flask were coated with a pale yellow gummy residue and the extraction liquor was turbid. The liquor was filtered, and the fine precipitate thus obtained washed back into the flask, where addition of a few cc. 48% HBr produced a clear solution. Since both the filtrate and the HBr solution gave negative tests for Ce, they were united and evaporated to 25 ml. The resultant solution, pale green in color, due to presence of small amounts of Pr, showed the same absorption spectra as that of the original oxide.

The apparatus was cleaned thoroughly and the residue remaining in the thimble was reextracted with Br₂ + H₂O for 12 hours more. The extraction liquor, treated as before, resembled that of the first extraction in appearance, absorption spectrum and test for Ce.

As a small portion of the residue remaining in the thimble still showed absorption bands on spectroscopic examination of its HNO₃ + H₂O₂ solution (indicating presence of undissolved Pr, Nd, and necessarily La), extraction was continued for a further 15 hours with fresh quantities of Br₂ + H₂O. Once again, the extraction liquor gave a negative Ce test and exhibited the characteristic absorption spectrum. However, an HNO₃ + H₂O₂ solution of the residue from the thimble showed no absorption spectrum, thereby indicating complete solvation of all earths but ceria.
A sample of oxide $Y_1$ treated in the same manner behaved in a similar fashion.

The method was abandoned because of the slow speed of filtration through the alundum thimble and lack of a satisfactory substitute.

6. With the object of developing a rapid extraction process, the following apparatus was devised:

1. 3-50 cm. condensers.
2. 1 graduated inlet tube.
3. 1 extraction flask.
4. 1 adapter.
5. 1 - 3 legged glass cup, 30 cm. long.

The extraction flask was constructed from a l.L. pyrex erlenmeyer, pyrex tubing and a pyrex 8 joint. The extraction cup consisted of a pyrex tube, sealed at one end, with 3 short lengths of 7mm. tubing blown into the sealed end for drainage purposes. Use of 3 condensers served to minimize extensive loss of $Br_2$ otherwise sustained through volatilization.

A ball of glass wool was packed into the base of the cup and sprinkled lightly with acid-washed asbestos. The ease of flow was tested by filling the cup with $H_2O$ and noting the drainage rate. A fairly fast flow is desirable yet sufficient asbestos must be present to prevent subsequent passage of the rare earth oxides.

Calculations were made on the assumption that solvation of the oxides proceeded on the basis of the following equations, based upon the reactions of other metal oxides.
APPARATUS FOR AQUEOUS BROMINE EXTRACTION OF RARE EARTH OXIDES.
La\textsubscript{2}O\textsubscript{3} + 5Br\textsubscript{2} \rightarrow LaBr\textsubscript{3} + La(OBr)\textsubscript{3}

3La(OBr)\textsubscript{3} \rightarrow La(BrO\textsubscript{3})\textsubscript{3} + 2LaBr\textsubscript{3}

or 3La\textsubscript{2}O\textsubscript{3} + 9Br\textsubscript{2} \rightarrow La(BrO\textsubscript{3})\textsubscript{3} + 5LaBr\textsubscript{3}

Cerium remains in the tetravalent state as insoluble Ce(OH)\textsubscript{4}.

10g. oxide \( X_1 \) were placed in the cup and washed to the bottom with the aid of a wash bottle. When the drainage was too slow, or when the oxide tended to pass through the asbestos pack, the material was removed, and a new pack prepared, as previously described, until a satisfactory one was obtained. 6 ml. Br\textsubscript{2} (excess over theoretical) and 500 ml. H\textsubscript{2}O were placed in the extraction flask, the apparatus assembled as shown, and heating commenced over a Meker burner whose flame was so adjusted to permit steady extraction without overflow of the cup.

Extraction was continued for 12 hours, after which the extraction liquor was treated with a few ml. 48\% HBr to dissolve the gummy suspensoid and evaporated to 25 ml. in a beaker. Tests performed on the resultant solution showed complete absence of Ce, but showed the usual absorption spectrum.

The residue remaining in the cup was dissolved in H\textsubscript{2}O\textsubscript{2} + concentrated HNO\textsubscript{3}. The clear solution obtained thereby showed no absorption spectrum and gave a heavy brown precipitate on treatment with NH\textsubscript{4}OH + H\textsubscript{2}O\textsubscript{2}, thus indicating it consisted wholly of Ce(OH)\textsubscript{4} free of other rare earths.

The apparatus was considered unsatisfactory due to the trouble involved in preparing a satisfactory asbestos filter for use in the extraction cup. See discussion for suggested improvements.

7. The extensive work of Prandtl, Rauchenberger and Losch\textsuperscript{5}
has shown that rare earth oxides are soluble in solutions of ammonium salts, to an extent varying according to the conditions employed. It was thought that such treatment combined with simultaneous halogenation might permit rapid separation of Ce from the other earths, by means of reactions expressed by the following equations:

\[
4La_2O_3 + 6NH_4Br + 9Br_2 \rightarrow 8LaBr_3 + 12H_2O + 3N_2
\]

\[
4La_2O_3 + 6NH_4NO_3 + 9Br_2 \rightarrow 2La(NO_3)_2 + 6LaBr_3 + 12H_2O + 3N_2
\]

These equations are based upon the fact that solutions of ammonium salts are slowly oxidised by Br\(_2\) with release of N\(_2\) gas.

As a rough qualitative test, the procedure outlined in the following was carried out. 15g. oxide \(X\) + 25g. \(NH_4NO_3\) (excess) was simmered gently with 100 ml. \(H_2O\) + 7ml. \(Br_2\) (excess) until most of the \(Br_2\) had vaporized. The hot mixture was filtered and evaporated to 25 ml. The residue was washed with a little \(H_2O\), dried in a hot air oven at 130\(\circ\), weighed (8g.) and dissolved in concentrated \(HNO_3 + H_2O_2\).

Both the filtrate and the solution of the residue showed the usual absorption spectrums on spectroscopic examination; however, whilst the residue solution gave a heavy brown flocculent precipitate with \(NH_4OH + H_2O_2\), the filtrate gave only a faint yellow coloration, indicating relatively good elimination of Ce.

Lack of time did not permit further investigation along this line.

**Discussion.**

Contrary to the ideas of early investigators, it is evident from the foregoing that an alkaline medium is not an essential pre-requisite for separation of ceria from congener earths by bromination.
The acidity of the hot Br₂ - H₂O mixture is sufficient to dissolve La, Pr, Nd, Sm, etc., but does not affect tetravalent Ce. It is apparent that reaction involves equilibria expressed by the equations:

\[
\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOB}_2 + \text{H}^+ + \text{Br}^-
\]

\[K_{eq} = 5.8 \times 10^{-9}\]

\[
\text{HOB}_2 \rightleftharpoons \text{H}^+ + \text{OBr}^-
\]

\[K_{eq} = 2.06 \times 10^{-9}\]

In the hot solutions employed, equilibria are predominately to the left due to decreasing solubility of Br₂ with rising temperature. Further, as the earths are dissolved to form bromates and bromides (cf. equations, p.6), the increasing value of [Br⁻] displaces equilibria to the left and solvation is brought to a standstill. For this reason, refluxing can not be expected to result in complete separation of Ce from other rare earth elements, whereas extraction, involving removal of the products formed from the sphere of action, should do so. Such has been shown experimentally true. However, the extraction apparatus herein employed is impractical due to the time and precautionary measures required. It is suggested that sintered glass thimbles used with the apparatus described under section § might yield worthwhile results. Lack of same prevented further study in this direction.

Solvations of Ce noted under section § is due to the formation of ammonium salts, solutions of which dissolve rare earth oxides. Introduction of HBr into the aqueous Br₂ medium induces similar solvation of Ce due to the high [H⁺].

The alundum thimbles employed for the Soxhlet extractions are unaffected by Br₂ + H₂O, as shown by blank runs performed under the conditions already described.

The result of the qualitative test of reaction between rare earth oxides, Br₂, ammonium salts and H₂O indicate that further
study along this line would be advantageous. The quantity of NH$_4$NO$_3$ employed was almost twice that required by the equation, hence the very slight solvation of Ce, due to the action of NH$_4$NO$_3$ solution on CeO$_2$ (as shown by Prandtl et al$^6$) is to be expected. However, it is evident that the presence of ammonium salts in the reaction mixture produces a considerable increase in the rate of solvation of the other earths, due to formation of a volatile product, without materially affecting CeO$_2$.

It is suggested that the study of extraction methods be extended to rare earth carbonates, sulfates, phosphates, and also to sparingly soluble organic salts.

B. Phosphate Precipitation.

Neokers and Kremers$^1$ developed a satisfactory method for quantitative separation of Ce from congener earths in acid solution by addition of a soluble phosphate to a slightly acid solution containing Ce(NO$_3$)$_4$, whence Ce precipitates completely as ceric phosphate, leaving the other rare earths in solution as the nitrates. The oxides, which have first been ignited to ensure maximum conversion to CeO$_2$, are dissolved in sufficient concentrated HNO$_3$ to give 5% free acid upon subsequent dilution to a 10% rare earth content. Sodium phosphate solution is slowly added at 80°C until precipitation is complete. The filtrate is further treated with excess sodium phosphate and titrated with K$_2$MnO$_4$ until oxidation of Ce to the tetravalent form and removal as phosphate is complete. By this means, Neokers and Kremers succeeded in reducing the Ce content of the filtrate to 0.02%.
Experimental.

Oxides X₁, Y₁ and Z₁ were treated according to the method of Neckers and Kremers with the following variations.

1. The free acid content of the dilute rare earth nitrate solutions was reduced to 4%.

2. The temperature of admixture of the rare earth nitrate and sodium phosphate solutions was raised to 90-95°C.

Coprecipitation of up to 20% of the other rare earths with Ce, as fine phosphate precipitates which filtered only with considerable difficulty resulted. However, the nitrate filtrate of the other earths gave absolutely no coloration when a 5cc. portion was treated with dilute NH₄OH + H₂O₂, thereby indicating removal of all Ce.

Discussion

Neckers and Kremers noted that 5% free HNO₃ sufficed to prevent precipitation of all rare earths but Ce⁴⁺ as phosphates. Their inference that reduction of this acid content would cause coprecipitation of other earths is herein found true experimentally. The higher temperature of admixture of the solutions employed by the author probably favors such precipitation. One obvious advantage of the described changes of procedure is that the Ce content of the final filtrate is reduced to < 0.00008%, the value of the sensitivity of the hydrogen peroxide test for Ce⁴⁺.

The endpoint of the titration of Ce³⁺ to Ce⁴⁺ with KMnO₄ solution is reached slowly and is frequently vague, when sodium phosphate is employed for precipitation. The finding⁹ that H₃PO₄, used as the precipitation agent, permits rapid attainment of a sharp endpoint can be advantageously applied.
II. SYNTHESIS OF ANHYDROUS RARE EARTH BROMIDES.

Since anhydrous metallic bromides are frequently employed as initial reagents in the preparation of organometallic compounds, it was necessary to investigate current modes of synthesizing these salts of the rare earth elements. Most of the methods described in the literature involve elevated temperatures, and are unsatisfactory for making large quantities of anhydrous rare earth bromides. Further, the technique required is usually elaborate and time consuming. Frequently, the products are contaminated with varying quantities of the oxybromides.

Three representative methods have been studied in the following.

At

Sulfur Monochloride Process.

Bourion prepared anhydrous rare earth bromides by passage of dry HBr + S₂Cl₂ over the oxides at temperatures slightly below red heat.

Experimental.

Some assistance was given by the author to D.B. Tonks and to R.R. Shinobu, who studied Bourion's Process in partial fulfillment of the requirements for their Bachelor of Arts degrees at the U.B.C. in 1940 and 1941 respectively. The interested reader is referred to their theses for details of the experiments carried out.

Discussion.

Bourion's Process was found unsatisfactory in this laboratory for synthesis of anhydrous rare earth bromides for the following reasons:
Conversion of the oxides to the bromides was incomplete under conditions prescribed by Bourion.

Contamination of the products with $H_2O$ and $S$ frequently occurred unless the most rigid precautions were exercised.

Quartz apparatus used in the process was badly eroded and often vitrified by the action of unconverted rare earth oxides at higher temperatures.

Further study of the method was not attempted.

B. Sublimation Process.

Reed, Hopkins and Audrieth successfully obtained anhydrous rare earth chlorides and bromides by heating a mixture of rare earth oxides with an excess of the corresponding ammonium halide to 200°C until the reaction mixture was completely water soluble. The remainder of the ammonium salt was then removed by vacuum sublimation at 300-320°C. Partial hydrolysis to the basic salts does not occur during the processing by virtue of the fact that the excess ammonium halide, acting as a strong acid in accordance with the Brönsted concept, produces favorable displacement of the equilibrium given by:

$$La_2O_3 + 6NH_4Br \rightarrow 2LaBr_3 + 3H_2O$$

Experimental.

Following is a modification of the apparatus designed by Reed, Hopkins and Audrieth for vacuum sublimation of the free ammonium bromide, (diagramatic form).

The reaction mixture is placed in the 500 ml. pyrex flask equipped with S.T. 29/42 joints. This flask is inserted in furnace
(Cenco Multiple Unit, 18 amps., 115 volts, with built in rheostat), and other parts of the apparatus are assembled as shown. bb, is a two piece lid, consisting of an asbestos board, perforated to permit egress of delivery tube f, surmounted by an iron lid to which 3 sheets of asbestos board are bolted. The delivery tube leads to a 500 ml. flask, into which the excess NH₄Br sublimes. A small bulb h, removed from a Kjeldahl trap, is blown onto the sublimation condenser, and serves to retain any fine particles of rare earth bromide carried over by the NH₄Br. Stopcock i controls the inrush of air on dismantling the apparatus at the conclusion of the sublimation. A 500 ml. pyrex flask j, equipped with S.T. 29/42 joint, and filled with lumps of fused KOH, dries the admitted air. The apparatus is connected by pressure tubing k through a closed end manometer l to a Cenco Hivac pump. The sublimation temperature is followed by means of thermometer d inserted in a pyrex well c.

When the above described sublimation condenser was in use, violent implosion frequently occurred on evacuation, due to presence of weak points in the glass. More satisfaction in performance was obtained with condenser m, constructed from two S.T. 29/42 pyrex joints, two short lengths of 24 mm. pyrex tubing and 50 cm. of 46 mm. pyrex tubing. No implosions occurred, a vacuum was more rapidly created and more easily maintained, and the length of cooling surface proved sufficient to retain all sublimate. Drying flask j was modified with 3-way stopcock n, which served as the air inlet valve. No lubricant was necessary on the S.T. joints in the furnace. Glass hooks attached to each joint were wired together to keep the parts in place.

Two samples each of oxides X₁ and Y₁ were converted to the
Sublimation Apparatus

for

Removal

of

Excess Ammonium Bromide
anhydrous bromides by this method. In all cases, the treatment was identical:

1. 25g. (0.07 moles) of rare earth oxide were ground together with 100g. (1.0 moles) NH₄Br(A.R.) in a glass mortar and transferred to a vitreosil casserole, which was heated on a wire gauze over a Meker burner whose flame was so adjusted to permit maintenance of a temperature ca.275°C. The contents were stirred continuously during heating, otherwise lumps tended to form. Reaction was accompanied by a rapid characteristic color change, as the dark oxides passed to the bromides. Heating was continued until a test sample of the reaction mixture dissolved in water with no appreciable turbidity, the average time required being 1 1/2 hours.

2. The contents of the casserole were transferred to flask e, the apparatus connected as shown, a vacuum ca.1mm. applied by means of a Cenco Hivac pump, and the temperature of the furnace raised over 3 hours to 310°C, at which point it was maintained until sublimation of the NH₄Br was complete. (Remove the outer lid of the furnace and note whether any sublimate forms on the exposed parts of the delivery tube at f). Sublimation required 24-30 hours.

3. After cooling, dry air was admitted to the apparatus by opening cock 1 or n, and the product was quickly transferred to a dry weighed stoppered bottle by means of a funnel fashioned from a 125ml. erlenmeyer (cut off the bottom with a hot wire).

4. Small samples of each product were tested with like results –

(a) on heating in a dry test tube, no water vapor, or
white sublimate, condensed on the cooler parts of the tube indicating the product to be perfectly anhydrous and free from \(\text{NH}_4\text{Br}\).

(b) solvation in \(\text{H}_2\text{O}\) was accompanied by characteristic fizzling and slight opacity was evident, showing traces of oxybromide had been formed through hydrolysis.

**Discussion**

The sublimation process developed by University of Illinois investigators is generally satisfactory for preparation of anhydrous rare earth bromides in quantity, requiring a minimum of manipulative skill, and no great outlay of time or costly apparatus. When necessary, traces of oxybromides may be separated from the neutral salts by extraction with absolute alcohol, followed by evaporation of the solvent and final removal of alcohol of crystallization from the solute by heating in a current of dry air\(^17\) (vide infra, p. [8]).

C. Extraction Process

Brauman and Takvorian\(^14\) found that when anhydrous rare earth benzoates were extracted with dry ether saturated with \(\text{HCl}\) gas, quantitative conversion to the anhydrous chlorides occurred. The following represents an attempt to extend their method to synthesis of anhydrous rare earth bromides.

**Experimental**

35g. (0.2 moles) each of oxides Y and Z were carefully treated with 40 ml. concentrated \(\text{HNO}_3\), and the resultant solutions diluted
to 1750 ml., thus giving a 2% rare earth and approximately 0.2% free acid content. After warming each solution to 80°C, excess 2N NaOH solution was slowly added with constant stirring, which was continued for 1 hour more. The heavy flocculent precipitates thus obtained were filtered off, washed with a little water, transferred to casserole, dried in a hot air oven at 110°C for 40 hours, (the long drying period was necessitated by the large quantities handled), and transferred to tightly stoppered bottles. The dehydration temperature of the benzoates must not exceed 125°C, otherwise noticeable pyrolytic decomposition occurs. Small amounts of dissolved rare earths were subsequently recovered from the filtrate and washings. The yield of benzoates averages 95% by the above.

Apparatus was assembled as shown in the subsequent diagram. Dry HBr is generated by the action of Br₂ on dry benzene \( \text{(Erdmann's process)} \) \( \text{C}_6\text{H}_6 + 2\text{Br}_2 \rightarrow \text{C}_6\text{H}_4\text{Br}_2 + 2\text{HBr} \). 100g. dry benzene are poured into flask \( m \), containing a few grams of finely divided Al powder. 135 ml. Br₂ are placed in tap funnel \( n \), whose tip is drawn to a fine point. Flask \( m \) is seated in a closely fitting beaker and its upper surface packed with ice chips in order to minimize subsequent vaporization of its contents. Br₂ is allowed to drip slowly into the benzene. The issuing current of HBr is scrubbed free of \( \text{C}_6\text{H}_6 \) and \( \text{Br}_2 \) vapors by passing it through paraffin oil contained in wash bottle \( l \) which is immersed in a \( \text{CaCl}_2 \) - ice mixture at -20°C. Traces of \( \text{H}_2\text{O} \) and organic vapors are absorbed during subsequent passages over freshly fused \( \text{CaBr}_2 \) in drying tube \( k \) which is directly connected to the extraction assembly by adapter \( j \), fitted with a stopcock and S.T. 29/42 joint.
APPARATUS FOR HBr-Ether Extraction

OF

Anhydrous Rare Earth Benzoates
Worm condenser \( h \), which prevents vaporization of the extraction medium into drying tube \( k \) when the HBr gas line is open, leads to 3-necked extraction flask \( a \), of 500 ml. capacity and fitted with 3 S.T. 29/42 necks. Temperature is followed by means of thermometer \( g \) inserted through adapter \( f \). \( e \) is a Soxhlet extractor, equipped with S.T. joints and a small tap \( d \) for withdrawal of test samples. The top of bulb condenser \( b \), which condenses the extraction solvent, is fitted with an inverted drying tube \( f \), which is filled with fused CaBr\(_2\) to prevent ingress of atmospheric water vapor. Escaping acid fumes are tubed thence to the fume closet.

All apparatus was washed with a cleaning solution consisting of a 1:1 mixture of concentrated H\(_2\)SO\(_4\) + HNO\(_3\), rinsed thoroughly, dried for 3 hours in a hot air oven at 150°C and then washed with a little anhydrous ether prior to assembly.

A blank test was made by pouring 300 ml. dry ether (A.R.) into flask \( e \), and passing in a slow current of dry HBr. Within two to three minutes, developed a golden color which deepened to a maximum within 15 minutes. Four hours passage of HBr failed to darken the color further, even when the ether was boiled. The HBr current was then cut off, drainage tap \( d \) opened and the ether allowed to distill over. The distillate was pale yellow in color, boiling at 34.5°C, and fuming violently due to dissolved HBr. A few cc. of a reddish-brown high boiling liquid remained in the flask. This residual liquor was heavier than and immiscible with water, burned slowly with a smoky flame, and carbonized upon prolonged heating.

14g. benzoate \( Y \) were weighed into a paper extraction
thimble which was placed in the extraction chamber of the apparatus. 300 ml. of ether saturated with HBr (obtained by distillation from the blank runs) was poured into flask e and extraction was commenced by heating over an electric hotplate. Reaction, as given by the equation

\[ \text{Nd}(O\text{Bz})_3 + 3\text{HBr} \rightarrow \text{NdBr}_3 + 3\text{HOBz} \]

was so rapid that the siphoning liquor consisted of a heavy suspension of HOBz crystals. Extraction was discontinued when the siphoning liquor was clear. Meanwhile, the liquid in the extraction flask had once again assumed a golden hue. Since some HOBz crystals still adhered to the walls of the extractor and to the outer surface of the thimble, the thimble was quickly transferred to a clean dry apparatus and extracted 1 hour more with fresh dry ether. A small deposit of rare earth bromide settled out in the extraction flask due to slight ether solubility (vide infra). A small sample of material removed from the thimble dissolved in 5 ml. H_2O with considerable fizzling to give a transparent lilac solution, free from opacity and devoid of any detectable odor of HOBz. The thimble and contents were transferred to a clean dry bottle fitted with a 2-holed cork and glass tubes, the whole was placed in the hot-air oven at 70°C, and a current of air, predried over concentrated H_2SO_4 and fused KOH pellets, passed in until the emerging gas current was free from odors of HBr and Et_2O. (1 1/2 hours). The product was quickly scooped out of the thimble into a dry weighing bottle, weighed (8.15g. = 81.5% yield) and stored in a desiccator over fused KOH. Since the salt thus obtained was entirely water soluble, without turbidity, even after heating to 350°C., conversion to the anhydrous bromide may be assumed complete.

14g. of benzoate Z were converted to the corresponding bromide by the same method with analogous results.
The products were analyzed for bromide according to Mohr's method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Bromide Found</th>
<th>% Bromide Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>65.39 : 62.70 : 63.85</td>
<td>62.45 (assuming NdBr₃)</td>
</tr>
<tr>
<td>ZZ</td>
<td>65.89 : 63.66 : 65.49</td>
<td>65.18 (assuming 60%LaBr₃+40% PrBr₃)</td>
</tr>
</tbody>
</table>

Attempts made to determine the rare earth contents of the products by precipitation with 8-quinolinol were unsuccessful (vide Sect. III).

During trial runs with the extraction apparatus, 14g. of benzoate Y were placed in paper thimble, and extraction initiated with 300 ml. dry ether (qR.), with the simultaneous passage of dry HBr from the generator. The aforementioned golden color developed in the ether within a few minutes and the siphoning liquor became turbid with HOB₃ crystals. Surprisingly, the extraction liquor in the flask gradually developed the characteristic Nd absorption spectrum which became intensified as the color of the medium deepened. After 5 hours processing thusly, the extraction liquor was quite transparent, free from residual crystals, a deep red in color and showed heavy Nd absorption spectrum bands.

The liquor was transferred to a well-stoppered flask overnight. By the following morning, two layers had formed, each showing the Nd absorption spectrum. These were separated by means of a tap funnel. Neither showed presence of H₂O when small amounts were tested with KMnO₄ crystals. On standing two days more, both solutions deposited fine granular crystals, lilac in color after washing with fresh dry ether, and completely water soluble without turbidity. These crystals were probably anhydrous NdBr₃.
A sample of benzoate Z tested under the same conditions showed parallel ether solvation.

Finally, 52g. NdBr₃ (Series Y₁), prepared in the anhydrous state by the Sublimation Process, were extracted in a paper Soxhlet thimble with 500 ml. dry ether (A.R.) in the apparatus previously described. After one hour, a fine suspension of lilac crystals was noted in the extraction liquor, indicating slight ether solvation of the NdBr₃. A steady current of dry HBr was then passed in over a four hour period, with simultaneous ether extraction. The suspended crystals dissolved rapidly, and the golden color developed in the ether within a few minutes. Nd absorption spectrum lines were visible in the colored solution, gradually becoming denser as extraction proceeded. The mixture was allowed to stand for 2 days in the apparatus, atmospheric moisture being excluded by drying tubes 3 and 4. 300 ml. of fresh ether were then introduced into the extraction flask; two sharply defined layers formed. Extraction was carried out once more (no HBr was passed in) over a 30 hour period. After 10 hours extraction, only one uniform layer was apparent, with a heavy deposit of NdBr₃ crystals carried down from the thimble. Thirty hours sufficed to extract all NdBr₃ from the thimble to the extraction flask. The mixture was boiled with simultaneous passage of dry HBr for 5 hours. The NdBr₃ gradually dissolved to give a deep red transparent solution in which Nd absorption bands were extremely dense. This solution was quickly filtered through a fritted glass gooch to remove any solid matter (none), then transferred to a well stoppered flask. After standing 2 days, a heavy crop of well formed crystals, comparable to those described in the preceding paragraph, settled out. The Nd content of the supernatant solution, a dark brown in color, was still high, as shown by the heavy
absorption spectrum bands. A few ml. poured carefully into 5 ml. \( \text{H}_2\text{O} \) settled to the bottom of the test tube (indicating density greater than 1), but on shaking the mixture well for several minutes, all rare earth went into aqueous solution, and a transparent brown etheric layer rose to the surface.

Lack of time prevented further investigation of the cause of these anomalous effects.

All rare earths were recovered from the ether residues by aqueous extraction.

Discussion

The close approximation of the bromide content of the products herein obtained to theoretical values indicates that the method of Brauman and Takvorian is applicable to the synthesis of anhydrous rare earth bromides. Due to slight ether solvation of the products, yields attained only 30% in the runs made. However, the short period of less than 8 hours required to effect the transformation to the anhydrous rare earth bromide, free from traces of basic salt, speaks in favor of the process, as compared to those in current use.

This investigation was only preliminary in scope; further work should greatly increase the yield, and clarify certain anomalies in behavior of the ether described in the experimental record. The apparatus employed requires two outstanding improvements:

1. Sintered pyrex thimbles (not at present available in this laboratory) Paper thimbles used herein proved rather troublesome, tending to become somewhat brittle through deleterious action of \( \text{HBr} \) gas, and charring slightly if the drying temperature was allowed to greatly exceed 70°C.
2. Rubber corks j. and connection o should be replaced by standard taper pyrex ware to ascertain their influence on the changes observed in ether upon passage of HBr.

Other parts of the apparatus, designed and assembled as shown only after considerable deliberation and experimentation, require but slight attention, having been found very satisfactory. No great manipulative skill is required for successful operation.

Preparation of dry HBr by interaction of Br₂ and C₆H₆ is superior to wet inorganic methods, (e.g. P + Br₂ + H₂O), and with the freezing trap described, permits steady generation of gas with but scant attention. Some workers prefer to use naphthalene instead of benzene.

It is suggested that dry saturated hydrocarbons known to dissolve benzoic acid be substituted in place of ether as the extraction medium, in order to eliminate the peculiar behavior of the latter substance. Such solvents would conceivably permit extension of the method to synthesis of pure anhydrous rare earth iodides, which can not be prepared by extraction of benzoates by extraction with dry ether saturated with HI due to mutual reaction (vide infra.)

Although the cause of the color change observed when dry HBr was passed into dry ether was not ascertained, some speculation as to the nature of the reaction is necessary. The thought that vapors of Br₂, C₆H₆, or products thereof from the HBr generator may be the causative agent (2) falls into discard quickly, since such substances should be completely removed by the iced paraffin: furthermore, the same effects were noted when the HBr was generated by interaction of P, Br₂ and H₂O - a method avoiding all organic substances. Although rubber stoppers j. and connection o expanded and hardened considerably due to action of HBr,
no volatile product should be formed therefrom, since such action primarily involves addition of HBr to the double bonded system of an isoprene polymer. Sulfur, used in vulcanization, does not react with dry HBr, according to Mellor (vol. II). Antimony, present in rubber, forms a tribromide which melts at 96°C. and hence is not volatile. Nevertheless, all glass connections should be introduced in place of the rubber, in case this should have some effect.

HCl gas dissolves copiously in ether without chemical reaction, while HI promotes hydrolytic decomposition, as given by

\[
\text{Et}_2\text{O} + \text{HI} \rightarrow \text{EtI} + \text{EtOH} \quad \text{(cold)}
\]

\[
\text{Et}_2\text{O} + 2\text{HI} \rightarrow 2\text{EtI} + \text{H}_2\text{O} \quad \text{(hot)}
\]

HBr may react to a limited extent in the same fashion.

\[
\text{Et}_2\text{O} + \text{HBr} \rightarrow \text{EtBr} + \text{EtOH}
\]

\[
\text{Et}_2\text{O} + 2\text{HBr} \rightarrow 2\text{EtBr} + \text{H}_2\text{O}
\]

although no mention of such hydrolysis could be found in any current test of organic chemistry. Further, such reaction does not explain the coloration which developed in the ether. Also, no water was detected in the extraction liquors with KMnO₄ crystals, which would indicate presence of any more than a trace.

Ether usually contains traces of peroxide to atmospheric oxidation on prolonged standing. This peroxide could conceivably act with HBr as follows:

\[
\text{Et}_2\text{O}_2 + 2\text{HBr} \rightarrow 2\text{EtOH} + \text{Br}_2.
\]

The Br₂ in a dissolved state lending the golden color to the solution and brominating the alcohol formed to give high boiling substituted derivatives.
None of the above hypothetical reactions provide adequate explanation for the complete solvation of the rare earth bromides up to 10% concentration, followed by the subsequent crystalline deposition already described. Diethyl ether is known to act in an electrodomic fashion, by virtue of the presence within the molecule of two unshared electron pairs. This feature, considered in conjunction with the electronic structure of the rare earth halides, permits the hypothetical postulation of an unstable ether soluble complex ion formation, according to the following equation:

\[
\begin{align*}
\text{Et}_2\text{O}^+ + \text{HBr}^- + \text{NdBr}_3^- &\rightarrow \left[\text{Et}_2\text{O}^+\text{H}^-\right]^+ + \left[\text{Nd}^{3+}\text{Br}_4^-\right]^- + \left[\text{Br}^{+}\right]^- \\
\text{Et}_2\text{O}^+ &+ \text{Br}^- &+ \text{NdBr}_3^- \\
\text{Et}_2\text{O}^+ &+ \text{Br}^- &+ \text{NdBr}_3^- \\
\end{align*}
\]

Although no such derivatives of the rare earths have yet been described, their existence is quite possible in non-aqueous solvents.
III. QUANTITATIVE ESTIMATION OF RARE EARTHS AND DETERMINATION OF MEAN EQUIVALENT WEIGHT WITH 8-QUINOLINOL

Pirtea successfully developed procedures with a sensitivity of 1/500000 for quantitative determination of cerium and lanthanum with 8-quinolinol (oxine). Alcoholic oxine reacts with ammoniacal NH₄OAc solutions of La salts to give a flocculent precipitate which filters readily, and dries to constant composition at 150° C. Gravimetric determination is thus readily effected, or the precipitate may be dissolved in HCl, and the La estimated therefrom by bromometric titration.

The aim of the author was to extend Pirtea's method to the quantitative estimation of other rare earth elements, and to apply the results of such analyses to computation of the mean equivalent weight of mixtures of rare earth elements in their salts in a fashion to be subsequently explained. (cf. Discussion) Unfortunately, insufficient time allowed only a cursory study to be made.

Experimental.

0.1 g. (0.001 moles) samples of bromides Y and Z, prepared by the ether extraction process, were accurately measured from a weighing bottle and dissolved in 200 ml. freshly distilled water. Each solution was warmed almost to the boiling point, treated with 25 ml. 2n. HNO₃, then a slight excess of 5% alcoholic oxine solution added (ca. 5 ml.). 6n. NH₄OH was then added dropwise until the solution smelled strongly of NH₃ (ca. 20 ml.). Heavy flocules of the rare earth oxinates settled out. The suspensions were warmed almost to boiling to facilitate precipitation, then allowed to digest at room temperature for 1 hour. After warming once more for several minutes, the precipitates
were filtered off by passage through accurately weighed dry sintered glass gooches of fine porosity, with the aid of a water pump. On some occasions, the rare earth oxinates tended to pass through the filter during the initial stages of filtration. However, this was readily recovered by passing the liquor repeatedly through the filter until a clear filtrate resulted. If the precipitate passing through the filter dissolves on heating, it is merely excess oxine, which is much less soluble in cold than in hot water. On the other hand, if the precipitate fails to dissolve on heating, this shows that heavy metal oxinates have slipped through the filter, and further filtration is required.

After washing the precipitates with 5 ml. portions of hot distilled water until the wash liquor was colorless (ca. 25 ml.), in order to remove excess oxine, the gooches were transferred to the hot air oven at 150° C. and dried to constant weight (90 min. proved ample). The weighed oxinates were then dissolved in 2n. HCl, by pouring small portions into the gooch (up to 100 ml.), and applying the water pump. 2 g. KBr (A.R.) were added to each resulting solution, which was subsequently titrated with 0.1002n. KBrO₃ until a drop of the mixture gave a positive test with a drop of KI starch indicator on a spot plate. 10 ml. of freshly prepared KI solution and 2 ml. starch solution were added, and the excess KBrO₃ then determined by backtitration with 0.1138n. Na₂S₂O₃.
Following are the Analytical Results.

<table>
<thead>
<tr>
<th></th>
<th>Series Y 1</th>
<th>Series Y 2</th>
<th>Series Z 1</th>
<th>Series Z 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of bromide</td>
<td>0.1090</td>
<td>0.1288</td>
<td>0.0523</td>
<td>0.1694 g.</td>
</tr>
<tr>
<td>Wt. of oxinate</td>
<td>0.1136</td>
<td>0.1257</td>
<td>0.0756</td>
<td>0.1555 g.</td>
</tr>
<tr>
<td>0.1002n·KBrO₃</td>
<td>21.47</td>
<td>22.10</td>
<td>17.00</td>
<td>28.00 ml.</td>
</tr>
<tr>
<td>0.1136n·Na₂S₂O₃</td>
<td>0.90</td>
<td>0.10</td>
<td>0.37</td>
<td>0.10 ml.</td>
</tr>
<tr>
<td>KBrO₃ reacting</td>
<td>20.45</td>
<td>21.39</td>
<td>16.59</td>
<td>27.89 ml.</td>
</tr>
</tbody>
</table>

Now \[ 2 \text{KBrO}_3 = 3 \text{C}_3\text{H}_7\text{ON} = 3 \text{C}_3\text{H}_6\text{ON}^- \]

or \[ 1 \text{L. 0.10n·KBrO}_3 = 3.6056 \text{ g. C}_3\text{H}_6\text{ON}^- \]

From this the oxinate content of the precipitates is readily computed.

<table>
<thead>
<tr>
<th></th>
<th>Series Y 1</th>
<th>Series Y 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series Y 1</td>
<td>20.45 x F = 64.72%</td>
<td>0.1136</td>
</tr>
<tr>
<td>Series Y 2</td>
<td>21.39 x F = 63.04%</td>
<td>0.1257</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Series Z 1</th>
<th>Series Z 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series Z 1</td>
<td>16.59 x F = 79.06%</td>
<td>0.0756</td>
</tr>
<tr>
<td>Series Z 2</td>
<td>27.89 x F = 52.01%</td>
<td></td>
</tr>
</tbody>
</table>

where \[ F = \frac{3.6056 \times 100}{1000} \]

The analytical results are so irregular that further computation is without purpose.
Discussion

The quantities of reagents employed in this determination are exact multiples of those quantities employed by Pirtea in determination of La.

The rare earths should be completely precipitated by oxine under the conditions described according to the general equation.

\[ MX_2 + 3C_6H_7ON + 3HX + M (C_3H_6ON)_3 \]

HCl treatment liberates the oxine from the precipitate. KBrO₃ used for titration reacted with KBr which acts on oxine in a quantitative fashion thusly:

\[ KBrO_3 + 5KBr + 6HCl \rightarrow 6KCl + 3Br_2 + 3H_2O \]

\[ C_6H_7ON + 2Br_2 \rightarrow C_6H_5ONBr_2 + 2HBr. \]

thereby making volumetric determination feasible.

Further investigation is required to explain the irregular analytical results herein obtained. The oxinate content of the precipitates should have closely approximated 75% (e.g. oxinate content of the pure La = 75.67%). Taking 75% as a hypothetical example, further calculation may be made: 1 mole of the oxinate of a trivalent metal contains 432.458 g. oxinate radical

75 g. oxinate = 25 g. rare earth metal.

432.458 g. oxinate = 144.146 g. rare earth metal.

= mean molecular weight

or, mean equivalent weight = 48.048

Knowing the mean equivalent weight, the rare earth content of a salt is quickly computed from the weight of oxinate obtained by gravimetric precipitation.

It is generally easier and certainly less
costly to use compounds of rare earth mixtures rather than those of the pure elements in synthetic studies, hence the need for an all embracing method of determining the mean equivalent weight. Older procedures involving calcination of the oxalates, sulfates, etc. to the oxides are worthless when dealing with mixtures containing Ce, Nd, Pr, Tb, due to the tendency of these elements to form higher oxides of indeterminate composition. Neither volumetric nor potentiometric methods are of value for the same reason. Thus, if further study shows that oxine can be successfully applied to the determination of rare earth elements, a new rapid method is provided whereby not only the rare earth content of a newly synthesized compound may be found, but also the mean equivalent weight of any group of metals concerned.
The initial purpose of this investigation was to attempt synthesis of organometallic derivatives of the rare earth elements. With this view, correspondence was carried on with Dr. B.S. Hopkins and Dr. L.F. Audrieth of the University of Illinois to ascertain whether any such work had been undertaken there. Following is a resume of unsuccessful reactions attempted at the University of Illinois:

A. From the salts in ether

1. \[ C_7H_7MgBr + LaCl_3 \rightarrow (C_7H_7)_2LaCl_2 \]
2. \[ C_3H_7MgBr + CeCl_3 \rightarrow (C_3H_7)_2CeCl_2 \]
3. \[ (C_2H_5)_2Zn + LaCl_3 \rightarrow (C_2H_5)_2LaCl + ZnCl_2 \]
4. \[ (C_2H_5)_2Zn + CeCl_3 \rightarrow (C_2H_5)_2CeCl + ZnCl_2 \]

B. From the metals in ether

1. \[ 4La + 6C_4H_9Br \rightarrow 3(C_4H_9)_2LaBr + LaBr_3 \]
2. \[ 2La + 3(C_2H_5)_2Zn \rightarrow 2(C_2H_5)_3La + 3Zn \]
3. \[ misch metal + (C_2H_5)_2Zn \]
4. \[ 2La + 3(C_2H_5)_2Hg \rightarrow 2(C_2H_5)_3La + 3Hg \]
5. \[ misch metal + (C_2H_5)_2Hg \]
6. \[ 2Ce + 3(C_2H_5)_2Hg \rightarrow 2(C_2H_5)_3Ce + 3Hg \]

This reaction was attempted in March, 1937. Appropriate quantities of reactants were heated in a sealed tube at 100 - 150°C. for one week. Subsequent distillation of the reaction mixture in an atmosphere of helium under 13 mm. pressure resulted in a distillate free of rare earth. The residue contained the powdered rare earth metal in a
slightly amalgamated state.

Dr. LiF. Audrieth proposed study of the reaction given by:

\[ 3\text{NaR} + \text{CeX}_3 \rightarrow 3\text{NaX} + \text{CeR}_3. \]

Since the sodium alkyl compounds are difficult to prepare and are generally spontaneously inflammable, the author recommends that a study be made of possible reaction between sodium amalgam + EtBr + LaBr₃ and between Na rare earth alcohols + EtBr in an etheric medium, under an inert atmosphere to minimise danger of explosion.

The author does not propose to discuss the various points offered pro and con existence of rare earth organometallics. The interested reader is referred to the bibliography kindly offered by Dr. LiF. Audrieth, now in possession of Dr. J.Ai Harris of the U.B.C. Department of Chemistry. Although time did not permit experimental studies on this field in this laboratory, preliminary problems relating thereto have been sufficiently clarified to permit direct attack on the problem.
V. SUMMARY

1. Mosander's process of separating Ce from related earths by bromine treatment has been studied with the object of improving its efficiency. This was accomplished by -
   (a) use of extraction methods.
   (b) refluxing rare earth oxides, Br₂ and H₂O in presence of ammonium salts.

2. Necker's and Kremer's method of separating Ce by phosphate precipitation has been examined, and the effect of varying acid concentration and temperature of mixing the reagents confirmed.

3. Bourion's S₂Cl₂ process for preparing anhydrous rare earth halides has been found unsatisfactory for reasons described herein.

4. The synthesis of anhydrous rare earth chlorides and bromides by sublimation of rare earth oxides with the corresponding ammonium halide, as proposed by Reed, Hopkins and Audrieth, has been found satisfactory. Improvements in the apparatus used are described and means of removing traces of basic salt from the product are suggested.

5. Anhydrous rare earth bromides have been successfully prepared by extraction of anhydrous benzoates with ether saturated with dry HBr. Tentative explanations have been offered of the anomalous behaviour of ether + HBr + rare earth bromides.

6. Attempts were made to employ 8 - quinolinol for quantitative estimations of the rare earth elements in their compounds and for determination of the mean equivalent weight of mixtures of rare earth elements including Ce, Pr, Nd and Tb. Insufficient time prevented success in this direction. Exemplary hypothetical
comparisons are given.

7. A resume of unsuccessful reactions studied at the University of Illinois for synthesis of organometallic derivatives of the rare earth elements, together with ideas of the author on the subject, have been included.
VI. BIBLIOGRAPHY


5. (a) Prandtl, W. Z. anorg. allgem. Chem., 145, 277-84 (1925)

       (b) Prandtl, W. and Huttner, K. ibid, 126, 289-94 (1924)

       (c) Prandtl, W. and Losch, J. ibid, 122, 159 - 66, (1922) ibid, 127, 209-14, (1923)


7. Latimer, W.M. "Oxidation Potentials", p.54 Prentice-Hall, Inc. (1938)


11. Mellor, J.W.
"Comprehensive Treatise on Inorganic and Theoretical Chemistry"
V, 645, (1924)
Longmans, Green and Co.

12. Bourlon, M.F.
Compt. rend., 145, 243-9, (1907)

13. Reed, J.B., Hopkins, B.S. and Audrieth, L.F.
J.A.C.S., 57, 1159, (1935).

14. Brauman, P. and Takvarian, S.
Compt. rend., 194, 1579 (1932)

15. Mellor, J.W.
"Comprehensive Treatise on Inorganic and Theoretical Chemistry"
II, 170 (1922)
Longmans, Green and Co.

16. Dennis, L.M.
"Gas Analysis", p.254
MacMillan Co. (1916)

17. Gér. patent 268827,
cf. Chem. Abstr., 8, 1861, (1914)

18. Vogel, A.I.
"Quantitative Inorganic Analysis" p.310
Longmans, Green and Co. (1959)

19. Luder, W.F.
Chem. Rev., 27, 562, (1940)

20. Pauling, L.
"The Nature of the Chemical Bond"

21. Pirtea, Th. I.
Z. anal. chem., 107, 191, (1936),
cf. also C.A. 54, 2277 (1940)

22. Vogel, A.I.
"Quantitative Inorganic Analysis" pp.161, 455-8

23. ibid., p.451

24. ibid., p.408

25. ibid., p.406

26. ibid., p.405.