thallium in an infinite amount of mercury would be accompanied by a heat evolution of 2970 joules. From the electromotive forces and temperature coefficients of thallium amalgam concentration cells, Richards and Daniels calculated the heat effects of the cells by use of the Helmholtz equation. From these results, Lewis and Randall[5] calculated the partial molal heat contents of thallium and mercury in the amalgams and, by the use of these heat contents and the data of Richards and Daniels upon the heats of solution of thallium in the amalgams, calculated the heat evolved when 1 gram-atom of thallium dissolves in an infinite amount of mercury. The value thus obtained is 730 calories, or 3053 joules, at 30°, with a probable error of 20 calories or 83 joules. The corresponding value at 20° may be calculated by the Kirchhoff equation to be 3220 joules, which is 250 joules higher than the value obtained by extrapolation of the curve in Fig. 1. In view of the possible errors in both results, the agreement is not unsatisfactory.

Summary

The heats of solution of thallium in dilute thallium amalgams have been determined in a preliminary series of measurements. The results are consistent with those obtained by Richards and Daniels for concentrated amalgams. A short extrapolation of the curve for the variation of the heat of solution with concentration of the amalgam gives a value for the heat of solution of thallium in an infinite quantity of mercury in fair agreement with the value calculated by Lewis and Randall.

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STUDIES ON THE QUANTITATIVE DETERMINATION OF PRASEODYMIUM

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The gravimetric determination of praseodymium is attended by some uncertainty, and while the single determination of this element is not at present required in the routine of industry, it is a matter of fundamental importance in many studies of the chemistry of the rare earth elements. The precipitation as oxalate is commonly followed by ignition in air. Contrary to the action of the majority of the rare earth elements, praseodymium does not form an oxide of the R_2O_3 type on ignition in air, but gives an intermediate oxide to which the formula Pr_4O_7 is commonly assigned, and this is used as the basis of calculation in the majority of analytical directions.

In previous work[1] difficulty had been experienced in getting satisfactory results by this method, and it had been found necessary to reduce in hydrogen to the sesquioxide, Pr_2O_3, for weighing.

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[1] Brinton and James, THIS JOURNAL, **43**, 1446 (1921).

The behavior of the oxides of praseodymium on ignition has been the subject of considerable research, but the results up to this time have been inconclusive. Von Welsbach[2] arrived at the formula Pr_4O_7 for the oxide ignited in air, by an iodimetric determination of the "excess oxygen." In acid solution it was held that the oxygen in excess of that required by the formula Pr_2O_3 liberated its equivalent of iodine from potassium iodide. Schottländer[3] by reduction in hydrogen obtained values which pointed to the formula Pr_6O_{11} for the composition of the oxide obtained on ignition in air, but of the purity of his praseodymium he was by no means certain. H. C. Jones[4] in the course of atomic weight determinations reduced the ignition product of the oxalate to the sesquioxide by heating it in hydrogen and found a loss of 2.50% of oxygen. He considered, therefore, that the higher oxide was Pr_4O_7. (The theoreticall oss of oxygen should have been 2.37%.) Von Scheele,[5] working on the transition of the dioxide to the sesquioxide by reduction in hydrogen, heated some of his reduced oxide in air to constant weight, and found a gain of 3.65%. This would correspond to a formula between Pr_6O_{11} and PrO_2, but he does not seem to have considered any oxide other than the dioxide and sesquioxide, attributing any intermediate proportions to various mixtures of these two oxides. Brauner[6] deduced the formula Pr_5O_9 by considerations of specific gravity and atomic volumes. The formula Pr_6O_{11} for the oxide resulting from ignition in air is held by Meyer[7] to be correct. His assumptions are based on titration of the iodine liberated by heating his oxide with potassium iodide and concd. hydrochloric acid, distilling the free chlorine into potassium iodide solution, and then titrating the liberated iodine. The gravimetric reduction in hydrogen and reoxidation in oxygen led to essentially the same results. It must be said, however, that the agreement of Meyer's figures with those theoretically calculated for Pr_6O_{11} was not quite as close as might be desired, but it should also be noted that Meyer's praseodymium was not absolutely pure. Marc[8] has shown that contamination of praseodymium by other rare earth elements exercises a decided influence on the degree of oxidation shown by the praseodymium. Baxter and Griffin[9] also, interested in atomic weights, obtained certain results which cast doubt on the formula Pr_4O_7 as the ignition product of the oxalate.

It will be readily seen that the exact composition of the oxide of praseodymium obtained by ignition in air is still an open question. Realizing that the composition of the oxide may vary according to the conditions under which the ignition is made, we have conducted a series of experiments with a view to establishing the formula for the oxide which may be used as the basis for calculation in the gravimetric determination of praseodymium.

Experimental Part

Praseodymium oxalate, free from all other rare earths except a trace of cerium, was made available by the kindness of Professor C. James of New

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[2] Von Welsbach, *Monatsh.*, **6**, 477 (1885).

[3] Schottländer, *Ber.*, **25**, 569 (1892).

[4] Jones, *Am. Chem. J.*, **20**, 345 (1898).

[5] Von Scheele, *Z. anorg. Chem.*, **17**, 310 (1898).

[6] Brauner, *Proc. Chem. Soc.*, 17, 66 (1901).

[7] Meyer (a) *Z. anorg. Chem.*, **41**, 119 (1904). See also (b) Meyer and Koss, *Ber.*, **35**, 3740 (1902).

[8] Marc, *Ber.*, **35**, 2370 (1902).

[9] Baxter and Griffin, This Journal, **28**, 1690 (1906).

Hampshire College. The last trace of cerium was removed, at the expense of a little of the praseodymium, by the addition of ammonium hydroxide to the acid solution until a faint turbidity persisted, after which a little hydrogen peroxide was added. The small amount of praseodymium hydroxide with which was associated all of the cerium was filtered off. The filtrate contained praseodymium which we believe to have been of the very highest purity.

The first question to answer was the possibility of obtaining constant weight by ignition of the oxalate in air. Previous experiments, made with the praseodymium before the trace of cerium had been removed, had shown that constant weight was not easily obtained.

Samples of the purified solution were precipitated by the addition of oxalic acid in moderate excess to the faintly acid solution. The moist precipitates with the paper were ignited in platinum crucibles, slightly inclined, with covers slipped to one side so that about $^1/_3$ of the mouth of the crucible was open to the air. After the preliminary incineration of the paper and expulsion of the gases, ignition over the full flame of a Bunsen burner for 15 minutes gave a weight which remained constant (within 0.0001 g. on a 0.13g. sample) upon several successive ignitions of 20 minutes each, over the blast lamp. The experiments were repeated in crucibles of alundum and porcelain with the same satisfactory results. The oxides which had been intensely heated were then subjected to ignition at barely visible red heat for periods as long as 90 minutes, but there was no appreciable loss or gain in weight.

The fact having been established that with pure praseodymium a constant weight for the oxide could be obtained by ignition of the oxalate in air—and this, too, with considerable latitude in the conditions of the ignition—the next point to be investigated was the composition of the oxide so obtained.

The oxide obtained by ignition in air was weighed into a porcelain boat and heated in an electric combustion furnace in a silica tube through which was passing a current of hydrogen, highly purified by the conventional absorbents. The temperature was registered by an accurately calibrated platinum thermocouple. The oxide was always cooled in the current of pure, dry hydrogen, and then transferred to a desiccator in which was left a stick of potassium hydroxide in addition to calcium chloride, as praseodymium oxide has been found to absorb carbon dioxide quite rapidly.

A sample of 0.7876 g. of "air-ignited" oxide was heated for 60 minutes in hydrogen at 900–950°. The loss was 0.0244 g. (3.10%). Further heating for 45 minutes under the same conditions caused a loss of 0.0001 g. (0.01%). The reduced oxide was next heated for 45 minutes at 950°, with a current of air passing through the tube. The gain in weight was 0.0244 g. (3.10%). The oxide was next heated for 40 minutes in pure oxygen and cooled in the same gas. A gain in weight of 0.0010 g. was found, and further heating for 20 minutes in oxygen caused no change. Reheating in air to 900–950° for 20 minutes caused a loss of 0.0008 g., which was increased by 0.0001 g. by further heating in air for 30 minutes. This shows that the gain of 1 mg. from heating in oxygen is practically exactly lost by again heating in air. The oxide was now once more heated in a current of hydrogen at a temperature of 900–1000° for 65 minutes, and a loss of 0.0245 g. was determined. Another heating in the same way for 35 minutes caused a further loss of 0.0001 g. This loss corresponded to 3.13%.

The behavior of the oxide when heated in oxygen will be discussed later. From this cycle it will be seen that the "excess oxygen" taken up by heating the fully reduced oxide in air was found in the two series to be 3.11% and 3.13%.

As a check on these figures the oxide previously used was dissolved in acid, and reprecipitated as oxalate in the presence of filter pulp, thus furnishing on ignition a porous, easily reducible oxide. This substance was subjected to a cycle of three sets of alternate ignitions in air and in hydrogen, the previously described conditions being maintained. The losses observed were 3.11, 3.06 and 3.09; the corresponding gains were 3.06, 3.10 and 3.13%. Once more an ignition in pure oxygen gave a gain of 1 mg. which was again given up when the oxide was heated in air. The average of all these oxidations and reductions gives 3.10% of "excess oxygen."

In the light of work by previous investigators, and in view of the constancy of weight readily obtained by reduction in hydrogen, it seems fair to assume that the formula Pr_2O_3 can be assigned to the oxide obtained by reduction. The oxygen taken up by ignition in air in excess of that required for the formula Pr_2O_3 was found to be 3.10%. For the higher oxides of praseodymium which have been proposed we have the following calculated percentages of "excess oxygen:" Pr_4O_7, 2.37%; Pr_5O_9, 2.83%; Pr_6O_{11}, 3.13%; PrO_2, 4.63%. From our experiments it seems highly probable that the formula Pr_6O_{11}, suggested by Schottländer and by Meyer, most nearly corresponds to the oxide obtained by ignition in air, and should be used as a basis for analytical calculations rather than the more generally recommended Pr_4O_7. The fact that our results accord with the theory much more closely than did those of Meyer may be explained by the higher degree of purity of our praseodymium.

The slight gain of 1 mg. when the oxide constant in air is heated in pure oxygen, and the loss of this weight when again heated in air, suggested the probability that the composition of the oxide was influenced by the pressure of oxygen to which it was subjected, and that doubtless while the formula Pr_6O_{11} is justified for the oxide ignited in air at ordinary pressure, it would not be justified for other conditions. The correctness of this view was proved by a series of tests in which weighed amounts of Pr_6O_{11} were heated in the same apparatus in which the hydrogen reductions had been made, but with the tube connected with an exhaust pump. A complete study of the behavior of the oxides of praseodymium at various pressures of oxygen will be made the subject of a later paper. It is sufficient now to say that on heating Pr_6O_{11} in a vacuum the sesquioxide seems to form readily, and the brown color of the former gives place to the characteristic green of the latter. Only on the surface did the dark color remain, and this was undoubtedly due to incomplete evacuation.

It has been shown [8,7b] that in its tendency toward formation of higher oxides praseodymium is appreciably influenced by the presence of other rare earths, cerium favoring the formation of higher oxides and lanthanum and neodymium having the opposite effect. In presence of even slight contamination by other rare earths, then, we are hardly justified in accepting the formula Pr_6O_{11} as representing the composition of the oxide resulting from the ignition of the oxalate. In the presence of traces of other earths a method for the determination of praseodymium which is independent of the tendency of this element to form higher oxides is desirable, and this had led to a study of the volumetric oxalic acid-permanganate process.

Krüss and Loose[10] found that by adding an excess of standard oxalic acid to a solution of a pure rare earth salt, filtering off the rare earth oxalate and titrating back the excess of oxalic acid with potassium permanganate, they obtained results for the atomic weights of rare earth elements which were approximations only, and invariably high. These high atomic weights they attributed to the formation of basic salts. If this method were used for the analytical determination of praseodymium, the formation of basic salt would make the results for praseodymium low, since a greater excess of oxalic acid would be left to be titrated back. Krüss and Loose claim that when they multiplied the atomic weights found by $^{16}/_{17}$ approximately correct results were obtained; but the concordance obtained by this correction is still far from satisfactory.

Our preliminary experiments pointed to the correctness of the views of Krüss and Loose as to the basic nature of the oxalates, and our first results by their method were all decidedly low. Even a sample of praseodymium containing an unknown amount of lanthanum gave low results by this method, whereas lanthanum should cause the results to be high, because of its lower atomic weight and because of its repressing action on the oxidation of praseodymium which would cause a lower weight of the oxide weighed for the determination.

If it is true, as Krüss and Loose contend, that the oxalates ordinarily precipitated are basic, then the nearest approach to a neutral oxalate should be obtained by precipitation in a fairly strongly acid solution; but in such a solution the solubility of the rare earth oxalates is appreciable. How-

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[10] Krüss and Loose, *Z. anorg. Chem.*, **4**, 161 (1893).

ever, advantage may be taken of the presence of considerable mineral acid for the precipitation of the greater part of the oxalate, and that portion still remaining in solution can then be precipitated as oxalate by the gradual neutralization of the strong acid by ammonium hydroxide.

It has been found[11] that the purest oxalate is obtained from a nitric acid solution, so it would seem advisable to dissolve the oxide in nitric rather than in hydrochloric acid.

The following method is, therefore, based on these considerations.

The sample is added to concd. nitric acid, about 1 cc. for 0.1 g. of oxide, and the mixture heated to effect solution. About 100 cc. of water is now added, the solution heated to 60–70°, and an excess of 0.1 *N* oxalic acid is slowly added with constant stirring. The mixture is kept warm for an hour or more, and stirred occasionally. The excess of nitric acid is now gradually neutralized with ammonium hydroxide, which is added a few drops at a time at intervals of several minutes until the liquid shows only a faintly acid reaction. The oxalate precipitate is filtered and washed, and the excess of oxalic acid in the filtrate, heated to 80°, is titrated back with potassium permanganate solution, after the addition of 10 cc. of 1 – 1 sulfuric acid.

Sample	Oxide taken G.	Pr_6O_{11} found G.	Sample	Oxide taken G.	Pr_6O_{11} found G.	Sample	Oxide taken G.	Pr_6O_{11} found G.
Pure Pr	0.1213	0.1209	Pr and Ce	0.1382	0.1383	Pr and La	0.1515	0.1539
Pure Pr	.1540	.1535		.1376	.1377		.1520	.1543
Pr and Ce	.1390	.1389		.1377	.1376		.1520	.1543

The results for pure praseodymium and for praseodymium with the addition of less than 1% of cerium show a very satisfactory degree of concordance. For the sample of praseodymium containing a fairly large amount of lanthanum (the exact percentage is not known) the results are high as would be expected. It seems fair to assume, then, that by following the directions as above outlined the oxalates of the rare earth elements may be precipitated reasonably free from basic salts, and that the volumetric method is satisfactory.

Summary

The formula Pr_6O_{11} has been shown to be correct for the ignition product of praseodymium oxalate, obtained in air at ordinary pressure, over a wide range of temperatures.

Details have been given for the volumetric determination of praseodymium by precipitation of the oxalate and titration of the excess of oxalic acid.

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[11] Lenher, THIS JOURNAL, **30,** 577 (1908). Job, *Compt. rend.*, **126,** 246 (1898). Matignon, *Ann. chim. phys.*, [8] **8,** 245 (1906).