

peratures are given in Table IV. They range from 0.0011 at 1270° K to 0.15 at 2770° K.

9. Applying the principles of the kinetic theory to an analysis of the experimental data, we are led to the following conception of the mechanism of the reaction.

The oxygen molecules that strike the filament do not react directly with tungsten atoms, but as a first step become negatively charged by taking up an electron from the metal. On the average, about 30 electrons in the metal collide with the oxygen molecule during the time that it is in contact with the metal. Only those electrons which have a velocity of 62×10^6 cm. per sec. or more, succeed in charging the oxygen atoms. When we say that 30 electrons collide with each oxygen molecule, we mean that 30 electrons reach such positions with respect to the oxygen molecule that they would combine with it if their velocities were greater than 62×10^6 cm. per sec. The number of electrons in the metal that have velocities as high as this is so small that only a few of the oxygen molecules that strike the tungsten become negatively charged. For example, with the tungsten wire at 1270° , only one electron out of about 24,400 has a velocity as high as 62×10^6 . Therefore the number of oxygen molecules that receive a charge is only $30/24400$, or only about one out of a thousand.

The number of electrons in the metal must be at least one-seventh as great as the number of tungsten atoms.

The oxygen molecule, after taking up a negative charge, is held by electrostatic forces to the positively charged tungsten atoms and soon, by secondary reactions, combines with the tungsten and with oxygen atoms to form WO_3 . The present experiments do not throw much light on the nature of these secondary reactions.

This theory accounts quantitatively for the observed values of ϵ between the temperatures 1270 and 1770° K, and for the fact that ϵ does not depend on the temperature of the oxygen. It also leads to several interesting deductions which do not appear to be inconsistent with known facts.

The writer wishes to express his indebtedness to Mr. S. P. Sweetser, who has carried out most of the experimental part of this investigation.

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SEBACATES AND CACODYLATES OF THE RARE EARTHS.

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The sebacates appeared to be worthy of special consideration, inasmuch as they afford a separation of the rare earths from thorium in a faintly

acid solution, and from the alkalis in a neutral solution. The cacodylates seemed especially interesting on account of their characteristic properties.

The Sebacates.

Lanthanum Sebacate, $[\text{C}_8\text{H}_{16}(\text{COO})_2]_3\text{La}_2 \cdot 2\text{H}_2\text{O}$, was obtained as a white precipitate by adding a solution of ammonium sebacate to a neutral solution of lanthanum chloride. The whole was kept at 100° for a short time, the liquid separated by filtration and the salt washed first with water containing sebacic acid, and finally with alcohol and ether. This compound formed a white voluminous powder, which was soluble in dilute mineral acids and insoluble in water.

The lanthanum oxide was determined by igniting to constant weight, while the carbon and hydrogen were estimated by combustion. The following results were obtained:

Calculated: La_2O_3 , 35.67; H, 5.73; C, 39.40.

Found: La_2O_3 , 35.63; H, 5.88; C, 39.44.

Praseodymium Sebacate, $[\text{C}_8\text{H}_{16}(\text{COO})_2]_3\text{Pr}_2 \cdot 2\text{H}_2\text{O}$.—This substance was prepared in a similar manner to the lanthanum compound. It formed a very pale green voluminous powder, soluble in dilute mineral acids and insoluble in water. The sebacates appeared to form no double salts with ammonium sebacate. The composition of this substance was ascertained by determining the amounts of hydrogen and carbon present.

Calculated: H, 5.71; C, 39.22. Found: H, 5.67; C, 39.43.

Neodymium Sebacate, $[\text{C}_8\text{H}_{16}(\text{COO})_2]_3\text{Nd}_2 \cdot 3\text{H}_2\text{O}$, was obtained by the method used in the two preceding preparations. It was a light powder of a very pale amethyst color with properties similar to those of the corresponding lanthanum and praseodymium compounds. A simple ignition gave the following results:

Calculated: Nd_2O_3 , 35.70. Found: Nd_2O_3 , 35.60.

After drying at 100° for some time, the amount of water of hydration remained practically unchanged.

Samarium Sebacate, $[\text{C}_8\text{H}_{16}(\text{COO})_2]_3\text{Sa}_2 \cdot 4\text{H}_2\text{O}$, was prepared as described above. This compound formed a nearly white powder, which resembled the former sebacates in its reactions.

By igniting, it was found that the composition corresponded to four molecules of water of crystallization.

Calculated: Sa_2O_3 , 35.84. Found: Sa_2O_3 , 35.82.

Yttrium Sebacate, $[\text{C}_8\text{H}_{16}(\text{COO})_2]_3\text{Yt}_2 \cdot 4\text{H}_2\text{O}$, was prepared by adding a solution of ammonium sebacate to the neutral chloride solution, as in the preparation of the former cerium earth compounds. This sebacate consisted of a light white powder, soluble in dilute mineral acids and insoluble in water.

The analysis of this salt showed that it contained four molecules of water of crystallization, which is similar to the amount carried by the

samarium compound. This resemblance between yttrium and samarium salts has often been observed before.

Calculated: Yt_2O_3 , 26.57. Found: Yt_2O_3 , 26.48.

The Use of the Sebacates for the Quantitative Estimation of the Rare Earths.

In a previous paper,¹ the authors have shown that yttrium can be quantitatively separated from the alkalis by precipitation with ammonium sebacate. Recently this reagent has been applied to several members of the cerium group, with the following results:

Lanthanum (a) from Sodium.—A solution of lanthanum nitrate was standardized by precipitation with ammonium sebacate, as follows: 25 cc. of the solution were diluted to about 100 cc., heated to boiling, a slight excess of ammonium sebacate added and the whole allowed to stand for a short time at 100°. This precipitate was filtered off, washed dried and ignited. Twenty-five cc. were found to contain 0.2789 gram of La_2O_3 .

In the same manner, the lanthanum was precipitated from a similar quantity of the standard solution to which 5 cc. of a 10% solution of sodium chloride had been added.

Standard: 0.2789. Found: 0.2791.

(b) *From Potassium.*—Following the procedure described above, lanthanum was precipitated from the same amounts of standard solution to which 10 cc. of a 10% solution of potassium chloride had been added.

Standard: 0.2789. Found: 0.2790.

It will be seen that lanthanum differs from yttrium, inasmuch as it can be separated from potassium by one precipitation.

Cerium (a) from Sodium.—The separation of this element was studied in a similar way to the lanthanum. Twenty-five cc. were found to contain 0.1272 gram CeO_2 , and the cerium in like amounts was precipitated in the presence of 10 cc. of 10% sodium chloride solution.

Standard: 0.1272. Found: 0.1274.

(b) *From Potassium.*—In this case, potassium chloride was substituted for sodium chloride.

Standard: 0.1272. Found: 0.1275.

Neodymium (a) from Sodium.—Neodymium chloride was standardized and treated as above.

Standard: 0.1474. Found: 0.1475.

(b) *From Potassium.*—It was found that one precipitation gave a complete separation as in the preceding cases.

Standard: 0.1474. Found: 0.1476.

¹ THIS JOURNAL, 34, 772.

The Cacodylates.

Lanthanum and Cerium Cacodylates.—These salts are extremely difficult to obtain pure, owing to their great solubility. The lanthanum solution readily becomes milky, and it cannot be filtered because of its colloidal nature.

Perhaps the most remarkable property of the rare earth cacodylates is the ease with which they form double salts with rare earth compounds, such as chlorides, nitrates, sulfates, etc. Some of these substances will be described further on.

Praseodymium Cacodylate, $[(\text{CH}_3)_2\text{AsO}_2]_6\text{Pr}_2 \cdot 16\text{H}_2\text{O}$, was prepared by dissolving praseodymium hydroxide in a boiling solution of cacodylic acid. It is absolutely necessary that the hydroxide be thoroughly washed free from all traces of chlorides, etc., since these impurities would cause the formation of a certain amount of double salts. The solution of praseodymium cacodylate was filtered, evaporated and allowed to crystallize. The crystals were filtered off and carefully washed with alcohol.

This cacodylate forms pale green crystals, which are soluble in water. One hundred parts of water dissolve 8.43 parts at 25° . Since strong solutions of the more soluble cacodylates form jelly-like masses with alcohol, this reagent cannot be used to throw down crystals of these salts.

In the analysis, praseodymium oxalate was titrated with potassium permanganate.

Calculated: Pr_2O_3 , 23.67. Found: Pr_2O_3 , 23.46.

Neodymium Cacodylate, $[(\text{CH}_3)_2\text{AsO}_2]_6\text{Nd}_2 \cdot 16\text{H}_2\text{O}$, was obtained in a similar manner to the praseodymium compound by using the same precautions.

This salt formed small crystals of a very pale amethyst color, soluble in water. One hundred parts of water dissolve 5.13 parts of the compound at 25° . After heating for some time at 100° , all water of hydration was given off.

Calculated: Nd_2O_3 , 24.05; H_2O , 20.61. Found: Nd_2O_3 , 24.19; H_2O , 20.39.

Samarium Cacodylate, $[(\text{CH}_3)_2\text{AsO}_2]_6\text{Sa}_2 \cdot 16\text{H}_2\text{O}$.—This cacodylate was prepared and described in an earlier paper.¹

It forms nearly white crystals, which are very soluble in boiling water and much less in cold. One hundred parts of water at 25° dissolve 1.60 parts of the cacodylate.

Yttrium Cacodylate, $[(\text{CH}_3)_2\text{AsO}_2]_6\text{Y}_2 \cdot 18\text{H}_2\text{O}$.—A boiling neutral solution of yttrium chloride was treated with a slight excess of sodium cacodylate. A precipitate of the yttrium salt soon formed. The mass was kept at 100° for sometime, when practically all of the yttrium was thrown out of solution. The crystallin precipitate was washed with hot water containing a little cacodylic acid; finally, alcohol removed the small amount

¹ THIS JOURNAL, 34, 276.

of acid remaining. In this case the presence of a chloride does not affect the purity of the compound, since the normal cacodylate is less soluble than the double salt.

Yttrium cacodylate forms a powder of small white crystals, which are only very slightly soluble in boiling water, and insoluble in cold. The salt became anhydrous at 100° .

Calculated: Y_2O_3 , 17.07. Found: Y_2O_3 , 17.16.

Thulium Cacodylate, $[(CH_3)_2AsO_2]_{16}Tm_2 \cdot 16H_2O$.—This was prepared by heating thulium hydroxide with a solution of cacodylic acid. A crystallin powder formed, which was separated by filtration and washed.

This salt is nearly insoluble in boiling water.

Thulium cacodylate was shown to possess sixteen molecules of water of crystallization, by heating to 100° and weighing the anhydrous salt.

Calculated: H_2O , 19.91. Found: H_2O , 19.81.

Fractionation by Means of the Cacodylates.

The material first studied was rich in yttrium, dysprosium and holmium. The crude oxides were dissolved in hydrochloric acid, the solution diluted and precipitated with oxalic acid. The oxalates were washed, dried, ignited and dissolved in hydrochloric acid. A neutral solution was obtained by gradually adding the acid drop by drop towards the end of the reaction. The chlorides were diluted, heated to boiling and stirred rapidly by a motor. Sodium cacodylate was slowly added, causing at first no precipitate, owing to the formation of double salts. After a time the normal cacodylates were deposited as a crystallin powder. When a sufficient quantity had formed, it was separated by filtration, the liquid was returned to the beaker and again submitted to the same process. In this way, four fractions were obtained. The oxide from fraction 1 was colored yellowish and was richer in yttrium than the original material. Fraction 4, obtained by precipitating the filtrate from fraction 3 by means of oxalic acid, gave upon ignition an orange-brown oxide. A nitric acid solution of this oxide gave absorption bands of neodymium, dysprosium and holmium. Practically all the rare earth metals from lanthanum to samarium were concentrated in this last fraction. It was also rich in gadolinium and contained most of the terbium of the original crude oxides. Owing to the presence of neodymium, it was difficult to observe whether there had been any separation between holmium and dysprosium.

Finally, material consisting chiefly of neodymium, samarium and gadolinium was employed. The hydroxides were boiled with cacodylic acid, and the resulting cacodylates fractionated by boiling out with water and crystallizing by evaporation. Neodymium rapidly collected in the more soluble portions, while nearly all the terbium and dysprosium remained in the portion only slightly soluble in cold water. Although

the neodymium compound is very soluble in boiling water, it tends to cling somewhat to those elements forming slightly soluble cacodylates.

Double Salts.

Lanthanum Chloride Cacodylate, $2\text{La}[(\text{CH}_3)_2\text{AsO}_2]_3 \cdot \text{LaCl}_3 \cdot 18\text{H}_2\text{O}$.—Lanthanum cacodylate forms double salts with the sulfate, nitrate, chloride, bromide, iodide, methane-trisulfonate, etc., of lanthanum. Although lanthanum cacodylate and lanthanum nitrate are both very soluble in water, their dilute solutions, upon mixing, give a precipitate which is nearly insoluble.

When solutions of lanthanum chloride and the cacodylate are mixed, a double salt rapidly separates as a mass of fine crystals. These were filtered off, washed, dried and analyzed. The results showed that one molecule of lanthanum chloride united with two molecules of lanthanum cacodylate.

Calculated: La_2O_3 , 29.28; Cl, 6.37. Found: La_2O_3 , 29.43; Cl, 6.24.

Cerium Chloride Cacodylate, $2\text{Ce}[(\text{CH}_3)_2\text{AsO}_2]_3 \cdot \text{CeCl}_3 \cdot 18\text{H}_2\text{O}$.—This compound separated upon mixing solutions of cerium chloride and cerium cacodylate. It consisted of white fibrous crystals. The CeO_2 content showed that its composition resembled that of the corresponding lanthanum salt.

Calculated: CeO_2 , 30.87. Found: CeO_2 , 30.88.

Cerium Sulfate Cacodylate was obtained as a thick precipitate by mixing the sulfate and cacodylate solutions. The mass filtered badly, but was finally washed and dried. The analysis indicated that it probably consisted of one molecule of cerous sulfate in combination with half a molecule of cerous cacodylate.

Neodymium Chloride Cacodylate, $2\text{Nd}[(\text{CH}_3)_2\text{AsO}_2]_3 \cdot \text{NdCl}_3 \cdot 18\text{H}_2\text{O}$, was prepared in a similar manner to the double chlorides described above. It formed very pale amethyst crystals, which were of a fibrous nature.

Calculated: Nd_2O_3 , 30.00; Cl, 6.31. Found: Nd_2O_3 , 30.04; Cl, 6.31.

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THE PREPARATION OF OXAN AND THE PROPERTIES OF SALTS OF α - AND β -OXAN.

By A. P. LIDOV.

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In the account of my paper to the VIIIth International Congress of Applied Chemistry, "The Preparation of Oxan and of the Existence of a Higher Grade of its Oxidation, Peroxan," there is a small inaccuracy, occasioned possibly by my having employed a not quite correct terminology, borrowed from Comey's "Dict. of Chemical Solubilities, Inorganic," p. 268, 1896.

¹ C. A., 6, 3093 (1912).