THE RARE EARTH ELEMENTS AND THEIR COMPOUNDS: THE PURIFICATION AND PROPERTIES OF PRASEODYMIUM OXIDE

By

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INTRODUCTION

The development of new techniques for the separation of the rare earth metals is the ultimate goal of practically all rare earth research. Because of the chemical similarities of the rare earth elements, the utilization of fractional procedures[29,85,38] has been necessary. Any method which lends itself to both continuous operation and automatic control would be highly desirable. Two such methods, fractional distillation and liquid-liquid counter-current extraction, have been suggested, but as yet not developed. Appleton and Selwood[2] proposed the utilization of rare thiocyanates for extraction procedures; later, Templeton and Peterson[86] had considerable success in extracting saturated rare earth nitrate solutions with n-hexyl alcohol.

For this dissertation the original research problem consisted of a study of the distribution of rare earth compounds between water and various organic solvents to find qualitatively a suitable combination of solvents which might be used in the development of a liquid-liquid counter-current extraction separation.

Rare earth acetylacetonates, nitrates, acetates, n-valerates, benzoates, p-hydroxybenzoates, 8-hydroxyquinolates, mono-, di-, and trichloroacetates were prepared and their solubilities in a number of common organic solvents investigated.

In this study the rare earth trichloroacetates were observed to decompose in hot solutions to form insoluble compounds, identified as rare earth carbonates. When a water solution of both lanthanum and praseodymium trichloroacetates was heated, the carbonate precipitate was found to be enriched in praseodymium. Because of this discovery, attention was focused upon the development of separations by homogeneous phase reactions, such as the precipitation of carbonates due to the decomposition of the trichloroacetates and the precipitation of oxalates upon the hydrolysis of dimethyloxalate.

It was also observed that trichloroacetic acid precipitated ceric ions from aqueous solutions and formed extremely soluble salts with the trivalent rare earths. These observations suggested a procedure for the separation of cerium.

In order to follow the separation of rare earth mixtures, new analytical procedures were developed:

a) an iodometric procedure for the determination of praseodymium in binary mixtures, and b) an iodometric correction for "excess" oxygen in the oxalate-oxide average atomic weight determination.

During the development of the analytical procedures, the nature of praseodymium oxide was observed to vary considerably in the presence of different rare earth oxides. Although the character of praseodymium oxide has been the subject of extensive work by many investigators, a complete answer has not been obtained. Accordingly, this problem was studied to clarify the behavior of these praseodymium compounds in binary rare earth mixtures.

A number of research ideas were formulated during this study and one section is devoted to them.

SECTION I

Qualitative Solubility and Distribution Studies

The solubilities of several neodymium salts in water and various organic solvents were studied qualitatively. Neodymium was chosen for this study because of its strong and characteristic absorption spectrum and because an adequate amount of pure neodymium material was available. If the saturated solution were pink, the salt was considered soluble; if the neodymium spectrum were visible through 10 cm. of solution with a hand spectroscope, the salt was considered as moderately soluble; if visible through 20 cm. of solution, slightly soluble; if not visible through 20 cm., insoluble. The results are listed in Table I. The trichloroacetates show a greater range of solubilities in a larger variety of solvents than do the normal acetates, suggesting the possibility of using the rare earth trichloroacetates in liquid-liquid counter-current extraction techniques.

The extraction of 0.1 N neodymium nitrate solutions with various organic solvents was also studied. The organic solvent layer in each case was examined for dissolved neodymium compounds with a hand spectroscope. Neodymium nitrate could be extracted from a 0.1 N aqueous

TABLE I

Qualitative Solubilities of Neodymium Salts

Salt	Soluble	Moderately Soluble	Slightly Soluble	Insoluble
Acetate	Water	Methyl Salicylate Carbon Disulfide Benzyl Chloride Benzyl Alcohol Benzyl Carbinol	Chloroform Nitrobenzene Chlorobenzene n-Amyl Alcohol	Ethyl Acetate Benzene Hexane Carbon Tetrachloride Butyl Bromide Xylene Hexone* Toluene Methyl Iodide
Monochloroacetate	Water	Ethyl Alcohol	Acetone	Ethyl Ether Benzene
Dichloroacetate	Water	Ethyl Alcohol Acetone	Ethyl Ether	Benzene
Trichloroacetate	Water Acetone Alcohol	Hexone* Ethyl Acetate n-Amyl Alcohol Water	Ethyl Ether Chloroform	Benzene Hexane
n-Valerate				
Acetylacetonate	Hexone* Acids		Water	
Benzoate	Acids		Water	Organic Solvents
p-Hydroxybenzoate	Acids			Water Organic Solvents
8-Hydroxyquinolate	Acids		Chloroform Carbon Disulfide Carbon Tetra-chloride	Benzene Hexone* Ethyl Acetate Water

* - Methyl Isobutyl Ketone

solution with n-butyl alcohol and n-valeric acid, but probably not with hexane, carbon tetrachloride, n-amyl alcohol, t-amyl alcohol, or hexone (methyl isobutyl ketone). Mayper[55] indicated a distribution of rare earth nitrates between water and methyl butanol. Templeton and Peterson[86] succeeded in extracting saturated nitrate solutions with n-hexyl alcohol.

SECTION II

Preparation and Properties of the Rare Earth Trichloroacetates

Since trichloroacetic acid and its salts are not widely used in inorganic chemistry a brief resume of their properties will be outlined.

Dumas[21] first prepared trichloroacetic acid by adding dry chlorine gas to crystalline acetic acid in a glass-stoppered flask and placing the flask in sunlight for a day. The chlorine disappeared and large rhombohedral crystals of trichloroacetic acid formed. Dumas analyzed this acid and characterized many of its properties. He prepared the silver, ammonium, and potassium salts by evaporating their water solutions at room temperature. He observed that when solutions of the trichloroacetates were heated, chloroform was liberated and a carbonate was formed. Barium carbonate was prepared by boiling a solution of barium hydroxide and trichloroacetic acid. This decomposition reaction is of particular importance since it offers a method for the preparation of many carbonates which cannot be easily prepared as pure and crystalline compounds.

Although trichloroacetic acid has been known for over a hundred years, only a few of its inorganic salts have been studied. It is a strong acid, comparable to hydrochloric acid, and forms ionic salts with the more basic elements, e.g. the alkali and alkaline earth elements. Trichloroacetic and acetic acids have many of the same properties, such as the tendency to form complex ions with certain transition elements and insoluble basic acetates with the amphoteric elements. The normal and basic trichloroacetates which have been reported are listed in Table II.

The normal trichloroacetates are ionic salts which are highly soluble in water, alcohol, and acetone, but practically insoluble in carbon tetrachloride and benzene. They will decompose in aqueous solutions to produce carbonates. Verhoek[93] studied the kinetics of the decomposition of trichloroacetic acid and its sodium and barium salts; Hall and Verhoek[21] studied its sodium, barium, calcium, and lithium salts (Section IV).

The basic trichloroacetates are sparingly soluble in water, but may be recrystallized from 95 per cent ethyl alcohol.[45] This solubility phenomenon usually indicates the formation of an internal complex between the metal and organic acid.

TABLE II

Inorganic Salts of Trichloroacetic Acid

Normal Compounds

Metal	Formula of Salt	Reference
Ammonium	$NH_4C_2Cl_3O_2$	5
Barium	$Ba(C_2Cl_3O_2)_2 \cdot 3H_2O$	93
	$Ba(C_2Cl_3O_2)_2 \cdot 2H_2O$	83
Beryllium	$Be(C_2Cl_3O_2)_2 \cdot 2H_2O$	83
Cadmium	$Cd(C_2Cl_3O_2)_2 \cdot 1\text{-}1/2H_2O$	28
Cerium	$Ce(C_2Cl_3O_2)_3 \cdot 3H_2O$	100
Cobalt	$Co(C_2Cl_3O_2)_2 \cdot 3\text{-}1/2H_2O$	28
	$Co(C_2Cl_3O_2)_2 \cdot 4H_2O$	1
Copper	$Cu(C_2Cl_3O_2)_2 \cdot 3H_2O$	4
	$Cu(C_2Cl_3O_2)_2 \cdot 6H_2O$	43
Lead	$Pb(C_2Cl_3O_2)_2 \cdot H_2O$	43
Manganese	$Mn(C_2Cl_3O_2)_2 \cdot 3H_2O$	28
Potassium	$KC_2Cl_3O_2 \cdot H_2O$	21
Silver	$AgC_2Cl_3O_2$	21
Sodium	$NaC_2Cl_3O_2$	93

Basic Compounds

Beryllium	$BeO(C_2Cl_3O_2)_2$	33
Cobalt	$Co(OH)_2 \cdot 2Co(C_2Cl_3O_2)_2 \cdot 4H_2O$	1
Copper	$Cu(C_2Cl_3O_2)_2 \cdot 3Cu(OH)_2 \cdot xH_2O$	12
Indium	$In(OH)(C_2Cl_3O_2)_2$	22
Thorium	$Th(OH)_2(C_2Cl_3O_2)_2 \cdot H_2O$	44,45
Uranium	$UO(C_2Cl_3O_2)_2 \cdot 3H_2O$	57

Mandl[50] precipitated zirconium from a nitrate solution by the addition of trichloroacetic acid and suggested the formation of a basic salt, but failed to report an analysis of the compound.

In the present research basic ceric trichloroacetate was prepared and studied (Section V).

Solutions of ferric trichloroacetate may be rendered colorless by the addition of excess trichloroacetic acid. Absorption studies[47] give evidence for the formation of a soluble complex ion $[Fe(C_2Cl_3O_2)_6]^{-3}$. There is some indication that chromium may form a similar complex ion with trichloroacetic acid.

Beilstein lists mercuric trichloroacetate as having been prepared by Clermont. However, other workers[4,13,46] have not been successful in preparing this salt since apparently it immediately decomposes to form insoluble mercurous chloride when mercuric oxide is added to trichloroacetic acid in water.

Wolff[100] prepared cerous trichloroacetate, $Ce(C_2Cl_3O_2)_3 \cdot 3H_2O$, as long needles by concentrating its water solution in a vacuum desiccator. A thorough search of the available literature did not reveal the preparation of any of the other rare earth trichloroacetates, although Urbain[90] did attempt to fractionally precipitate the rare earths as acetates and chloroacetates.

The preparation of the rare earth trichloroacetates consists of dissolving the oxide in a concentrated solution of trichloroacetic acid, heating the solution until rare earth carbonate begins to precipitate, cooling the solution in an ice bath, filtering the carbonate, and crystallizing the salt at room temperature by evaporating the water in a vacuum desiccator. The salt may be dried over phosphorous pentoxide or concentrated sulfuric acid. If recrystallized from alcohol, there is evidence that some of the solvent is retained as alcohol of crystallization.

The procedure for the preparation of neodymium trichloroacetate follows. Neodymium oxide, 25 g., is dissolved in 300 ml. of 25 per cent trichloroacetic acid solution. The excess acid is decomposed by heating the solution to about 90° C. When neodymium carbonate begins to precipitate, the solution is quickly cooled to room temperature and the carbonate filtered. The filtrate is a solution of neodymium trichloroacetate free of excess trichloroacetic acid. The salt is crystallized at room temperature by evaporating the water in a vacuum desiccator. Yields of 90 per cent or better are obtained.

The composition of neodymium trichloroacetate prepared by the above method and air dried was determined.

Analysis for neodymium oxide was made by dissolving a weighed sample of the salt in water, precipitating neodymium oxalate with oxalic acid, igniting the oxalate in a muffle furnace, and weighing the resulting oxide. For the chlorine analysis a weighed sample was decomposed by the method of Umhoefer.[89] This consisted of refluxing the salt with sodium in isopropyl alcohol for two hours. After the solution was neutralized with 6 N nitric acid, chloride was determined by the Volhard method.[96]

Comparison of the theoretical and experimental values for the neodymium oxide and chlorine (Table III) indicates that the formula for the neodymium trichloroacetate is $Nd(C_2Cl_3O_2)_3 \cdot 3H_2O$.

TABLE III

The Analysis of Neodymium Trichloroacetate

For $Nd(C_2Cl_3O_2)_3 \cdot 3H_2O$

Per Cent	Nd_2O_3	Cl
Experimental	24.4	46.3
Theoretical	24.6	46.5

Neodymium trichloroacetate forms heavy pink needles when crystallized from water. The crystals are very soluble in water, acetone, and alcohol; less soluble in ether, hexone, ethyl acetate, n-amyl alcohol, and chloroform; and insoluble in benzene and n-hexane.

The anhydrous salt was not obtained by moderate heating since the salt and its water of hydration react. The neodymium trichloroacetate is contaminated with carbonate. Upon ignition the salt does not melt but decomposes to yield neodymium oxide and a gas which has an odor similar to phosgene. In warm water the course of the decomposition reaction appears to be represented by the equation

$$2Nd(C_2Cl_3O_2)_3 + 3HOH \longrightarrow 3CO_2 + 6CHCl_3 + Nd_2(CO_3)_3.$$

Decomposition of neodymium trichloroacetate is not observed in anhydrous acetone, but proceeds at room temperature upon the addition of water.

The solubility of neodymium trichloroacetate was determined at 25° C. A known volume of the saturated solution was weighed, diluted with water, and the neodymium oxalate precipitated with oxalic acid, and ignited in a muffle furnace. The solubility of neodymium trichloroacetate was calculated from the weight of oxide obtained and found to be 225.8 g. of $Nd(C_2Cl_3O_2)_3 \cdot 3H_2O$ per 100 g. of water. The density of the saturated solution at 25° C. was 1.636 g. per ml.

It is of interest to compare the solubilities of the neodymium acetate and trichloroacetate. Meyer and Muller[66] reported the solubility of a monohydrated neodymium acetate as 20.76 g. per 100 g. of water,

whereas Thomas[87] gave the solubility in terms of anhydrous salt as 20.19 g. of acetate per 100 g. of saturated solution. It is observed that the solubility of the acetate is very appreciably lower than that of the trichloroacetate. From these data, and from observations made during the separation studies involving the trichloroacetates, it may be stated that the latter salts of the rare earth ions are definitely more soluble than the acetates, the increase in the case of the neodymium compounds being approximately tenfold.

SECTION III

Preparation of Rare Earth Carbonates

Two methods have been used to prepare rare earth carbonates, neither of which is entirely satisfactory for producing a pure crystalline compound. The older method was first used by Vauquelin,[91,92] who precipitated cerous carbonate by the addition of an alkali carbonate to a cerous salt solution. This method usually produces amorphous flakes which become crystalline only after standing in the liquid several days. Priess and Dussik[77] obtained a more crystalline product by using alkali bicarbonates for the precipitation. Nevertheless, the carbonate is usually contaminated with alkali carbonates because the rare earths also form insoluble alkali double carbonates.[64] A second method for preparing rare earth carbonates was proposed by Cleve.[19,20] He obtained them by passing a current of carbon dioxide through a suspension of the rare earth hydroxides in water. Such a conversion of one solid to another is seldom complete. Rare earth carbonates free from hydroxide impurities are not obtained.

For this study pure crystalline rare earth carbonates were prepared by the decomposition of rare earth trichloroacetates according to the following procedure.

Approximately 10 g. of a rare earth oxide is dissolved with warming in slight excess of 25 per cent trichloroacetic acid. This solution is diluted to 500 ml. with distilled water and heated on a steam bath for about 6 hours after the first precipitate of carbonate is formed. The carbonate is filtered by suction, washed with distilled water, and air dried. The precipitated carbonate may be washed with alcohol and then ether in order to hasten drying. Since all of the rare earth is not precipitated by this method, the filtrate should be treated with oxalic acid to recover the rare earth as the oxalate.

An excess of trichloroacetic acid is required to dissolve the rare earth oxide, but the carbonate will not precipitate until the excess acid has been removed. The time required for this operation is dependent upon the amount of the excess acid and the temperature of the bath.

The carbonates as described in the above procedure appear to be normal carbonates of the formula $R_2(CO_3)_3 \cdot xH_2O$. This conclusion is based upon the experimental determination of the percentages of rare earth oxide and carbon dioxide and the calculation of the mole ratio CO_2/R_2O_3. This ratio is 3 only for normal carbonates. A value less than 3 is obtained for basic

carbonates and greater than 3 for acid carbonates. For example, the mole ratios CO_2/R_2O_3 would be 2 and 6 respectively for $R(OH)CO_3$ and $R(HCO_3)_3$.

Weighed samples of a particular carbonate were ignited in a muffle furnace at a temperature of 925° C. The resulting oxides were weighed and the per cent rare earth oxide in the carbonate calculated. Other weighed samples were treated in a CO_2 gas analysis apparatus[96] with dilute hydrochloric acid. The liberated carbon dioxide was collected in an absorption bottle and weighed. The per cent carbon dioxide in the carbonate and the mole ratio CO_2/R_2O_3 were calculated.

Lanthanum, neodymium, and samarium carbonates were prepared and analyzed. The results are listed in Table IV.

TABLE IV

The Analysis of Rare Earth Carbonates

Carbonate	% R_2O_3	% CO_2	% H_2O*	$\frac{CO_2}{R_2O_3}$	$\frac{H_2O}{R_2O_3}$	Formula
Lanthanum	58.55	23.60	17.85	2.98	5.51	$La_2(CO_3)_3 \cdot 5.5H_2O$
Neodymium	65.80	25.35	8.85	2.95	2.51	$Nd_2(CO_3)_3 \cdot 2.5H_2O$
Samarium	65.88	23.43	10.69	2.82	3.14	$Sm_2(CO_3)_3 \cdot 3H_2O$

* - $(100 - \%R_2O_3 - \%CO_2)$

Since the mole ratios CO_2/R_2O_3 indicate normal carbonates, the difference between 100 and the sum of the percentages of rare earth oxide and carbon dioxide must be the per cent of water in the carbonates. The mole ratio H_2O/R_2O_3 in each case may then be calculated. These results were not verified experimentally.

The mole ratio CO_2/R_2O_3 is smaller for samarium carbonate than for the other two. This indicates a slight tendency toward basic salt formation; a condition which might be expected for the less basic rare earth elements (yttrium group).

The preparation of anhydrous neodymium carbonate was attempted. Samples of neodymium carbonate were dried under different conditions and analyzed for neodymium oxide as before and for carbon dioxide by a volumetric procedure which consisted of dissolving weighed samples in an excess of standard 1 N nitric acid, diluting with water, boiling to remove the carbon dioxide, and determining the excess acid by titration with a standard 0.1 N sodium hydroxide solution using methyl red as the indicator. The mole ratios CO_2/Nd_2O_3 and H_2O/Nd_2O_3 were calculated and are listed in Table V.

The mole ratio CO_2/Nd_2O_3 remained approximately 3 for the above drying conditions; the mole ratio

TABLE V

Effect of Heat on Hydrated Neodymium Carbonate

Sample	Drying Conditions	% Nd_2O_3	% CO_2	% H_2O	$\frac{CO_2}{Nd_2O_3}$	$\frac{H_2O}{Nd_2O_3}$
A	Air dried*	65.8	25.4	8.8	2.96	2.50
B	1 hr. at 110°C.	68.2	26.7	5.1	3.00	1.40
C	12 hrs. at 110°C.	70.8	27.9	1.3	3.02	0.34
D	3 days at 120°C.	71.4	27.8	0.8	2.98	0.21
$Nd_2(CO_3)_3$ (theoretical)		71.8	28.2	0.0	3.00	0.00

* - Washed with alcohol and ether.

H_2O/Nd_2O_3 decreased continually, indicating dehydration. For an extended drying period, as in the case of Sample D, a carbonate was obtained which was essentially anhydrous.

The preparation of rare earth carbonates by the decomposition of the trichloroacetates from hot water solutions is more satisfactory than older preparations. Pure normal carbonates are produced since no interfering ions are introduced.

SECTION IV

Separation of Praseodymium and Lanthanum

Among the reactions used for fractional precipitation methods of separating the rare earths, homogeneous phase reactions have been very satisfactory even though some of them have certain disadvantages. The hydrolysis reactions that have been used are listed by Moeller and Kremers[68] in an excellent review article on the basicity characteristics of the rare earths. Some of the more important ones involve the separation of cerium by oxidation to the ceric form followed by hydrolysis of rare earth nitrites, phthalates, lactates, sulfites, citrates, tartrates, m-nitrobenzoates, phenoxyacetates to form basic salts. In most of these methods the desired anion was added in the form of an alkali salt. The resulting high concentration of alkali ions in the reaction mixtures is disadvantageous.

Willard and Gordon[97] separated thorium and the rare earths from monazite by a homogeneous phase reaction involving the hydrolysis of dimethyloxalate to precipitate insoluble thorium and rare earth oxalates. Thorium was separated from the rare earths by the hydrolysis of urea in the presence of formic acid; an insoluble basic thorium formate precipitated. A more recent method[35] involves the

hydrolysis of tetrachlorophthalic acid to produce an insoluble thorium compound. No data about these homogeneous phase separations being applied to the rare earth group have been published.

Since praseodymium and lanthanum salts have very similar chemical and physical properties, their separation is difficult. Slight differences in solubilities and basicities are the important criteria in such separations. Methods which depend upon the immediate formation of a precipitate after addition of a reagent resulting in local action do not give maximum efficiency. This difficulty is minimized by the use of homogeneous phase reactions in which the reagents are formed in solution.

Two homogeneous phase reactions which have been investigated for the separation of praseodymium and lanthanum are the decomposition of the trichloroacetate ion in the presence of rare earth ions to form the insoluble rare earth carbonates, and the hydrolysis of dimethyloxalate in rare earth solutions to yield insoluble rare earth oxalates.

Part A

The Trichloroacetate Separation

The rate of decomposition of the trichloroacetate ion to form chloroform and carbon dioxide has been studied rather extensively by Verhoek.[37,93,94,95] In water the rate of decomposition of the trichloroacetate ion is dependent upon the temperature and concentration but almost independent of the nature or size of the accompanying cation. Verhoek[37] claims that for a fixed temperature and salt concentration there is very little difference in the rate of decomposition of sodium, ammonium, barium, and even tetraethylamine trichloroacetates in water. Because of the dissimilarities in properties of the above mentioned cations, it may be assumed that lanthanum and praseodymium trichloroacetates decompose at essentially the same rate and that the separation of these two rare earths does not depend upon a difference in the rate of decomposition of their respective trichloroacetates.

Verhoek[93,94] has shown that it is the trichloroacetate ion which decomposes and not the free acid or its salts. The trichloroacetate ion under the influence of heat yields carbon dioxide and the strongly basic trichloromethyl ion, which immediately reacts with water to form chloroform.

$$CCl_3C\bar{O}O \longrightarrow CCl_3^- + CO_2$$

$$CCl_3^- + H_2O \longrightarrow CHCl_3 + \bar{O}H$$

Since chloroform is insoluble in water it is evolved; the carbon dioxide reacts with the water and any cation present to form a carbonate. If the carbonate is an insoluble one, such as an alkaline earth or rare earth carbonate, a precipitate forms. When several different cations are present, the carbonate of the one which is the least soluble has the greatest tendency to precipitate. For a lanthanum-praseodymium mixture, the praseodymium has the greater tendency to precipitate as the carbonate leaving the mother liquor enriched in lanthanum. If the reaction continues until all the trichloroacetate ion has decomposed, the filtrate contains only a small quantity of rare earth chloride. The chloride ion is formed during the reaction by the secondary oxidation of chloroform in the hot solution.

Praseodymium may be concentrated by the following method. The lanthanum and praseodymium oxide mixture is dissolved in the theoretical quantity of hot 25 per cent trichloroacetic acid solution by sifting the oxide gradually into a flask containing the acid. A slight excess of acid may be necessary to effect complete solution. Oxides containing a high praseodymium content are more difficult to dissolve. The rare earth trichloroacetate

solution is diluted with water until the rare earth concentration is approximately 10 grams of oxide per liter. The solution is heated to 90° C. on an electric mantle. This temperature is maintained for 20 minutes after the first appearance of a precipitate. During the heating the solution is stirred continuously. The reaction is stopped by cooling the flask to room temperature in an ice water bath. The carbonate precipitate, containing about 30 per cent of the rare earth, is filtered in a Buchner funnel and washed with a small quantity of water. The filtrate is reheated to 90° C. and the decomposition reaction carried on for 35 minutes. The mixture is cooled and the precipitate (another approximately 30 per cent of the rare earth) filtered as before. Its praseodymium content exceeds that of the original sample by about 10 per cent. The filtrate from the second precipitation is treated with oxalic acid to recover the remaining rare earth.

A typical example illustrating the concentration of praseodymium consisted of treating 72 grams of an oxide sample containing 36 per cent Pr_6O_{11} by the method outlined (Separation I, Table VI). Upon ignition the first carbonate precipitate yielded 22 grams of an oxide containing 53 per cent Pr_6O_{11}, indicating an enrichment of 18 per cent. A second precipitate gave 21 grams of oxide containing 46 per cent Pr_6O_{11}, or a praseodymium oxide enrichment exceeding

the original by 10 per cent. The final filtrate yielded 29 grams of rare earth oxide which had been reduced to 21 per cent Pr_6O_{11}.

The rare earth obtained in the first precipitate was treated in similar fashion to further concentrate the praseodymium (Separation II, Table VI). The 53 per cent material yielded in the first precipitate 6.5 grams of an oxide which contained 72 per cent Pr_6O_{11}; in the second precipitate 6.5 grams of an oxide which contained 62 per cent Pr_6O_{11}; and from the filtrate 9 grams of an oxide, which by coincidence had the same composition as the original sample, namely 36 per cent Pr_6O_{11}.

The results of these two separations are listed in Table VI from which it can be seen that the praseodymium

TABLE VI

The Enrichment of Praseodymium by the Trichloroacetate Separation

Sample	Weight Per Cent Pr_6O_{11}*	
	Separation I	Separation II
Original	36	53**
First Carbonate	53	72
Second Carbonate	46	62
Filtrate	21	36

* - The oxides were analyzed for praseodymium by the absorption spectra method (Section VI).

** - This sample is the same as the first carbonate precipitate, Separation I.

content was doubled in two steps from 36 to 72 per cent Pr_6O_{11}.

The effects of two variables, temperature and concentration, upon this separation were investigated. The results obtained show that the degree of separation of lanthanum and praseodymium is dependent upon the concentration of rare earth trichloroacetates in solution, and essentially independent of the temperature at which the reaction is carried out.

The temperature effect was investigated by heating trichloroacetate solutions containing 10 grams of lanthanum-praseodymium oxide mixture per liter at 60°, 70°, 80°, and 90° C. Two fractions of carbonates, each containing about 30 per cent of the original oxide sample, were removed and analyzed for praseodymium. The reaction times and analyses are listed in Table VII.

TABLE VII

The Effect of Temperature on the Trichloroacetate Separation

Temp. (°C.)	Reaction Time (Hrs.)		Weight Per Cent Pr_6O_{11}*		
	Carbonate I	Carbonate II	Original	Carbonate I	Carbonate II
90	0.33	0.6	53	72	60
80	1.5	2.5	53	70	61
70	6.5	11.5	53	73	63
60	32.5	62.5	53	71	62

* - Analyzed by the absorption spectra method (Section VI).

The reaction time in each case was calculated using the rate constants reported by Verhoek[94] for the decomposition of sodium trichloroacetate in water. From these results it is evident that the separation of praseodymium is not improved by carrying out the decomposition at a lower temperature and a slower rate.

The effect of rare earth concentration was investigated in a similar manner. The decomposition reaction was carried out at 90° C. with trichloroacetate solutions containing 10 and 20 grams of rare earth oxide per liter. The first carbonate fraction was removed 20 minutes after the appearance of a precipitate, the second after an additional 35-minute period. Each fraction contained approximately 30 per cent of the original rare earth. The carbonates and the final filtrate were analyzed for praseodymium and the average results of several reactions are listed in Table VIII.

TABLE VIII

The Effect of Rare Earth Concentration on the Trichloroacetate Separation

Rare Earth Oxide Concentration (g./l.)	Weight % Pr_6O_{11}*			
	Original	Carbonate I	Carbonate II	Filtrate
10	53	72	62	36
20	53	65	61	41

* - Analyzed by the absorption spectra method (Section VI).

The results clearly indicate that a better separation of praseodymium is obtained in the more dilute solutions. In other experiments it was observed that if the concentration is less than 10 grams per liter, the carbonates tend to be gelatinous and difficult to filter.

A comparison of the enrichment of praseodymium at 90° C. in carbonate fractions removed after permitting the trichloroacetate decomposition to run for long periods of time with those removed after short time intervals was made.

The mixed oxides of lanthanum and praseodymium were dissolved in 25 per cent trichloroacetic acid. The solution, diluted with water so that the rare earth concentration was 25 grams of oxide per liter, was heated to and maintained at 90° C. for two hours. During the heating the solution was stirred continuously. The carbonate was filtered off and dissolved in the minimum quantity of 5 per cent trichloroacetic acid. This solution was then heated for two hours in the same manner as the original solution to decompose the acid and precipitate another carbonate fraction. The carbonate was filtered, dissolved in the 5 per cent acid, and the decomposition again effected. This process of precipitating a carbonate fraction, dissolving it and reprecipitating was repeated several times.

The analyses of the different fractions obtained in one typical separation are given in Table IX. The original oxide sample weighed 26.2 grams and contained 67 per cent Pr_6O_{11}; Fraction 8, consisting of high purity praseodymium, weighed 4.5 grams and represented a yield of approximately 25 per cent with respect to the original praseodymium content. For this type of separation it is also observed that the carbonate precipitate is enriched in praseodymium.

TABLE IX

The Purification of Praseodymium by the Trichloroacetate Separation

Fraction	Weight % Pr_6O_{11}*
Original	67
1	74
2	79
3	86
4	91
5	94
6	97
7	99
8	99+

* - Analyzed by the absorption spectra method (Section VI).

Of the two procedures the former is the better for quickly concentrating small amounts of praseodymium from samples which contain less than 80 per cent praseodymium oxide. For samples containing more than 80 per cent praseodymium, the latter procedure is better. Although the

enrichment per step is less, the major part of the sample remains intact and much less praseodymium is sacrificed.

The latter procedure was utilized for the purification of some praseodymium oxide (about 16 grams) which contained about 5 per cent lanthanum oxide. The decomposition time was increased to 3 hours in order to precipitate a larger portion of the rare earth. After 10 fractionations the carbonate obtained was ignited. About 8 grams of oxide was secured. Arc spectrum analysis* showed the following elements to be present as impurities: lanthanum, less than 0.02 per cent; iron, less than 0.02 per cent; silicon, 0.04 per cent. Elements not detected were aluminum, calcium, cerium, cobalt, chromium, dysprosium, erbium, europium, gadolinium, holmium, lutetium, magnesium, manganese, molybdenum, neodymium, nickel, lead, scandium, samarium, strontium, terbium, thulium, titanium, vanadium, yttrium, ytterbium, and zirconium. It is evident that the method may be applied to the separation of small amounts of lanthanum from oxides rich in praseodymium.

Cerium interferes and should be removed before attempting to separate lanthanum and praseodymium. In a hot solution cerium is oxidized and precipitated as hydrated ceric oxide. Its presence imparts a gelatinous character

* - Analysis by Dr. F. S. Tomkins, Argonne National Laboratory, Chicago, Illinois.

to the carbonate precipitate and filtration becomes difficult. However, if a small quantity of cerium is present when the oxide is dissolved in trichloroacetic acid, it precipitates as an insoluble yellow basic ceric trichloroacetate which can be filtered. The filtrate is then treated for the separation of lanthanum and praseodymium.

The trichloroacetate separation of praseodymium and lanthanum is rapid, requires a minimum of labor and space, uses ordinary laboratory equipment, requires no expensive chemicals, and can be applied to large scale production.

Part B

The Dimethyloxalate Separation

Several procedures,[85] which may be classified into two groups, have been developed for the fractional precipitation of rare earth oxalates. In one type, oxalic acid solution is added drop by drop to a hot acidic rare earth solution until a slight permanent precipitate is formed. The solution is then allowed to cool after which some rare earth oxalate precipitates. The mixture is filtered and the filtrate subjected to the same treatment as the original solution. The order of decreasing solubility from the most to the least soluble oxalate is lanthanum, cerium, praseodymium, neodymium, and samarium.[80] In the second type of separation a partial solution of rare earth oxalates in alkali oxalate solutions is effected. Due to the formation of soluble complex oxalates, the order of solubility is reversed; lanthanum oxalate is the least soluble and samarium oxalate the most soluble in alkali oxalate solutions. Recently Beck[10] developed a variation of the latter procedure by dissolving rare earth oxalates in a solution of sodium nitrilotriacetate, $N(CH_2COONa)_3$, and fractionally reprecipitating them as the solution is acidified. Lanthanum oxalate precipitated first, followed by the oxalates of the less basic rare earth elements. Willard[35,97] and

co-workers suggested the hydrolysis of dimethyloxalate in perchloric acid solutions for the separation of the rare earths and thorium from monazite. Complete precipitation was not obtained due to incomplete hydrolysis of the dimethyloxalate. A small quantity of oxalic acid was finally added to complete the precipitation. No report was given about the use of this reaction to separate the members of the rare earth group itself.

The fractional precipitation of rare earth oxalates based upon the internal hydrolysis reaction of dimethyloxalate to produce oxalate ions in solution minimizes the interference due to local action when oxalate solutions are added directly. The reaction may be represented as

$$2RCl_3 + 3(CH_3)_2C_2O_4 + 6HOH \rightarrow R_2(C_2O_4)_3 + 6CH_3OH + 6HCl.$$

It was found that praseodymium may be concentrated by the following method. About 5 g. of a mixture of lanthanum and praseodymium oxides is moistened with water and dissolved in the minimum quantity of concentrated hydrochloric acid. The solution is diluted with 600 ml. of 1 N hydrochloric acid. About 2.8 g. of dimethyloxalate is dissolved in 400 ml. of 1 N hydrochloric acid. (This is sufficient dimethyloxalate to precipitate half the rare earths in solution as oxalates if all the ester hydrolyzes.) The dimethyloxalate solution is added from

a dropping funnel to the rare earth solution at a rate of about one drop per 2-3 seconds. The reaction mixture is stirred continuously during the addition of the ester solution. After all the dimethyloxalate has been added, the solution is stirred for an hour. Approximately one-third of the original quantity of rare earth is precipitated as a very dense crystalline rare earth oxalate, which is filtered in a Buchner funnel and ignited to the oxide. The rare earth in the filtrate is precipitated with oxalic acid; the oxalate is filtered and ignited to the oxide.

The precipitation of rare earth oxalates by the hydrolysis of dimethyloxalate is rapid in neutral solution, but considerably slower in acid medium. If the concentration of rare earth and ester is low, the precipitation is still slower. Since rapid precipitations generally result in poorer products than slow ones, the conditions which favor a slow oxalate precipitation are utilized.

The original oxide and the oxides obtained from the precipitate and the filtrate were analyzed for praseodymium by the iodometric method. The results of two different dimethyloxalate separations are listed in Table X as Experiments 1 and 2.

In one variation of the above procedure, Experiment 3, all of the dimethyloxalate solution was added at

one time and the solution stirred for two hours before being filtered. In Experiment 4 the dimethyloxalate solution was added dropwise as in Experiments 1 and 2 except that 1 N sulfuric acid was used instead of 1 N hydrochloric acid as the solvent for the sample.

TABLE X

The Enrichment of Praseodymium by the Dimethyloxalate Method

	Weight Per Cent Pr_6O_{11}*		
Experiment	Original	Precipitate	Filtrate
1	64	85	59
2	64	85	60
3	64	80	58
4	64	70	-

* - Oxides analyzed by the iodometric procedure (Section VI).

Since the idea for the dimethyloxalate separation was conceived late in the research program, conditions which govern the degree of separation, such as concentration of rare earth and dimethyloxalate, temperature, pH, and effect of various acids and complexing agents, have not been studied as completely as in the trichloroacetate separation. However, the following facts may be observed from the values listed in Table X: a) the percentage of praseodymium in a rare earth sample may be increased by 20 per cent in one step, b) a poorer separation

is obtained if all the dimethyloxalate is added at one time, c) the separation is considerably better in chloride solutions than in sulfate solutions.

The dimethyloxalate procedure appears to have advantages over the trichloroacetate procedure in that cerium does not interfere and does not have to be previously separated and heating is unnecessary since the reaction proceeds at room temperature. Its principle disadvantage is that the oxalates must be ignited and the resulting oxide dissolved before carrying out a second fractionation, while the trichloroacetate decomposition produces a carbonate which is easily dissolved in a dilute trichloroacetic acid solution.

SECTION V

The Trichloroacetate Separation of Cerium

The usual separation of cerium from the other rare earths is based upon the facts that cerium may be oxidized to the tetravalent state and that ceric compounds are easily hydrolyzed to insoluble basic salts. The two methods most commonly used in the laboratory are the potassium bromate method[24,41,42] and the permanganate-ceric oxide method.[79] In the former, cerium is oxidized by potassium bromate in a solution buffered by lumps of marble. A basic ceric nitrate is precipitated slowly as the solution is boiled. The method is slow; the physical nature of the marble is important. If powdered marble is used, the pH will be too high and some rare earth hydroxide will contaminate the basic ceric salt. In the permanganate method cerium is oxidized by potassium permanganate and is precipitated as a hydrated ceric oxide by adjusting the pH to about 3.5 with dilute hydroxide solution. Although this method is faster than the bromate method, it has the disadvantage of adding manganese to the solution. Several precipitations of the rare earths as oxalates are often necessary to separate all the manganese. The adjustment of pH is critical. If it is too low not all the cerium is precipitated, if too high the trivalent earths precipitate.

When the hydroxide is added some of the trivalent earths have a tendency to precipitate due to a high local hydroxide concentration where the drops come in contact with the solution. The rare earth hydroxides are not always completely redissolved; hence the cerium is frequently contaminated with other rare earths.

While studying the properties of the rare earth trichloroacetates it was observed that tetravalent cerium and thorium form insoluble basic trichloroacetates. The compounds were similar to the basic acetates produced with acetic acid. The rare earth trichloroacetates are extremely soluble. This difference in solubility between the basic and normal salts immediately suggested a possible separation of cerium.

Trichloroacetic acid is used to separate cerium from lanthanum, praseodymium, and neodymium by the following procedure. One hundred grams of the freshly ignited rare earth oxide is dissolved in the minimum quantity of concentrated nitric acid. The solution is cooled and diluted to one liter with water. Seventy-five grams of trichloroacetic acid dissolved in a few milliliters of water is added to the rare earth solution. [This is approximately the quantity of trichloroacetic acid equivalent to the formation of the rare earth salt $R(C_2Cl_3O_2)_3$.] Although

the solution is strongly acid from the addition of the trichloroacetic acid, a large portion of the cerium separates immediately as a light yellow precipitate. The basic ceric trichloroacetate is filtered with gentle suction in a Buchner funnel supplied with a filter mat. (A suitable mat may be prepared from filter paper pulp.) The precipitate is washed with a 5-10 per cent trichloroacetic acid solution, which dissolves any trivalent earth hydroxides that may have coprecipitated with the cerium compound, but will not dissolve the basic salt. Water must not be used as a wash solution because the basic trichloroacetate becomes colloidal and is washed through the filter. The major portion of the cerium is removed in this first precipitation. Any remaining cerium may be removed from the filtrate by adding 6 N ammonium hydroxide slowly with stirring until the solution becomes neutral to litmus. At this higher pH the remaining cerium is precipitated along with some rare earth hydroxide. A few milliliters of 20 per cent trichloroacetic acid solution is added until the solution is again acid to litmus. The rare earth hydroxide redissolves, but the basic ceric trichloroacetate remains insoluble and may be filtered as before. The process of adding 6 N ammonium hydroxide followed by 20 per cent trichloroacetic acid is continued until the precipitate formed by the ammonia is soluble in the acid.

A clear solution upon the addition of a small quantity of the trichloroacetic acid is an indication that the solution is free of ceric cerium. The basic ceric trichloroacetate is dissolved in concentrated nitric acid and the cerium recovered as the oxalate.

A concentrated nitrate solution of the cerium obtained by this method yields a colorless solution when the cerium is reduced with hydrogen peroxide, and the absorption spectra of neodymium and praseodymium are not detectable. Cerium of rather high purity may be obtained by this trichloroacetate method.

The procedure given above is dependent upon all the cerium being in the tetravalent form. It has been shown by Barthauer and Pearce[7] that all of the cerium in freshly ignited rare earth oxide mixtures exists in the tetravalent form only. Unlike praseodymium, the oxidation state of cerium is not affected by the presence of other rare earth oxides.

The exact chemical composition of basic ceric trichloroacetate is not known, although basic thorium trichloroacetate, $(Cl_3C\cdot COO)_2Th(OH)_2$, was prepared by Karl[44] who recrystallized it from hot 95 per cent alcohol. He found the thorium compound to be only slightly soluble in water; 100 ml. of water at 25° C. dissolved 0.0091 g. $(Cl_3C\cdot COO)_2Th(CH)_2$. In this study qualitative solubility

determinations indicate that the cerium compound is even less soluble; the basic trichloroacetate separation of cerium depends upon a low solubility of the ceric compound in water and dilute trichloroacetic acid solutions.

Basic ceric trichloroacetate is an insoluble yellow compound of a slightly gelatinous nature. In physical appearance it resembles other basic salts of tetravalent cerium. It is not a normal trichloroacetate since these compounds are crystalline and extremely soluble in water, yet it is not gelatinous enough to be confused with hydrated ceric oxide. It is soluble in concentrated nitric acid, less soluble in alcohol, and almost insoluble in excess trichloroacetic acid solution. It becomes colloidal in very dilute solutions probably due to further hydrolysis. The compound is difficult to analyze, since any of the common drying techniques cause some decomposition of the trichloroacetate ion.

SECTION VI

Analytical Methods for the Rare Earth Elements

In any rare earth separation research the choice of a suitable analytical method is important. Methods which are both rapid and accurate are highly desirable. It is often necessary to develop new methods to suit the particular mixture being investigated.

The first part of this section is a discussion of the principal analytical methods for the determination of the rare earth elements. Since a large part of the present research deals with the separation of praseodymium and lanthanum, the methods used for the determination of praseodymium, including a new iodometric method, are dealt with in the second part of this section. The last part describes a correction for average atomic weight determinations of rare earth mixtures by the oxalate-oxide method.

Part A

Principal Analytical Methods

The five fundamental methods for the quantitative determination of mixtures of rare earth elements are average atomic weight determinations, special methods involving a change in valence state of a particular rare earth element, spectroscopic methods, magnetochemical analyses, and the use of radioactive tracers. The first two are based upon chemical reactions in common usage. However, the second method is applicable only to those rare earth elements which are capable of existing in more than one valence state. The last three methods are based upon physical properties, the measurement of which requires special equipment that is not always available in the ordinary chemical laboratory.

The relationships most frequently used to evaluate the average atomic weight of a rare earth mixture are the determinations of the acid equivalence of a weighed quantity of rare earth oxide,[23] rare earth chloride to silver ratio,[9] oxide to sulfate ratio,[81] and oxalate to oxide ratio.[8,24,32] The determination of the chloride to silver ratio is the most accurate, but also the most time consuming. It requires the preparation of a pure anhydrous chloride; weighed quantities of which are treated with silver nitrate solution. The resulting silver chloride is

collected and weighed. This method is impracticable for routine application. Similarly, the determination of oxide to sulfate ratio requires the preparation of an anhydrous sulfate from a weighed quantity of the oxide. Common sources of error in this method are the difficulty of removing the last traces of free sulfuric acid from the sulfate without causing decomposition, and the difficulty of weighing the anhydrous sulfates which are exceedingly hygroscopic. Since the oxalate to oxide method is rapid and fairly accurate, it is widely used. It involves the preparation of an oxalate, a weighed sample of which is ignited to the sesquioxide. A second sample is dissolved in sulfuric acid and titrated with a standard permanganate solution in order to determine the oxalate content. The average atomic weight is calculated from the oxide to oxalate ratio. In this ratio the two sample weights are directly proportional and no error is introduced due to the hydrated nature of the oxalate. This method becomes inaccurate due to the formation of an oxide higher than the sesquioxide if rather large quantities of cerium, praseodymium, or terbium are present. The positive error in the case of high purity praseodymium may amount to several atomic weight units and is frequently misinterpreted as indicating a high percentage of samarium and yttrium earths in the sample. Nevertheless, this method is one of the most frequently used.

A volumetric method which has had limited use depends upon dissolving a weighed sample of oxide in a known excess of 0.5 N sulfuric acid and titrating the excess acid with 0.1 N alkali using methyl orange as indicator. The average atomic weight is calculated from the number of acid equivalents required to neutralize the oxide. The rare earths differ in basicity, hence the hydrolysis effect may introduce an error. It is alsc important that the original oxide be ignited strongly enough to free it of carbonate. The above atomic weight determinations yield the average composition of the mixture and cannot be used if the percentage of any particular element is desired.

Certain of the rare earth elements, namely cerium, praseodymium, samarium, europium, terbium, and ytterbium, exist in more than one oxidation state. A few special analytical methods involving these changes in oxidation state have been developed for cerium, praseodymium, and europium.

The most common analytical procedures[16,30] for the determination of cerium are the iodometric method, the ferricyanide and permanganate method, the hydrogen peroxide and permanganate method, the alkaline permanganate method, the bismuthate and permanganate method, the persulfate method,[98,99] and the perchloric acid method.[84] In Bunsen's iodometric method[7,88] ceric oxide is dissolved in hydrochloric

acid in the presence of potassium iodide, and the liberated iodine determined with a standard sodium thiosulfate solution. This method gives inaccurate results if praseodymium or terbium are present since they also form higher oxides that are capable of liberating iodine. Potassium ferricyanide oxidizes trivalent cerium to the tetravalent form in alkaline solution. The ceric hydroxide is filtered off and the ferrocyanide formed titrated with permanganate in acid solution. The hydrogen peroxide and permanganate method is based on the fact that ceric sulfate is reduced in a dilute sulfuric acid solution by hydrogen peroxide. The excess hydrogen peroxide is then determined by titration with permanganate. The alkaline permanganate method depends upon the oxidation of cerous salts in alkaline solution by permanganate. Special care must be taken because of the oxidation of cerous hydroxide by air. One of the better methods involves the oxidation of cerium in dilute sulfuric acid by sodium bismuthate. The excess bismuthate is filtered off. A measured excess of standard ferrous ammonium sulfate is added to the filtered solution and the excess ferrous iron is then back titrated with standard permanganate. The cerium may be oxidized by adding solid ammonium persulfate and boiling the sulfate solution. A small amount of silver nitrate solution is added as catalyst. The tetravalent cerium is determined as in the bismuthate method, or it may

be titrated electrometrically with a ferrous sulfate solution which has been standardized against a ceric sulfate solution of known strength.

A later variation of this method utilizes the oxidation of cerium in a hot mixture of sulfuric and perchloric acids. The solution is then cooled, the cerium reduced by a standard ferrous ammonium sulfate solution, and the excess determined by a suitable standard oxidizing agent.

Europium may be reduced in a Jones reductor to the divalent state[58,59,60] and determined directly by titration with permanganate or iodine solutions.[61] In order to decrease the effect of air oxidation, the europous salt may be determined indirectly by collecting it in a standard ferric sulfate solution and titrating the equivalent amount of ferrous sulfate formed with permanganate. Ytterbium and samarium may interfere since they may be reduced to the divalent ions.

The black oxides of praseodymium are capable of liberating iodine from acidified potassium iodide solutions. It seems probable that the Bunsen iodometric method for cerium could be applied to praseodymium. This procedure has been proposed[6] but not completely investigated. The method would require a working curve of percentage composition of praseodymium oxide versus liberated iodine or

active oxygen. Since the function is not linear, the preparation of such a curve would require the mixing of pure rare earths in order to determine a series of points.

Three kinds of spectral methods, X-ray, absorption, and emission, are used in the determination of the rare earth elements; all require the use of special equipment. Absorption spectra analysis is almost indispensable in following the purification of these elements. The quantity of rare earth ions in a solution may be determined in two ways. A definite volume of the unknown solution is diluted until certain absorption bands begin to disappear. A standard solution of the pure element is diluted in a similar manner. The concentration of the element in the unknown solution is calculated by comparing the two dilutions.[76] A second way requires the application of Lambert's and Beer's laws.[15,73] A working curve consisting of a plot of extinction versus concentration may be prepared for the pure element. The extinction of the unknown solution is measured and the concentration of the colored ions determined from the graph. However, many of the absorption bands overlap, and the choice of the proper wave length is of extreme importance. Moeller and Brantley[67] made an extensive study of the application of the absorption spectra to the determination of the rare earths. The proper wave lengths for the determination of praseodymium, neodymium,

samarium, europium, gadolinium, erbium, thulium, and ytterbium are listed along with correction factors for interfering ions. Nevertheless, the accuracy of absorption methods is usually no better than one per cent.

The analysis of the rare earths by emission spectra is extremely sensitive. This type of analysis is usually applied to the determination of trace impurities in high grade samples. Unfortunately the emission spectra of the rare earths are enormously line rich. The classification of these lines is a complex problem. Gatterer and Junkes with the assistance of V. Frodl have prepared enlarged plates of the arc and spark spectra of the various elements along with a complete list of their emission lines.[31]

The most accurate of all the spectroscopic methods for the rare earths utilizes the well defined X-ray spectra. If a rare earth compound is bombarded with cathode rays, X rays are emitted. The spectra of these X rays differ for each element and are extremely simple.[29] Thus it has an immediate advantage over the analysis by emission spectra if proper equipment is available.

Most of the rare earth elements are paramagnetic. In some cases, such as with europium and gadolinium, they differ widely in magnetic susceptibilities

and magnetochemical analysis[82] may be applied. It is especially useful in the purification of the first and last members of the rare earth series, namely lanthanum and lutetium, which are diamagnetic. The measurement of magnetic susceptibilities requires the use of a magnetic balance, which is not always available to the rare earth chemist. For quantitative determinations a disadvantage is that magnetic methods are usually limited to binary mixtures.

A more recent analytical method for the rare earths uses radioactive tracers. This type of analysis has been used extensively in following separations by ion exchange methods. A known quantity of a radioactive isotope of one of the elements to be separated is added to the mixture. Chemically there is no difference between the radioactive and ordinary atoms of the element. Since the ratio of these two types of atoms should remain constant throughout any chemical process, the degree of separation may be determined by measuring the radioactivity with a Geiger-Muller counter or other suitable means. However, radioactive tracers and the special equipment needed for their measurement are not always available.

Part B

The Determination of Praseodymium

Two quantitative methods were used to follow the progress of separation of lanthanum and praseodymium: a) the absorption spectrum method, and b) the iodometric method. The latter was developed while attempting to improve the oxalate-oxide method for the determination of the average atomic weight of rare earth mixtures. After its development the iodometric method was used exclusively.

A mixture of lanthanum and praseodymium is especially easy to analyze by means of absorption spectrum since lanthanum ions are colorless and offer no interference to absorption measurements of the green praseodymium ions. Solutions approximately 0.01 M in Pr_6O_{11} were prepared by dissolving weighed samples of the unknown oxides in nitric acid and diluting to a known volume. The solutions were analyzed for praseodymium using 5 cm. cells in a Cenco-Sheard Spectrophotolometer, and measuring the extinction values in the 589 mμ region and by applying Beer's and Lambert's laws, $C = \frac{E}{kd}$, with C representing molar concentration of praseodymium oxide, E the observed extinction, k the extinction coefficient of a standard solution, and d the thickness of the solution. The percentage Pr_6O_{11} in

the original oxide was calculated as follows:

$$\%Pr_6O_{11} = C \times Pr_6O_{11} \times \frac{100}{S.W.}$$

with Pr_6O_{11} representing the molecular weight of praseodymium oxide and S.W. the sample weight.

The iodometric method was developed for this study by utilizing the fact that praseodymium exists in a higher oxidation state in oxides than it does in solution. The formula of the pure oxide has been found to be Pr_6O_{11}[7,70] which corresponds to an oxygen content 3.12 per cent in excess over that needed for sesquioxide formation. Under the proper conditions the "excess" oxygen in a weighed oxide sample liberates an equivalent amount of iodine from potassium iodide solutions. The iodine is titrated with standard thiosulfate, and the per cent "excess" oxygen calculated. However, in binary mixtures of praseodymium and lanthanum oxides the per cent "excess" oxygen varies with the ratio of the two oxides.[6,74] Accordingly, it was also necessary to determine the variation experimentally and construct a graph from which the per cent praseodymium oxide can be read.

The determination of praseodymium by the iodometric method consists of dissolving about 0.5 gram of the oxide in a slight excess of nitric acid. The nitrate solution is diluted to about 150 ml., heated to 90° C., and the rare earth precipitated with the minimum quantity

of hot dilute oxalic acid. After the solution has cooled the precipitate is filtered in a Buchner funnel, washed with 95 per cent ethyl alcohol, and air dried with suction. The oxalate is transferred to a crucible and ignited for 2-3 hours at 925° C. in a muffle furnace. The crucible is removed from the hot furnace and allowed to cool for about one minute; the oxide is transferred immediately to a weighing bottle and covered tightly. It is then allowed to cool to room temperature and is ready for weighing.

Three samples of 0.10-0.12 g. of the above oxide are weighed into 250 ml. iodine flasks. To the sample in each flask are added first 10 ml. of 0.1 M potassium iodide solution and then 25 ml. of 6 N sulfuric acid. The flask is immediately stoppered and gently swirled to dissolve the oxide. The solution time varies from 5 to 30 minutes depending upon the nature of the oxide. The liberated iodine is titrated with 0.01 N sodium thiosulfate using 3-4 ml. of 1 per cent starch solution as the indicator. A blank correction on water is made and the volume of thiosulfate required for the blank is subtracted from that of the sample. Blank corrections amount to approximately 0.02 ml. of thiosulfate for each 5 minutes of solution time.

The calculation for the per cent "excess" oxygen is % "Excess" Oxygen = $NV \times \frac{O}{2000} \times \frac{100}{S.W.}$. N represents the normality of the sodium thiosulfate solution, V the volume of the sodium thiosulfate solution, $\frac{O}{2000}$ the milliequivalent weight of oxygen, and S.W. the sample weight.

The graph used to determine the per cent praseodymium oxide in binary mixtures with lanthanum oxide with relation to "excess" oxygen was obtained by preparing synthetic mixtures covering the entire percentage range. Weighed samples of the two pure oxides were dissolved in dilute nitric acid, the rare earth ions coprecipitated as oxalates, and the mixed oxalates ignited at 925° C. for 2-3 hours in a muffle furnace. The "excess" oxygen was determined in these oxide mixtures by the iodometric method. The variation of per cent "excess" oxygen against per cent praseodymium oxide is graphed in Figure 1 and the data for it are listed in Table XI.

Since the curve for the praseodymium-lanthanum mixtures indicated such a variable behavior for the "excess" oxygen-oxide relationship, data were also obtained in the same manner for neodymium-praseodymium and samarium-praseodymium mixtures. These relationships are discussed in the section on the properties of praseodymium oxides.

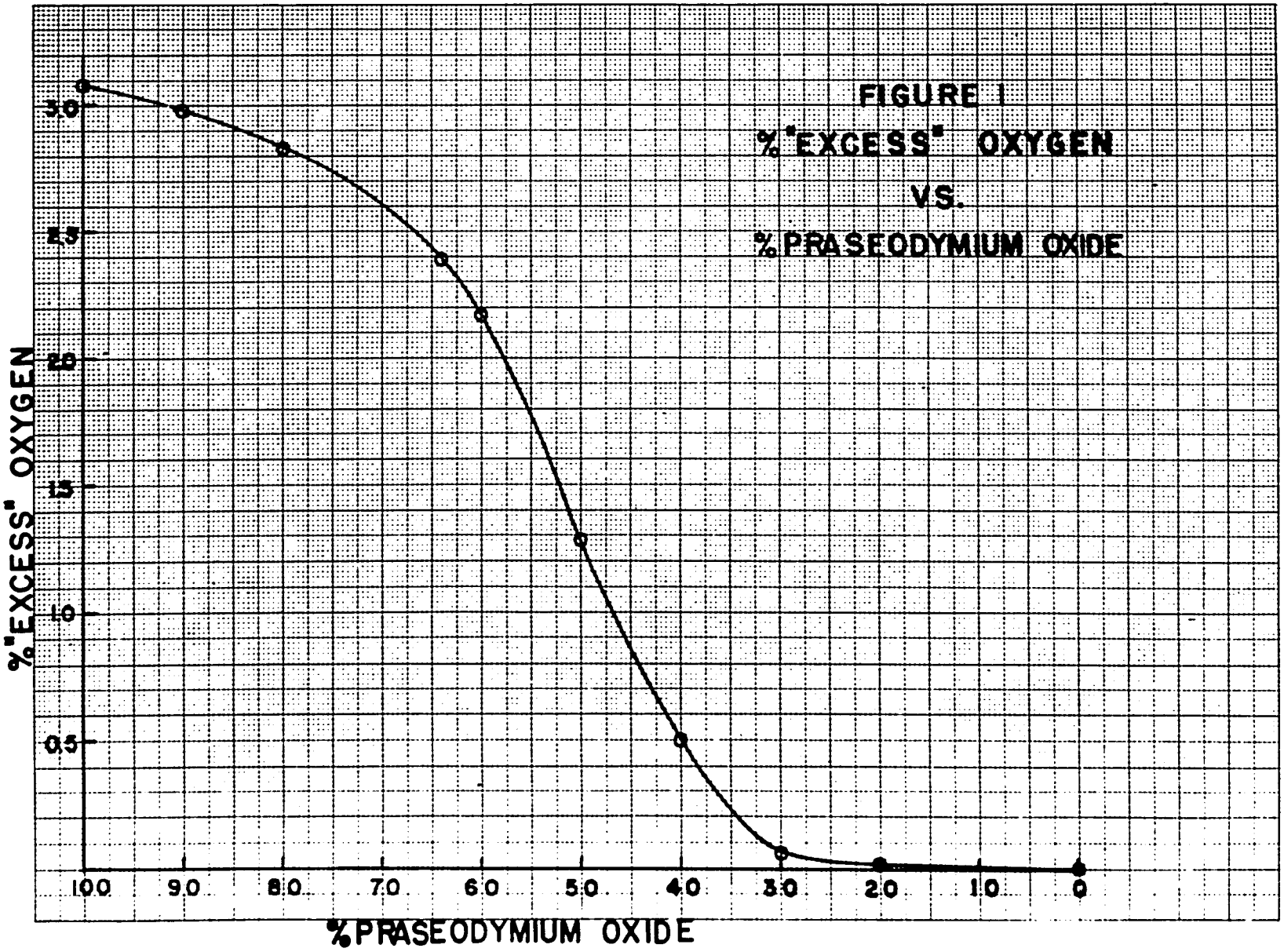


FIGURE 1
% "EXCESS" OXYGEN
VS.
% PRASEODYMIUM OXIDE
% "EXCESS" OXYGEN
3.0
2.5
2.0
1.5
1.0
0.5
100
90
80
70
60
50
40
30
20
10
0
% PRASEODYMIUM OXIDE

TABLE XI

Comparison of "Excess" Oxygen and Praseodymium Oxide Percentages in Lanthanum-Praseodymium Oxides

Per Cent Praseodymium Oxide	Per Cent "Excess" Oxygen
100.0	3.08
90.0	2.98
79.9	2.83
64.0	2.39
60.0	2.17
50.0	1.28
40.0	0.50
29.8	0.06
20.0	0.02
0.0	0.00

Factors which may affect the accuracy of the iodometric method are the conditions of ignition of the oxalate, the effect of air oxidation on the potassium iodide solutions, and the effect of other rare earths on the formation of praseodymium oxide. However, check values of two parts per thousand with an accuracy of $\pm$ 1 per cent may be obtained if the conditions given in the procedure are closely followed.

Since any carbonate character in the oxide would lead to low results, all oxalates must be ignited at a temperature exceeding 910° C., the temperature required for the complete decomposition of lanthanum carbonates.[78] (In this study a temperature of 925° C. was used.) The oxides must be cooled quickly because they have a tendency to absorb oxygen if cooled slowly. This effect is especially true at the surface of the oxide. Slowly cooled samples

yield high results. The effect of temperature conditions on praseodymium oxide and binary mixtures of it and other rare earths is discussed later.

The effect of air oxidation on acidified potassium iodide solutions must be considered in any iodometric method. Air oxidation is usually increased by heat, light, high acidity, and high concentration of iodide ion. In order to decrease the action of air to a minimum, the oxides are dissolved in a cold moderately dilute sulfuric acid solution protected from direct sunlight as is usual in other iodometric procedures.

In most iodometric methods a large excess of potassium iodide is used in order to take advantage of the law of mass action and to produce a solvent for the iodine, which is more soluble in potassium iodide solutions than in water. However, the higher concentration of iodide ions favors more oxidation by the air. For samples which may require a rather long solution time the concentration of potassium iodide should be reduced to a minimum, and the titration carried out in an iodine flask to prevent the escape of iodine.

In the procedure for the iodometric determination of praseodymium it was suggested that the oxides be dissolved in the acidified potassium iodide solution by gently swirling the iodine flask. The flask should

not be shaken since this increases the surface exposed to air. Samples that were shaken were found to have a larger and more inconsistent blank correction. By applying the suggestions given above the blank correction is seldom larger than 0.1-0.2 ml. of 0.01 N sodium thiosulfate solution.

To check the validity of the procedure, two samples were analyzed for praseodymium by the absorption spectrum method and the iodometric procedure. These results are given in Table XII.

TABLE XII

The Comparison of Absorption Spectrum and Iodometric Methods

	% Praseodymium Oxide	
Sample	Absorption	Iodometric
1	69	69
2	84	87

Since neither method may be considered more accurate than ± 1 per cent, the above determinations are reasonably good checks. Therefore, the iodometric method for the determination of praseodymium in binary oxide mixtures with lanthanum is both rapid and accurate.

Part C

Average Atomic Weight Determinations: An Iodometric Correction for "Excess" Oxygen

The oxalate-oxide average atomic weight determination[8,24,32] can be improved by applying an iodometric correction for "excess" oxygen to the weight of the oxide sample; the interference of praseodymium and other rare earth elements which form oxides higher than sesquioxides is eliminated. The suggested improved procedure follows.

The starting material for the analysis is freshly ignited rare earth oxide. The ignition temperature must exceed 910° C., the temperature of complete decomposition of lanthanum carbonate.[78] A sample of the oxide is analyzed for "excess" oxygen by the iodometric procedure. A second sample, about 0.2 g., is dissolved in 10 ml. of water containing 1-2 ml. of concentrated nitric acid. The solution is evaporated almost to dryness on a steam bath to remove the excess acid. The resulting rare earth nitrate is dissolved in 100 ml. of water. This solution is heated to boiling and the rare earth precipitated as an oxalate by the slow addition of a hot solution of one gram of oxalic acid dissolved in 50 ml. of water. The rare earth oxalate is digested on a steam bath for 15-20 minutes, allowed to cool to room temperature, and

filtered on an asbestos mat in a Gooch crucible or in a sintered porcelain crucible. The oxalate is washed several times with 50 ml. portions of cold water to remove any oxalic acid. The filtering and washing process is carried out by decanting the supernatant liquid into the crucible, thereby leaving most of the oxalate in the beaker. The crucible is placed in the beaker and the combined oxalates are dissolved in 40 ml. of 10 N sulfuric acid. This solution is diluted with 100 ml. of water and titrated with a 0.1 N potassium permanganate solution. About 75 per cent of the permanganate is added to the cold oxalate solution, but the titration is completed at 50-60° C.

The molecular weight of the rare earth sesquioxide is calculated as follows:

$$NV \frac{R_2O_3}{6000} = \left[S.W. - \left(S.W. \times \frac{\%\ "O"}{100}\right)\right]$$

$$R_2O_3 = \frac{6000}{NV}\left[S.W. - \left(S.W. \times \frac{\%\ "O"}{100}\right)\right].$$

N = normality of the potassium permanganate solution,

V = volume of the potassium permanganate solution,

R_2O_3 = molecular weight of rare earth sesquioxide,

$\frac{R_2O_3}{6000}$ = milliequivalent weight of the rare earth sesquioxide,

% "O" = per cent "excess" oxygen determined iodometrically,

S.W. = sample weight of original rare earth oxide,

S.W. $\times \frac{\%\text{"O"}}{100}$ = total weight of "excess" oxygen.

The average atomic weight of the rare earths may then be calculated from the molecular weight of the sesquioxide.

$$R = \frac{R_2O_3 - 48}{2}$$

The atomic weights of lanthanum, praseodymium, and neodymium determined using the above procedure are listed in Table XIII with the results of other workers[8,18,32] who also used an oxalate-oxide method for their determinations.

A comparison of the determined atomic weights with the international atomic weights indicates the accuracy of the method. This is especially true in the case of praseodymium, since the older method gives results that are often high by as much as 5-6 atomic weight units. In a statistical treatment of average atomic weight data obtained by the oxalate-oxide method described in Inorganic Syntheses, Audrieth and co-workers[18] found the mean of three atomic weight determinations will not deviate from the true mean by more than ± 1.28 atomic weight units in 95 per cent of the cases. All the results reported in Table XIII are well within this limit.

TABLE XIII

Atomic Weights of Several Rare Earths
by Oxalate-Oxide Methods

Lanthanum

Determined Atomic Weight	Audrieth[18] (La-29)	Pearce[8]	Gibbs[32]	International Atomic Weight
138.5	138.4	139.4	139.7	
139.1	139.0	140.0		
	139.1			
Av. 138.8	138.8	139.7	139.7	138.92

Praseodymium

Determined Atomic Weight	Audrieth[18] (Pr-1)	(Pr-8)	Inorganic Syntheses*	International Atomic Weight
140.7	146.1	146.6	145.3	
140.7	146.1	144.7		
	145.7	144.9		
Av. 140.7	146.0	145.4	145.3	140.92

Neodymium

Determined Atomic Weight	Pearce[8]	International Atomic Weight
143.5	144.5	
144.7	145.8	
Av. 144.1	145.7	144.27

* - One sample was analyzed by the method described in Inorganic Syntheses.

In agreement with Audrieth and co-workers[18] it was found that no error was introduced by standardizing the potassium permanganate against pure sodium oxalate instead of pure rare earth oxalates. Barthauer and Pearce,[8] however, claim a higher normality is obtained with the rare earth oxalates probably due to contamination of the oxalates with nitrato-oxalates. This possible source of error was not neglected, but reduced to a minimum by evaporating the excess nitric acid on a steam bath and then precipitating the oxalates from very dilute hot solutions; the mixture is cooled to room temperature before filtering.

Since the starting material is a rare earth oxide, it is extremely important that the sample be freshly ignited. The presence of carbon dioxide leads to inconsistent high results.

The average atomic weights of a few mixtures were determined by the procedure described above and results are listed in Table XIV. The values obtained, if no iodometric correction for "excess" oxygen is calculated, are given for comparison with the theoretical average atomic weight of the mixture.

The iodometric correction for "excess" oxygen is negligible for binary or ternary mixtures of praseodymium with lanthanum and neodymium oxides if the

TABLE XIV

Average Atomic Weights of Rare Earth Mixtures

50% La_2O_3-50% Pr_2O_3 Mixture

	Uncorrected for "Excess" Oxygen	Corrected for "Excess" Oxygen	Theoretical Average Atomic Weight
	141.6	139.9	
	142.1	140.5	
	142.2	140.6	
Av.	142.0	140.3	139.9

41.4% La_2O_3-25.0% Pr_2O_3-33.6% Nd_2O_3 Mixture

	Uncorrected for "Excess" Oxygen	Corrected for "Excess" Oxygen	Theoretical Average Atomic Weight
	140.8	140.8	
	140.7	140.7	
	140.9	140.9	
Av.	140.8	140.8	141.2

praseodymium content does not exceed 30 per cent as illustrated by the data for the second mixture in Table XIV. However, the presence of small quantities of cerium or samarium increases the "excess" oxygen content so that the iodometric correction is significant. (See Section VII.)

The advantages of this procedure over the one outlined in Inorganic Syntheses[24] are greater accuracy when elements which form higher oxides than sesquioxides are present and greater rapidity since no gravimetric determinations are necessary.

SECTION VII

The Praseodymium Oxides

The behavior of praseodymium in rare earth oxide mixtures has been a difficulty in average atomic weight determinations, magnetic susceptibility investigations, separations based upon the dry oxidation of praseodymium,[25,54,69] crystallographic studies, etc. The anomalous behavior of praseodymium is due to the existence of the element in more than one oxidation state in the rare earth oxide mixtures; this behavior cannot be completely explained without additional structural studies and perhaps magnetic susceptibility investigations.

A clarification of the chemistry of praseodymium has been attempted by a) reviewing the properties of the praseodymium oxides, b) determining the oxidation state of praseodymium in binary oxide systems with lanthanum, neodymium, and samarium oxides, c) suggesting an explanation for the behavior of praseodymium in oxide mixtures with the other rare earth elements. Several formulas are presented for which there is very meager evidence, e.g. the formation of pyropraseodymates. They are given to stimulate future research in this field of study.

Part A

Properties of the Praseodymium Oxides

Three oxides of praseodymium are known: a sesquioxide, Pr_2O_3; a dioxide, PrO_2; and an intermediate oxide, Pr_6O_{11}. The intermediate oxide is the most common. Special techniques are required for the preparation of the other two. Physical properties of the three oxides are listed for comparison in Table XV. In addition, two other oxides, a pentoxide, Pr_2O_5,[74] and a monoxide, PrO,[54] have been reported; but their existence has not been confirmed.

Praseodymium sesquioxide, Pr_2O_3, is prepared by the reduction of Pr_6O_{11} or PrO_2 in hydrogen.[70] Goldschmidt and co-workers[34] found that the sesquioxide had crystal structures belong to three types, A, B, and C. A is the high temperature form and C the low temperature form. Greenish-yellow flakes of Type A may be prepared by fusing the black oxide* in the flame of an acetylene blowpipe. The crystals belong to the trigonal trapezohedral class of the hexagonal system. The reduction of praseodymium sulfate by hydrogen at 900° C. gives, in addition to the A-modification, clear yellow crystals of a pseudotrigonal variety, Type B. If the reduction

* - This designation, black oxide, refers to Pr_6O_{11} throughthis thesis.

TABLE XV

Physical Properties of the Praseodymium Oxides

$$Pr^{+3} = Pr^{+4} + \bar{e};\ E^{o} < -1.6^{49}$$

	Pr_2O_3		Pr_6O_{11}	PrO_2
Color	Greenish-yellow	Yellowish-white	Black	Black
Symmetry	Hexagonal	Cubic	Cubic	Cubic
Structure Type	La_2O_3	CaF_2	CaF_2	CaF_2
Lattice Constants	a=3.851A[102]	a=5.570A[62]	a=5.468A[62]	a=5.394A[62]
	c=5.996A		5.488A[34]	5.41A[34]
Density (20° C.)[74]	7.07		6.61	6.82
Solubility in Water[17] at 20°C.(Moles/L.)*	0.61×10^{-6}		3.9×10^{-6}	
Heat of Solution in[71,74] 8 N HNO_3 (Calories)	54,750($1/2Pr_2O_3$)		45,100($1/6Pr_6O_{11}$)	42,800(PrO_2)
Magnetic Susceptibility ($\chi \cdot 10^6$)	(29)[82]		15.6[56]	(9)**
% Available Oxygen	0		3.13	4.63
Ratio "O":Pr_2O_3	0		0.667	1.000

* - Although the solubilities of Pr_2O_3 and Pr_6O_{11} reported by Bush[17] are correct in the order of magnitude, the actual values are questionable since the higher oxides of the rare earth elements are more insoluble than the sesquioxides.

** - Estimated value.

temperature is 500°-600° C., Type C, a yellowish-white cubic variety, is obtained. Foex[26] studied the allotropy of praseodymium sesquioxide and found that the B- and C-modifications are transformed irreversibly to the A-type at temperatures exceeding 600° C. The C-type cannot be prepared from the A-type, but only by the low temperature reduction of the black oxide. Praseodymium sesquioxide is converted quantitatively to Pr_6O_{11} when heated to a dull red color in a current of oxygen or air. Acids

$$3Pr_2O_3 + O_2 \xrightarrow{\text{heat}} Pr_6O_{11}$$

dissolve the oxide forming green praseodymium salts.

Praseodymium dioxide, PrO_2, is prepared by low temperature ignition of the sesquioxide. Prandtl and Huttner[74] prepared it by heating the sesquioxide at 300° C. for several days. This procedure was very slow and the dioxide was always contaminated with lower oxides. They also prepared the dioxide by fusing Pr_6O_{11} with several times its weight of potassium chlorate at a temperature of 270°-280° C. After cooling, the product was leached with water and dried at 120° C. Pagel and Brinton[70] prepared praseodymium dioxide of 99.2 per cent purity by heating the lower oxides in pure oxygen at high pressures and studied the stability of the oxide at different temperatures and pressures. When heated above 400° C. the dioxide

decomposes into Pr_6O_{11} and oxygen. The dioxide crystallizes in the fluorite structure analogous to cerium dioxide.

Praseodymium dioxide is a strong oxidizing agent, liberating iodine from hydriodic acid, chlorine from hydrochloric acid, and converting manganous salts to permanganates and cerous salts to ceric salts.[11] It oxidizes ferrous, stannous, and arsenious salts; but part of the available oxygen is always lost, probably due to the oxidation of water. Praseodymium dioxide is soluble in oxyacids, forming trivalent salts and liberating oxygen and, in some cases, traces of ozone. Since hydrogen peroxide is not formed when the dioxide is treated with cold sulfuric acid, it does not appear to be a peroxide but rather an oxide actually containing tetravalent praseodymium. It does not show acidic or basic properties; thus, the dioxide does not form tetravalent praseodymium or praseodymate ions in solution. Attempts to oxidize a suspension of praseodymium hydroxide in strongly alkaline solutions with chlorine, bromine, and ozone have been unsuccessful.[74]

The black oxide, Pr_6O_{11}, sometimes designated as praseodymium praseodymate, is prepared by the ignition of praseodymium sesquioxide, dioxide, hydroxide, or salts of volatile acids in air. This oxide is stable between 500°-900° C., but when heated at 1100° C. in a current of

nitrogen it undergoes appreciable decomposition with the loss of active oxygen. When ignited to red heat in a covered crucible, it is reduced to the greenish-yellow sesquioxide. However, as the crucible cools, the oxide reabsorbs oxygen; if the cooling is very rapid, only a surface layer of Pr_6O_{11} is formed. The sesquioxide is not oxidized by air at room temperature, but may be reconverted to the black oxide if heated in an open crucible. The chemical properties of the intermediate oxide are similar to those of praseodymium dioxide, for the intermediate oxide liberates chlorine from hydrochloric acid, iodine from hydriodic acid, and oxidizes manganous, cerous, stannous, ferrous, and arsenious ions.

Like praseodymium dioxide, Pr_6O_{11} has no peroxide characteristics but may be considered an oxide salt. Cold hydrofluoric acid, concentrated or dilute, attacks the oxide; the hot acid slowly gives the difficultly soluble salt, PrF_3. A complex potassium praseodymium fluoride, easily soluble in dilute acids, may be prepared by adding Pr_6O_{11} to fused potassium hydrogen fluoride.[72] Sulfuric and nitric acids react with the oxide more or less violently, depending upon the temperature and concentration, liberating oxygen containing traces of ozone and forming trivalent praseodymium salts.

When placed on the anticathode of an X-ray tube and bombarded with electrons, praseodymium praseodymate is rapidly converted into the sesquioxide.[71] X-ray studies of the oxide show that the microcrystalline black powder has the "fluorite" structure.[36]

The formula of this oxide has been definitely established,[7,70,74] although earlier workers[85] found other praseodymium oxygen ratios. Their error was probably due to impure praseodymium. If the oxide is treated with a slight excess of acetic acid and the dissolving action continued until only a fifth of the oxide remains, the product, after washing and drying at 120°-130° C., is a deep reddish-brown powder which has a formula of $Pr_4O_8 \cdot H_2O$.[74] The above experiment indicates that the intermediate oxide, Pr_6O_{11}, is actually a compound of praseodymium sesquioxide and dioxide, $Pr_2O_3 \cdot 4PrO_2$.

Praseodymates have never been prepared in solution because tetravalent praseodymium oxidizes water.

$$8H^+ + 2PrO_2 + 2\,\bar{e} \longrightarrow 2Pr^{+++} + 4H_2O; \quad E^\circ = (?)$$

$$HOH - 2\,\bar{e} \longrightarrow \tfrac{1}{2}O_2 + 2H^+; \quad E^\circ = -2.42$$

$$6H^+ + 2PrO_2 \longrightarrow 2Pr^{+++} + \tfrac{1}{2}O_2 + 3H_2O$$

However, they have been prepared in the dry state. Zintl and Morawietz[103] prepared sodium praseodymate, Na_2PrO_3, by heating praseodymium sesquioxide and sodium oxide at

470° C. in oxygen. It has a density of 4.60 and a rock-salt (face-centered) cubic structure with a 4.84A, analogous to sodium cerate,[103] Na_2CeO_3, with a 4.82A. The sodium and tetravalent praseodymium ions are distributed over equivalent positions, each unit cell containing 1-1/3 sodium atoms and 2-2/3 praseodymium atoms. The 4 chlorine atoms in the unit cell of rock salt have been replaced by 4 oxygen atoms. Barium cerate, $BaCeO_3$, a=4.377A,[39] a=4.386A,[27] has been prepared, but the corresponding praseodymate has not. Barium praseodymate, if it can be made, should have an analogous structure to $BaCeO_3$.

Goldschmidt[34] was the first to show a relationship between the crystalline form of the rare earth sesquioxides and ignition temperatures. Iandelli[40] verified this previous work; his results are tabulated in Table XVI.

Type A is a hexagonal form; Type B is a pseudo-trigonal form, and Type C is cubic. It is noted that with the increasing atomic number of the rare earths, the C-type is more stable over an extended temperature range; and that for the first members of the group the C-form is the low temperature type which changes to the A-form at moderately high temperatures.

Marsh[54] states that the sesquioxides and dioxides form solid solutions, if the sesquioxides have the C-type structure. The dioxides possess a fluorite structure;

TABLE XVI

Dependence of the Type Sesquioxide
Upon the Ignition Temperature

Temperature (° C.)	La_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
350	C + A					
450	C + A					
500	C + A	C		C	C	C
600	A	C	C			
700		A	C			
775			C			
850		A	A			
900					C	
1000	A	A	A	C	C	C
1100		A		C		
1200				B		
1300				B	C	C
1400				B	B	
1500						C
2000			A			

the C-type or cubic sesquioxide has a subtraction lattice of the fluorite type with slight modifications. (The trivalent metals replace the calcium ions, but only three-fourths of the fluorine positions are filled with oxygen ions.) Because of this similarity in structure, the two types of cubic oxides are able to form solid solutions with each other. The A-type sesquioxides have hexagonal structures and do not tend to form solid solutions with praseodymium dioxide. Their presence inhibits dioxide formation. Therefore, any conditions which promote C-type sesquioxide formation should also promote praseodymium dioxide formation.

The effect of temperature upon the oxidation state of praseodymium may be explained by Table XVI. Starting with praseodymium sesquioxide low temperature ignition favors the formation of the C-modification. Since this cubic type can form solid solutions with cubic PrO_2, the tendency to take up oxygen is increased and the formation of praseodymium dioxide from the sesquioxide is favored. However, the oxidation is seldom complete.[70] If the ignition temperature is raised, the small amount of sesquioxide remaining tends to change into the A-modification which inhibits oxygenation, and oxygen is liberated until Pr_6O_{11} results. In the absence of oxygen and at very high temperatures the A-type praseodymium

sesquioxide is formed. However, if this oxide is cooled slowly in the presence of oxygen, Pr_6O_{11} again results. Reactions involved can be represented as:

$$Pr_2O_3(C) + \tfrac{1}{2}O_2 \xrightarrow{\leq 400^\circ} 2PrO_2$$

$$6PrO_2 \underset{\leftarrow}{\xrightarrow{> 400^\circ}} Pr_6O_{11}(Pr_2O_3 \cdot 4PrO_2) + \tfrac{1}{2}O_2$$

$$Pr_6O_{11} \underset{\rightarrow}{\xleftarrow{\geq 1100^\circ}} 3Pr_2O_3(A) + O_2.$$

It can be assumed from the limited data reported that the first reaction is very slow, the second is rapid to the right, and the third is rapid to the left. Since praseodymium sesquioxide (C-type) cannot be prepared by the low temperature ignition of the dioxide,[26] the first reaction apparently is not an equilibrium reaction. If the C-type sesquioxide is ignited above 400° C., it forms Pr_6O_{11} immediately.

Recently Gruen, Koehler, and Katz[36] have obtained evidence for a continuous transition from Pr_2O_3 to PrO_2. Several intermediates were prepared and their lattice

TABLE XVII

Oxygen Content and Lattice Parameters of Praseodymium Oxide

Formula	Oxygen/Metal Ratio	Constant	Reference
Pr_2O_3	1.50	5.570	62
$PrO_{1.65}$	1.65	5.530	36
Pr_6O_{11}	1.83	5.468	62
$PrO_{1.99}$	1.99	5.399	36
PrO_2	2.00	5.394	62
$PrO_{2.02}$	2.02	5.380	36

constants measured. A contraction in the lattice was observed as the oxidation state increased. Thus, the extent of oxidation was indicated by changes in the lattice parameters.

Part B

Effect of Other Rare Earth Oxides on Praseodymium Oxides

The tendency of praseodymium to form three oxides has been very troublesome in studies of rare earth oxide mixtures. This effect of the composition of rare earth mixtures is reviewed in the next few paragraphs. Marc[51] claimed that the presence of a little cerium was necessary for the higher oxidation of praseodymium and that lanthanum and neodymium hindered its oxidation. These effects were confirmed by Meyer and Koss.[65] In addition, Brauner[14] stated incorrectly that a small quantity of praseodymium in neodymium sesquioxide caused the production of a higher oxide of neodymium, probably a dioxide.

However, more recent studies by Barthauer,[6] Marsh,[54] Prandtl and Huttner,[74] and Prandtl and Rieder[75] indicate that in praseodymium-cerium oxide mixtures of very low cerium content, the cerium dioxide seems to inhibit oxidation of the praseodymium. In binary oxide mixtures of lanthanum-, neodymium-, or samarium-praseodymium, containing praseodymium in excess of the ratio $2R_2O_3/3Pr_2O_3$, the oxidation state of this latter element is increased. Likewise, if larger amounts of lanthanum, neodymium, or samarium oxides are present, the degree of oxygenation of the praseodymium is decreased. The reduction in the

amount of oxygenation is greatest with the addition of lanthanum oxide, intermediate with neodymium oxide, and least with samarium oxide.

Marsh[54] has correlated the types of sesquioxides with the ionic radius ratios of the rare earths, Table XVIII. He states that the C-type sesquioxide is stable for the ionic radius ratios of 0.53 to 0.86 (R_m=ionic radius of rare earth, R_o=ionic radius of oxygen), and that larger values than 0.86 favor the A-modification.

TABLE XVIII

Dependence of the Type Sesquioxide Upon the Ionic Radius Ratio

R^{+++}	Ionic Radii (A)*	Ionic Radius Ratios (R_m/R_o)	Type Sesquioxide**
La	1.22	0.92	A
Ce	1.18	0.89	A
Pr	1.16	0.88	A
Nd	1.15	0.87	A
Sm	1.13	0.86	C
Eu	1.13	0.86	C
Gd	1.11	0.84	C

* - Goldschmidt
** - Marsh

Observations by Prandtl and Rieder[75] and by Marsh[54] indicate complete oxygenation of praseodymium oxide

to form praseodymium dioxide in binary mixtures with samarium oxide (R_m/R_o=0.86), gadolinium oxide (R_m/R_o=0.84), and yttrium oxide (R_m/R_o=0.80), but not with the earlier (lower atomic number) rare earth oxides such as lanthanum oxide (R_m/R_o=0.92). However, complete oxygenation is also obtained with neodymium oxide (R_m/R_o=0.87), if the mixture is heated moderately in an atmosphere of oxygen. The above examples illustrate the dependence of the oxidation state of praseodymium upon ionic radius ratios.

It will be recalled that an iodometric analysis for praseodymium in binary oxide mixtures (Section VI) containing the element was developed. Since most analyses for praseodymium are on mixtures, it was necessary to learn how the degree of oxygenation varied with the composition of the mixture. In Tables XIX, XX, and XXI the results of these analyses for 0-100 per cent ranges for binary mixtures of praseodymium oxide with the oxides of samarium, neodymium, and lanthanum are tabulated. In Figure 2, weight per cent of R_2O_3 (R=Sm, Nd, or La) is plotted against weight per cent "excess" oxygen. The straight line is the theoretical curve expected if praseodymium oxide remains as Pr_6O_{11} without change for the various ratios. In Figure 3, mole per cent R_2O_3 is plotted against mole ratio of "excess" oxygen. The straight line corresponds to the composition of pure Pr_6O_{11}. Figure 2 is more valuable

in analytical work; Figure 3 in theoretical discussions since it shows the apparent oxidation state of praseodymium.

TABLE XIX

Samarium-Praseodymium Oxide System

Wt. % Sm_2O_3	Wt. % "Excess" Oxygen	Mole % Sm_2O_3	"Excess" Oxygen Moles Pr_2O_3
0.0	3.08	0.0	0.658
20.6	2.92	20.3	0.787
30.2	2.69	29.8	0.825
40.1	2.34	39.7	0.844
50.2	1.95	49.8	0.839
60.2	1.55	59.8	0.835
70.1	1.09	69.6	0.779
80.0	0.67	79.5	0.714
90.0*	0.23	89.6	0.485
94.0*	0.16	93.8	0.565
100.0	0.00	100.0	0.000

* - Errors in the determinations rather large due to the small quantity of standard thiosulfate solution required.

TABLE XX

Neodymium-Praseodymium Oxide System

Wt. % Nd_2O_3	Wt. % "Excess" Oxygen	Mole % Nd_2O_3	"Excess" Oxygen Moles Pr_2O_3
0.0	3.08	0.0	0.658
19.9	2.94	20.2	0.785
30.0	2.71	30.4	0.831
40.1	2.32	40.5	0.830
50.0	1.89	50.4	0.810
60.0	1.35	60.3	0.719
60.4	1.29	60.7	0.694
62.1	0.55	62.0	0.304
63.8*	0.18	63.5	0.103
70.1*	0.04	69.7	0.028
80.0*	0.03	79.6	0.031
100.0	0.00	100.0	0.000

* - Errors in the determinations rather large due to the small quantity of standard thiosulfate solution required.

TABLE XXI

Lanthanum-Praseodymium Oxide System

Wt. % La_2O_3	Wt. % "Excess" Oxygen	Mole % La_2O_3	"Excess" Oxygen Moles Pr_2O_3
0.0	3.08	0.0	0.658
10.0	2.98	10.4	0.707
20.1	2.83	20.9	0.758
30.0**	2.61**	31.5	0.799
36.0	2.39	37.2	0.800
40.0	2.17	41.2	0.774
50.0	1.28	51.0	0.542
60.0	0.50	60.6	0.261
65.1*	0.13	65.6	0.077
70.2*	0.06	70.6	0.042
80.0*	0.02	80.2	0.021
100.0	0.00	100.0	0.000

* - Errors in the determination rather large due to the small quantity of standard thiosulfate solution required.

** - Values taken from a plot of weight per cent La_2O_3, and weight per cent "excess" oxygen.

The curves indicate considerable differences in the behavior of praseodymium oxide in the presence of the oxides of samarium, neodymium, or lanthanum. The changing oxidation state of praseodymium with mole per cent samarium will be considered first. It is observed that the amounts of "excess" oxygen are greatest for the lowest percentages of Sm_2O_3 and exceed the theoretical amount for about 85 per cent of the composition range. The maximum "excess" oxygen (0.84 atom per mole Pr_2O_3) is noted in the region 40-50 per cent Sm_2O_3; the composition of this oxide may be represented by the formula $4Sm_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$. For the upper 15 per cent the amounts of "excess" oxygen are slightly less than that expected.

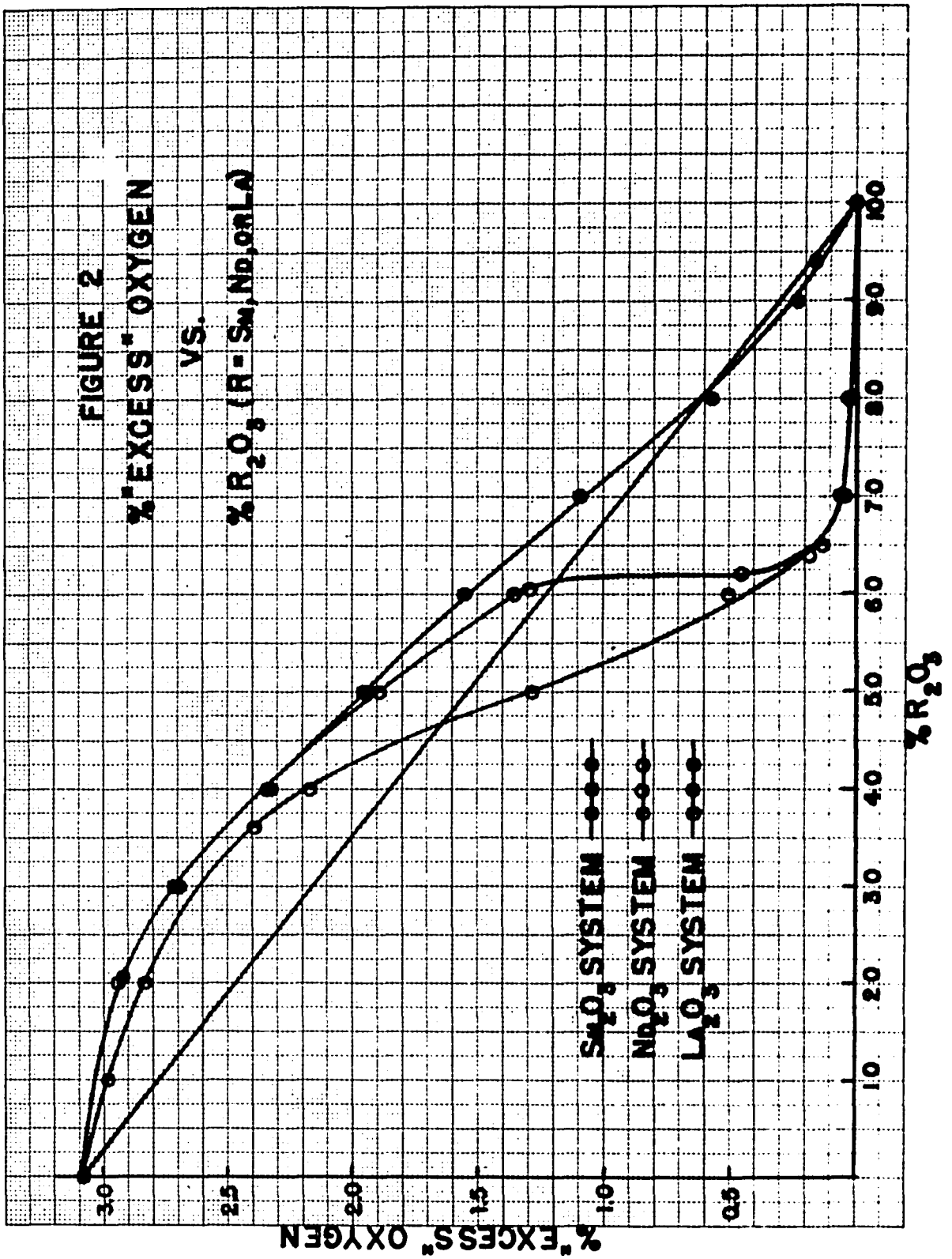
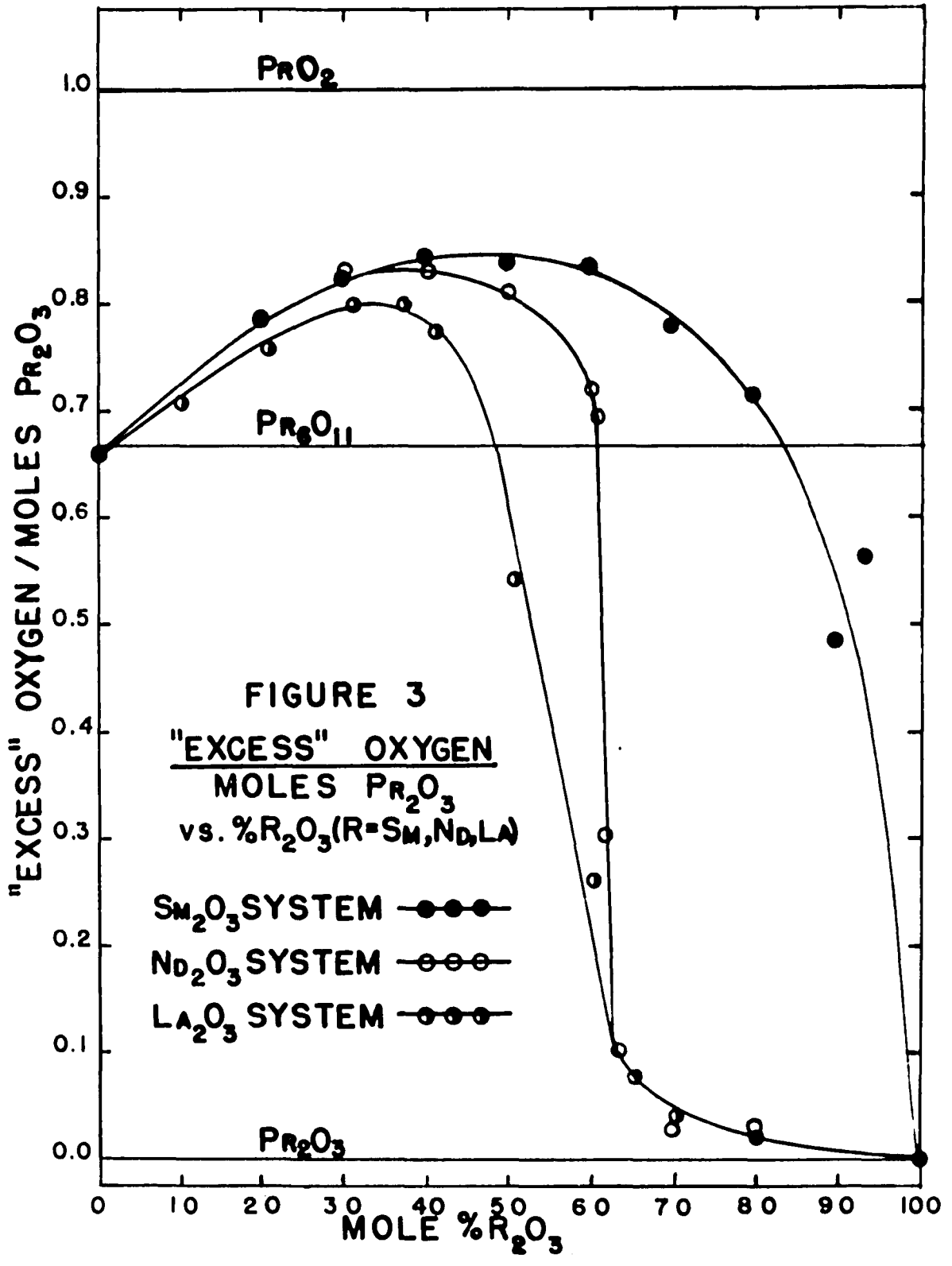


FIGURE 2
% "EXCESS" OXYGEN
VS.
% R_2O_3 (R = Sm, Nd, or La)
% "EXCESS" OXYGEN
% R_2O_3
Sm_2O_3 SYSTEM
Nd_2O_3 SYSTEM
La_2O_3 SYSTEM
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
90
100


PrO2
Pr6O11
Pr2O3
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
"EXCESS" OXYGEN / MOLES Pr2O3
0
10
20
30
40
50
60
70
80
90
100
MOLE %R2O3
FIGURE 3
"EXCESS" OXYGEN
MOLES Pr2O3
vs. %R2O3(R=Sm,Nd,La)
Sm2O3SYSTEM
Nd2O3SYSTEM
La2O3 SYSTEM

From the work of Goldschmidt[34] and Iandelli,[40] it is learned that Sm_2O_3 tends to form the C- or cubic-sesquioxide structure in the temperature range used for this study. The ionic radius ratio of samarium oxide also favors the formation of the C-type sesquioxide. It has been stated that both PrO_2 and Pr_6O_{11} exist in cubic forms. It appears reasonable, therefore, that the cubic Sm_2O_3 and one of the cubic praseodymium oxides might form solid solutions. If such were the case, it could also be expected that oxygenation of praseodymium towards the highest oxide, PrO_2, might occur. Such a behavior is indicated by the curves for the samarium-praseodymium system. Complete oxygenation to PrO_2 was not observed. However, the results in this study are in agreement with those of Prandtl and Rieder[75] who reported 0.80 to 0.85 atom of "excess" oxygen per mole of Pr_2O_3 for a mixture of $3Pr_2O_3/2Sm_2O_3$ (approximately 40 mole per cent Sm_2O_3).

In considering the oxide system for lanthanum-praseodymium, the ionic radius ratio of lanthanum oxide (0.92) and the ignition temperature (925° C.) favor the formation of the A- or hexagonal-type sesquioxide. As Marsh[54] points out, the hexagonal La_2O_3 and the cubic Pr_6O_{11} would not tend to form solid solutions. This would suggest that the oxygenation of praseodymium is inhibited. In this study it was found that samples containing more than 70 mole per cent lanthanum oxide gave

very small ratios of "excess" oxygen to moles of Pr_2O_3. This observation would indicate that the degree of oxygenation is inhibited so that practically all the praseodymium is present as the sesquioxide. Samples containing 0-35 mole per cent lanthanum oxide show a steady increase in the amount of "excess" oxygen. Marsh made a similar observation and suggested that the increase was due to the formation of a lanthanum praseodymate, $4PrO_2 \cdot La_2O_3$; praseodymium sesquioxide is substituted by lanthanum sesquioxide in the fluorite-type structure of $4PrO_2 \cdot Pr_2O_3$ (i.e., Pr_6O_{11}).

Complete oxygenation is not obtained. The peak value of the "excess" oxygen/moles Pr_2O_3 is 0.80; the composition of the oxide mixture which produces this peak oxygenation value may be represented by the formula $3La_2O_3 \cdot Pr_2O_3 \cdot 8PrO_2$. Prandtl and co-workers[74,75] reported a ratio of 0.86 for a sample containing $3Pr_2O_3/2La_2O_3$. The tendency of the lanthanum oxide to form an A-type sesquioxide and suppress oxygenation may be observed even in the 0-35 mole per cent lanthanum oxide region; the rise in oxygenation is more gradual than with samarium oxide, which forms only a C-type sesquioxide under the conditions given. The region from 35-70 mole per cent lanthanum oxide represents a transition from the C-type to the A-type sesquioxide with a corresponding gradual

decrease in oxygenation. The La_2O_3-Pr_6O_{11} curve is in agreement with a statement by Marsh,[54] "In the presence of lanthanum oxide (up to $3Pr_2O_3/2La_2O_3$) there is an increase in the degree of oxygenation of the praseodymium, but larger amounts cause a rapid fall."

The curve obtained for the neodymium-praseodymium oxide system differs from those of the samarium- and lanthanum-praseodymium systems. It follows rather closely the Sm_2O_3-Pr_6O_{11} curve for samples containing low percentages of neodymium oxide, but breaks away and follows the La_2O_3-Pr_6O_{11} curve for high percentage samples. The two factors, the ionic radius ratio of neodymium sesquioxide (0.87) and the ignition temperature (925° C.) only slightly favor the formation of the A-type sesquioxide; actually both of these conditions correspond to the transition region between C- and A-modifications. If the conditions favor formation of the hexagonal Nd_2O_3, there should be little tendency for solid solution with the cubic PrO_2, but increased solid solution with Pr_2O_3; a combination of hexagonal Pr_2O_3 and Nd_2O_3 would not favor oxygenation. Also, cubic Nd_2O_3 and cubic Pr_2O_3 could form solid solutions with an increased tendency for oxygenation. For samples containing 0-40 mole per cent neodymium oxide, the degree of oxygenation of praseodymium sesquioxide is about the same as with samarium oxide (a typical C-type sesquioxide). From 40-60 mole per cent it appears that

the A-type neodymium sesquioxide is beginning to affect the degree of oxygenation, from 60-65 mole per cent a very large decrease occurs. It may be that this system does not tolerate over 60 mole per cent neodymium oxide with the maintenance of the cubic-type lattice. Solid solutions of PrO_2 and Nd_2O_3 probably are formed up to but not beyond this percentage composition. This concept is in agreement with the X-ray data recently obtained by McCullough[62,63] for rare earth sesquioxide-dioxide systems. He found that for samples containing over 65 mole per cent neodymium oxide the A-type sesquioxide is formed and the fluorite-type structure is not tolerated. This behavior corresponds with the data in this study on the oxygenation of praseodymium sesquioxide. For these conditions the amount of oxygenation is inhibited, producing results that follow closely the curve of lanthanum oxide (a typical A-type sesquioxide). The peak oxygenation value found is 0.83 atom of "excess" oxygen per mole Pr_2O_3 which agrees with the value obtained by Prandtl and Rieder.[75] For this study and that of Prandtl and Rieder the peak occurs at about 40 mole per cent neodymium oxide ($3Pr_2O_3/2Nd_2O_3$). The composition of the oxide which produces the peak oxygenation value may be represented by the formula $4Nd_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$.

It is obvious that the composition of praseodymium oxide in binary mixtures with other rare earth oxides varies continuously over the entire percentage range. The ratios of the oxides at peak oxygenation in each system are:

$3La_2O_3 \cdot Pr_2O_3 \cdot 8PrO_2$ or $3(La_2O_3 \cdot 2PrO_2) + Pr_2O_3 \cdot 2PrO_2$

$4Nd_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$ or $4(Nd_2O_3 \cdot 2PrO_2) + Pr_2O_3 \cdot 2PrO_2$

$4Sm_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$ or $4(Sm_2O_3 \cdot 2PrO_2) + Pr_2O_3 \cdot 2PrO_2$

It will be of interest to conjecture about these ratios or formulas. For example, it might be asked if there is any significance to the repetition of the $R_2O_3 \cdot 2PrO_2$ ratio. It might be stated that except in the case of praseodymium oxide, Pr_6O_{11}, this ratio of one mole of sesquioxide to two of praseodymium dioxide is common to each formula. Whether $R_2O_3 \cdot 2PrO_2$ represents compound formation or simply a particularly stable solid solution ratio can only be answered by more detailed crystallographic or other structural studies.

One suggestion is to assume that if compounds are formed, the above compositions could be represented generally as $R_2Pr_2O_7$, derived from a parent pyropraseodymic acid ($H_6Pr_2O_7$) which corresponds to the loss of one molecule of water from two molecules of orthopraseodymic acid. Neither this acid nor any of its salts have been reported in the literature. Continuing the assumption, it is

possible to explain the complex oxide ratios at peak oxygenation as salts of pyropraseodymic acid. No other simple formula will fit these oxide ratios. At peak oxygenation these ratios would be:

$3La_2O_3 \cdot Pr_2O_3 \cdot 8PrO_2$ or $3La_2Pr_2O_7 + Pr_2Pr_2O_7$

$4Nd_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$ or $4Nd_2Pr_2O_7 + Pr_2Pr_2O_7$

$4Sm_2O_3 \cdot Pr_2O_3 \cdot 10PrO_2$ or $4Sm_2Pr_2O_7 + Pr_2Pr_2O_7$

High ignition temperatures as used in preparing these oxides (925° C.) usually favor the formation of pyro- rather than ortho- compounds. This concept is suggested only for provoking thought. One can probably devise structures based on close packed ionic structures to explain the behavior although the meager X-ray data will not permit elaboration along this line at present.

Zintl and Morawietz[103] prepared a complex oxide composed of sodium, lanthanum, and praseodymium oxides, $Na_{1.8}Pr_{0.8}La_{0.2}O_{2.8}$. They reported that the complex oxide exhibited a rock-salt-type lattice similar in lattice constants to sodium praseodymate, Na_2PrO_3. No interference from $NaLaO_2$, which they found did not form a cubic-type lattice, was observed. They did not offer an explanation as to the nature of the complex oxide except to point out that the oxide is an example of the rock-salt-type lattice containing three kinds of cations.

The formula of the complex oxide of Zintl and Morawietz,[103] $Na_{18}Pr_8La_2O_{28}$, obtained by increasing the ratio $Na_{1.8}Pr_{0.8}La_{0.2}O_{2.8}$ tenfold, can be represented as a mixture of sodium oxide, lanthanum sesquoxide, and praseodymium dioxide or, as a mixture of sodium and lanthanum pyropraseodymates.

$Na_{18}Pr_8La_2O_{28}$ or $9Na_2O \cdot La_2O_3 \cdot 8PrO_2$ or $3Na_6Pr_2O_7 + La_2Pr_2O_7$

Since all oxides concerned can exhibit a cubic-type lattice, it might be assumed that their solid solutions exhibit a cubic-type lattice. When a binary mixture of La_2O_3 and Na_2O is fused, $NaLaO_2$ is formed which does not have a cubic-type lattice; when a binary mixture of Pr_6O_{11} and Na_2O is fused, a cubic-type compound, Na_2PrO_3, is formed. However, X-ray analysis did not reveal any $NaLaO_2$ or $NaPrO_2$ in the ternary oxide mixture, but as stated before, a cubic-type compound of approximately the same lattice constants as Na_2PrO_3.

Part C

Effects of Praseodymium Oxides on Magnetic Susceptibility Measurements of Rare Earth Oxides

The effect of the changing ratio Pr_2O_3/PrO_2 in oxide mixtures is of interest in connection with other properties, such as its relationship with respect to the magnetic susceptibilities of mixtures. The susceptibility of trivalent praseodymium should be considerably larger than tetravalent praseodymium (Table XV). Thus, the conditions which promote A-type sesquioxide formation and low oxygenation of praseodymium should correlate with higher magnetic susceptibilities, and those which promote C-type sesquioxide formation and high oxygenation should be accompanied by lower magnetic susceptibilities. This idea agrees with the data of Mazza,[56] who measured the specific magnetic susceptibilities of the following binary systems: Nd_2O_3-Sm_2O_3 and Pr_6O_{11}-Nd_2O_3, (Table XXII, Figure 4).

The rule of additive magnetic susceptibilities for mixtures is represented by a straight line. The graph for the Nd_2O_3-Sm_2O_3 data agrees with the rule. For the Pr_6O_{11}-Nd_2O_3 system the experimental and theoretical values do not agree and Mazza[56] considered this system anomalous. In view of the "excess" oxygen studies listed above, the behavior of the Pr_6O_{11}-Nd_2O_3 system can be explained.

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TABLE XXII

Magnetic Susceptibilities of
Binary Mixtures of Rare Earth Oxides

% Nd_2O_3	Pr_6O_{11}-Nd_2O_3 ($\chi \cdot 10^6$)	Nd_2O_3-Sm_2O_3 ($\chi \cdot 10^6$)
0	15.6	6.1
10	15.8	8.5
20	16.4	11.0
30	17.5	13.4
40	18.9	16.0
50	20.8	18.4
60	23.1	21.0
70	25.6	23.4
80	28.7	25.9
90	30.3	28.4
100	31.1	31.0

It can be assumed that Mazza actually had a ternary mixture of Pr_2O_3-PrO_2-Nd_2O_3 and that since the ratio Pr_2O_3/PrO_2 varies with each addition of neodymium oxide, a straight line relationship between magnetic susceptibility and per cent neodymium sesquioxide should not be expected. The curve (Figure 4) for 0-75 per cent neodymium oxide falls below the dotted straight line which represents a linear relationship. The oxides containing small quantities of neodymium favor the oxygenation of praseodymium. Since the specific magnetic susceptibility of praseodymium dioxide is much lower than that of the sesquioxides (Table XV), these samples have values lower than the susceptibility values obtained by the additive rule. Oxides containing

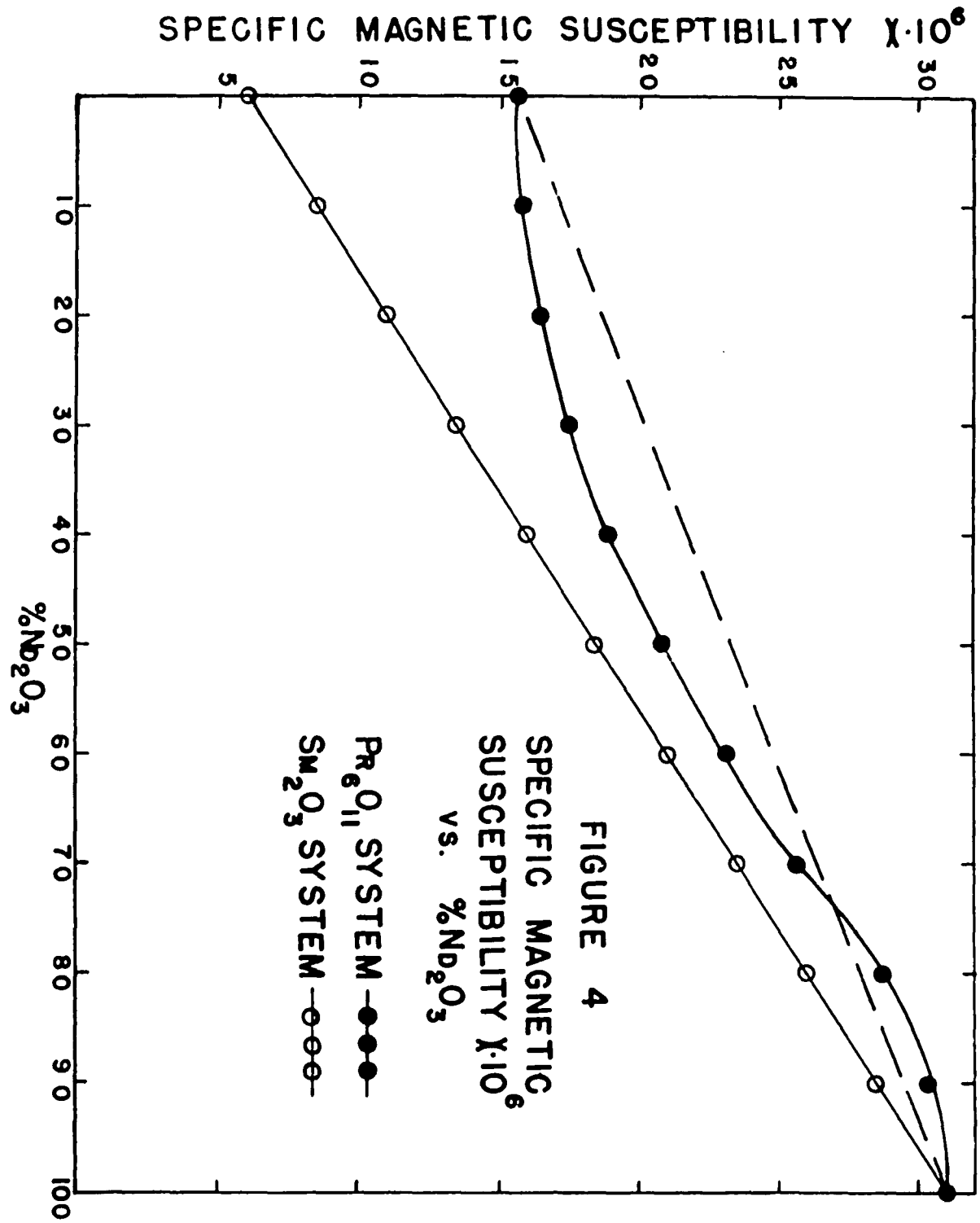

FIGURE 4

SPECIFIC MAGNETIC SUSCEPTIBILITY X·10⁶ vs. %Nd_2O_3

more than 75 per cent neodymium oxide have a specific magnetic susceptibility greater than that obtained by the additive rule (fall above the dotted line) because the oxygenation of praseodymium sesquioxide, which has a specific magnetic susceptibility almost as large as that of neodymium sesquioxide (Table XV) is inhibited in these samples. Hence, the curve obtained by Mazza does not seem to be anamolous. It is believed that the Pr_6O_{11}-Nd_2O_3 system might conform to the additive rule of specific magnetic susceptibilities if it is considered as a ternary system of Pr_2O_3-PrO_2-Nd_2O_3. This hypothesis can be confirmed only by a detailed study of the magnetic susceptibilities of the Pr_6O_{11}-Nd_2O_3 system in reducing and oxidizing atmospheres. That is, the binary systems, Pr_2O_3-Nd_2O_3 and PrO_2-Nd_2O_3 should conform to the additive rule to give a linear relationship of specific magnetic susceptibilities versus per cent neodymium sesquioxide.

Part D

Conclusion

The properties of the praseodymium oxides, Pr_2O_3, Pr_6O_{11}, and PrO_2, as well as their nature in binary mixtures with other rare earth oxides have been described. In general, praseodymium oxide exists as a combination of Pr_2O_3 and PrO_2 in rare earth oxide mixtures. For praseodymium rich samples it tends to form PrO_2 and for praseodymium poor samples, Pr_2O_3. The changing Pr_2O_3/PrO_2 ratio affects the physical properties of rare earth oxides. The failure of a Pr_6O_{11}-Nd_2O_3 system to conform to the additive rule of specific magnetic susceptibilities may be due to this effect.

The conditions which enhance oxygenation of praseodymium oxide in mixtures with other rare earth oxides have been listed. An ignition temperature of 925° C. was chosen to insure complete decomposition of rare earth carbonates[78] which are always formed as intermediate ignition products of the rare earth oxalates. It must be stated that the characteristics of binary rare earth oxides containing praseodymium may be different from those reported in this thesis if the conditions of ignition are changed. Lower ignition temperatures, shorter ignition periods, and greater oxygen pressure would enhance the oxygenation of the praseodymium.

The nature of praseodymium oxide is very complex, and its complete description will require the correlation of magnetic susceptibility, available oxygen, phase rule, X-ray and other structural studies.

SECTION VIII

Discussion and Suggestions for Future Researches

Rare earth separations which depend upon the fractional precipitation of a very slightly soluble compound may be improved by the slow even addition of the precipitating reagent and by reducing the rare earth ion concentration in solution to a minimum. One very good method of obtaining a slow even addition of the precipitating reagent with the minimum of local effects is by the use of internal decomposition or hydrolysis reactions, such as the decomposition of the trichloro-acetate ion in hot solutions to precipitate insoluble carbonates or the hydrolysis of dimethyloxalate in cold acid solutions to precipitate insoluble oxalates.

There are several ways to reduce the rare earth ion concentration in solution, the most common being by dilution. However, when working with extremely dilute solutions, the use of large quantities of solvent, the production of gelatinous precipitates, the difficulty of recovering the rare earth remaining in the filtrate, and other similar disadvantages present problems. Another method of reducing rare earth ion concentration is to employ a complexing reagent so that most of the rare earth ions are present as complex ions.

Nitrilotriacetic acid, $N(CH_2COOH)_3$, has been found to be a good reagent for the formation of soluble complex ions with the rare earths. Beck[10] found that this reagent would dissolve rare earth oxalates and fluorides in neutral or slightly basic solutions and that the oxalates could be fractionally precipitated upon the addition of dilute acetic acid. Under these conditions lanthanum oxalate precipitated first, followed by the oxalates of the less basic cerium earths as the pH was lowered. Beck and Gasser[11] applied a modification of this procedure to the yttrium earths. Although this method is fractional and presents the disadvantage that the change in pH is brought about by dropwise addition of acetic acid, it appears to be faster than most rare earth separations.

It is possible that the decrease in pH necessary to bring about precipitation in the method proposed by Beck may be produced by the application of homogeneous phase reactions. For example, dimethyloxalate may be added to the rare earth solution containing the nitrilotriacetate complexes and subsequently hydrolyzed to produce a gradual increase of oxalate ions and a decrease in pH. Both conditions would favor the slow formation of rare earth oxalates from a solution containing the nitrilotriacetate complexes.

Similarly, perhaps, rare earth carbonates could be fractionally precipitated from solutions of the nitrilotriacetate complexes by the decomposition of the rare earth trichloroacetates. The formation of carbon dioxide would result in a lowering of the pH of the rare earth solution. The probable order of precipitation of the carbonates for this type of reaction would be lanthanum carbonate followed by the carbonates of the less basic rare earths. If the nitrilotriacetate complex contained oxalate ions, the oxalates would probably precipitate in preference to the carbonates.

Other reagents which might have good complexing properties are amines, amides, imides, ureas, hydrazines, and hydroxylamines in which the hydrogen atoms attached to the nitrogen atoms have been replaced by alkanoic acids. Ethylenediamine tetra acetic acid $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$, and hydrazoformic acid, HOOCNHNHCOOH, are typical examples.

Meyer[64] found that concentrated potassium carbonate solutions readily dissolve rare earth carbonates and that the rare earths could be fractionally precipitated as double potassium carbonates upon the dropwise addition of water, the lanthanum double salt precipitating first. This procedure was used to obtain pure lanthanum compounds rather quickly. Although other workers[3,52,69] have since improved the method, it is still fractional. The separation

must be carried out in concentrated potassium carbonate solutions; the necessity of using these highly alkaline solutions is a distinct disadvantage.

In this study an attempt was made to purify some lanthanum oxide which contained 1-2 per cent praseodymium and neodymium oxides by decomposing trichloroacetate ions in a concentrated potassium carbonate solution containing the rare earths. The rare earth oxide mixture was dissolved in trichloroacetic acid, and the potassium double carbonates were precipitated and then redissolved with concentrated potassium carbonate solution. The rare earth solution was heated at 40° C., and the double carbonates reprecipitated by carbon dioxide, which is an acidic substance in strongly alkaline solutions, liberated in the decomposition of the trichloroacetate ions. The reaction was continued until most of the rare earth had been reprecipitated. The rare earths in the precipitate and in the filtrate were recovered as oxalates and ignited to oxides. The rare earth oxide obtained from the precipitated carbonate was white, whereas that from the filtrate was tan. The absorption bands of praseodymium and neodymium were observed for a nitrate solution prepared from the latter oxide, but not in the former. It is evident that small quantities of the other rare earths may be removed from

lanthanum by this method, which appears to be rapid; the chief disadvantage is the necessity of working with strongly alkaline solutions almost saturated with potassium carbonate. However, lack of time prevented a thorough investigation of the problem and continued research may prove profitable.

Samarium like europium may be reduced to a divalent state[101] and precipitated as an insoluble sulfate. Europium, but not samarium, may be reduced in a Jones reductor. Marsh[53] carried out the reduction of samarium with sodium amalgam. It seems possible that samarium might be reduced in a column containing a more electropositive metal than zinc, as for example, titanium. The titanous solution formed when titanium metal dissolves is probably an excellent reagent for collecting the samarous salt. The use of titanium hydride for the reduction of samarium should also be investigated.

In addition to the above suggestions many other research ideas were conceived during the problem and are listed briefly: a) the fractional precipitation of rare earth sulfates resulting from the decomposition of sulfamic acid,[48] b) the use of the rare earth trichloroacetates in liquid-liquid counter-current extraction separations, c) the determination of the solubilities and other properties of the rare earth trichloroacetates and carbonates,

d) phase rule studies based upon the decomposition of the rare earth carbonates, e) the application of the trichloroacetate and dimethyloxalate separations to other rare earth mixtures, f) the separation of cerium and thorium from monazite based upon the formation of insoluble basic trichloroacetates, g) further investigations of the effects of cerium, the other rare earths and related elements on the crystal structures, magnetic susceptibilities, oxidation states, densities, etc. of binary and higher oxide mixtures containing praseodymium or terbium oxides, h) the effects of ignition conditions on an oxide mixture containing praseodymium, and i) the preparation of insoluble praseodymates for the separation of praseodymium.

SUMMARY

1. The solubilities of neodymium salts in water and organic solvents and the distribution of neodymium nitrate between water and organic solvents were studied.

2. A brief resume of the properties of the inorganic salts of trichloroacetic acid and the procedure for the preparation of the rare earth trichloroacetates were given. Neodymium trichloroacetate was prepared and analyzed.

3. Lanthanum, neodymium, and samarium carbonates were prepared by the decomposition of their trichloroacetates from hot water solutions. The advantages of this decomposition method over older methods for preparing rare earth carbonates were discussed.

4. Two homogeneous phase reactions, the decomposition of the trichloroacetate ion in the presence of rare earth ions to form the insoluble rare earth carbonates and the hydrolysis of dimethyloxalate in rare earth solutions to yield insoluble rare earth oxalates, were investigated for the separation of praseodymium and lanthanum. The effects of conditions, such as temperature, pH, and rare earth concentration, are discussed. Praseodymium of high purity was obtained using these methods.

5. The advantages and disadvantages of various cerium separations, including a description of a new method based upon the insolubility of a basic ceric trichloroacetate, were discussed.

6. Five fundamental methods for the quantitative determination of the rare earth elements were reviewed. A new iodometric procedure for the determination of praseodymium and an improved procedure for the oxalate-oxide average atomic weight determination of rare earth mixtures were described, both of which depend upon the iodometric determination of "excess" oxygen in the oxide.

7. The properties of the praseodymium oxides, including a study of the oxidation state of praseodymium in binary oxide mixtures with lanthanum, neodymium, and samarium, were discussed.

8. Research ideas conceived during the problem were given.

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