[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE HIGHER OXIDES OF SOME RARE-EARTH ELEMENTS[1]

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Introduction

The sesquioxide, R_2O_3, may be assumed as the type of the normal oxides of the rare-earth elements; on that all are agreed, but the literature dealing with oxides of types higher than R_2O_3 is full of uncertainty and contradictions. Yet in the placing of these elements in the periodic table we find many assumptions of higher oxides, the existence of which has never been proved, and without this proof there seems little justification for placing several of the rare-earth elements in the columns with quadri- and quinquivalent elements. Of the oxides of the true rare earths those of praseodymium have been investigated most frequently, but with very uncertain results. The oxide resulting from the ignition of praseodymium compounds in air, formerly considered as Pr_4O_7, has been shown[2] to conform more nearly to the formula Pr_6O_{11}. Another oxide, PrO_2, has been prepared, although never quite pure, and divergent opinions have been expressed as to the methods of its formation and the conditions for its stability. Brauner[3] claimed to have prepared the dioxide by heating a mixture of praseodymium and potassium nitrates at 400°. He also reported[4] the preparation of Pr_5O_9, Pr_2O_5, Nd_2O_4 and Nd_2O_5, but failed to give details for their preparation. Marc[5] concluded that the presence of a little cerium is necessary for the higher oxidation of praseodymium, and that under these conditions neodymium is also oxidized. These results, as well as those of Meyer and Koss,[6] were obtained with mixtures, the relative proportions of which were arrived at indirectly, and the results cannot be regarded as entirely conclusive, as Meyer[7] admits in a later paper. Von Scheele[8] reported the preparation of the dioxide by heating praseodymium oxalate in air to incipient redness. His analyses showed from 4.09 to 4.97% "excess oxygen" "(that is, over that demanded by the

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[1] From a thesis submitted to the Graduate Faculty of the University of Minnesota by H. Armin Pagel in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Schottlander, *Ber.*, **25**, 569 (1892); (b) Meyer, *Z. anorg. Chem.*, **41**, 97 (1904); (c) Brinton and Pagel, THIS JOURNAL, **45**, 1460 (1923); (d) Prandtl and Huttner, *Z. anorg. allgem. Chem.*, **149**, 235 (1925).

[3] Brauner, *Proc. Chem. Soc.*, **14**, 70 (1898); **17**, 66 (1901).

[4] Brauner, *Z. anorg. Chem.*, **32**, 1 (1902).

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

[6] Meyer and Koss, *ibid.*, **35**, 3740 (1902).

[7] Meyer, *Z. anorg. Chem.*, **41**, 97 (1904).

[8] Von Scheele, *ibid.*, **17**, 310 (1898).

formula Pr_2O_3)." The calculated "excess oxygen" for PrO_2 is 4.64%, so his "yields" were approximately from 88 to 107%. Meyer[7] obtained a dioxide of about 97.5% purity by heating praseodymium nitrate with potassium nitrate at 440–450°, as recommended by Brauner. Prandtl and Huttner,[2d] attempting to duplicate the experiments of Meyer and Brauner, found a product corresponding to the formula $Pr_6O_{11}\cdot 7H_2O$ instead of PrO_2. Their purest dioxide was obtained by heating the sesquioxide for five days in an atmosphere of oxygen at about 300°. Neodymium was found to form no higher oxides when fused with sodium chlorate. Other investigations will be reviewed later in connection with our own conclusions.

In this paper we present the results of studies on the preparation and stability ranges of the oxides of lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium and ytterbium. It is hoped that oxides of other rare-earth elements, especially terbium, will be treated in a later paper.

Materials and Apparatus

The lanthanum, praseodymium, neodymium, samarium and gadolinium compounds were those described in a previous communication,[9] and further discussion of their high purity is not necessary. Before final precipitation as oxalates finely divided ashless filter pulp was added to the solutions in order to impart the desired fineness and porosity to the ignited oxides. Otherwise the oxides are so coarse and dense that reduction by hydrogen is very slow, and possibly not entirely complete.

The erbium and ytterbium compounds were purchased in the market. Special investigation of their purity was deferred, pending evidence of positive results in the formation of higher oxides.

For pressure oxidations tank oxygen of 99.5% purity was employed, after passage through a drying train. The use of hydrogen generated in the Laboratory was soon abandoned in favor of commercial electrolytic hydrogen, since after passage through the purification train the gas from the two sources gave identical results. The train consisted of (1) acid permanganate solution, (2) alkaline permanganate solution, (3) heated copper spirals in a copper tube, (4) moistened silver nitrate crystals, (5) potassium hydroxide solution, (6) concentrated sulfuric acid and (7) a tower of phosphorus pentoxide.

Balance.—It soon became evident that errors due to absorption of moisture and carbon dioxide by some of the very hygroscopic rare-earth oxides were quite appreciable, when dealing with small changes in weight, so a special balance was arranged to eliminate this source of error. A Christian Becker No. 8A chainomatic balance, having a graduated notched beam which allowed weights up to 1.1 g. to be adjusted without opening the door, was found entirely reliable as to constancy. The beam and chain

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[9] Sarver and Brinton, THIS JOURNAL, **49**, 943 (1927).

readings were accurately calibrated. The balance case was dismantled, all woodwork was varnished, and all cracks were filled with melted paraffin. The hole through the base accommodating the pan-arrest bar was covered with a thin rubber membrane (a dental rubber dam), which was sealed to the bar and base with adhesive tape. The front door was permanently sealed with tape and paraffin. Under the back door, which was raised about 10 cm., was sealed a board containing a brass tube, C, Fig. 1, of very slightly larger bore than the Pyrex tube, A. This tube was located directly behind the left pan of the balance. A nail driven into a wooden block, F, serves as a bumper to prevent disalignment of the pan when the boat is pushed onto it from the tube. B represents a wooden frame in which operates a snugly fitting metal slide-gate, D, which serves to seal the entrance when the Pyrex tube is not in place. A velvet lining, E, gives an almost air-tight joint between the wood and the glass tube. Behind the right pan a hole, ordinarily closed with a 1-hole stopper, allows the integral weights to be handled with a wire fork. A gentle stream of purified air passed through this stopper into the balance case at all times except when weighing. Thus it was never necessary to open the balance door except to change the desiccating and decarbonating reagents kept in the case. The technique of weighing will be described later.

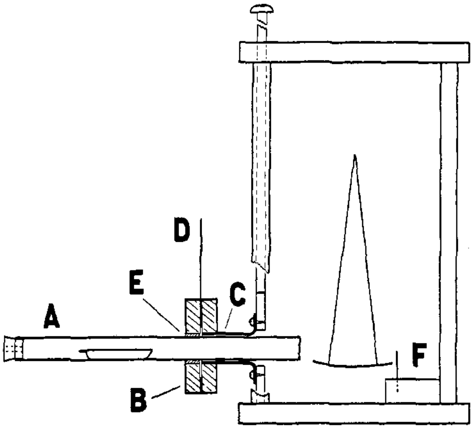

Fig. 1.—Side view of balance.

Pressure Furnace.—While a rebuilt Hoskins furnace with projecting core served for air ignitions and hydrogen reductions, a special furnace had to be built for the oxidations by oxygen under high pressures.[10] The furnace is diagrammatically shown in Fig. 2. A is the outer shell, 46 cm. long, of triple strength wrought iron, 8 mm. thick. The dotted lines just inside this shell, and at the ends, represent heavy wire screening, to facilitate the rapid distribution of oxygen when building up the pressure.

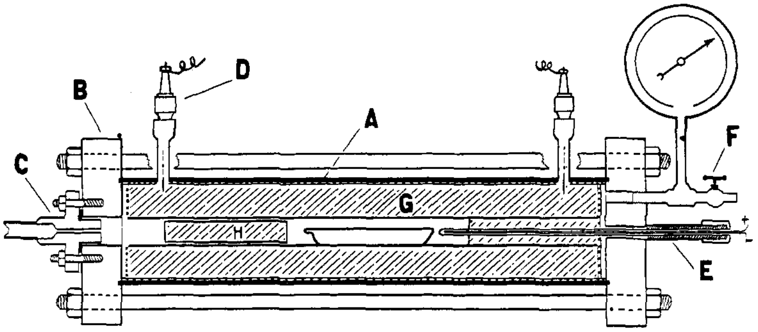

Fig. 2.—Pressure oxidation furnace.

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[10] After the completion of this work a somewhat similar type of furnace was found described by Fischer and Ploetze, *Z. anorg. Chem.*, **75**, 1 (1912).

The ends, B, are solid cast iron caps, 17.8 by 3.8 cm., grooved to take copper gaskets, and they were drawn against the accurately machined ends of the shell, A, by eight iron bolts, only two of which are shown in the cut. This gave a perfectly tight joint. C is a flanged bronze coupling, secured by four bolts, with copper–asbestos gaskets to prevent leakage. This coupling leads to the oxygen supply and provides an entrance to the silica tube, which is wound with 22-gage Chromel wire. To prevent too high a temperature at the junction points, 15 cm. of heavy Chromel wire was welded to each end of the heating wire. Eight-cm. lengths of regular $^3/_8$ inch iron pipe coupling were fitted into the jacket about 8 cm. from each end, and to these couplings Champion spark-plugs, D, were fitted by means of reducers, the joints being made air-tight with "Caulk" dental cement. Litharge-glycerin cement proved less satisfactory for joints which could not be water cooled, as there was a slight decomposition of organic matter at high temperatures. The terminals of the heating elements, insulated with Pyrex tubing, were attached to the spark-plugs with small hollow brass cylinders, slotted on each end, driven on the protruding end of the electrodes. After screwing the body of the plug into the reducer, the core of the plug was introduced, slipping the slot onto the terminal wire. This gave a very satisfactory contact. E shows a quartz thermocouple tube sealed into an iron nipple, fitted with a brass cap. This was made tight with litharge-glycerin cement and was water-cooled. The brass needle valve, F, was used for evacuating the furnace The pressure gage was calibrated at the Air Reduction Plant, in Minneapolis, by comparison with their standard test gages. The annular space between the furnace wall and the combustion tube was packed with ignited asbestos wool, G, as was also the end of the combustion tube into which the thermocouple extended. To prevent radiation toward the other end of the heating chamber an Alundum tube, H, loosely packed with asbestos fiber, was inserted. Acknowledgment is gratefully made to Mr. F. W. Fullerton, Mechanician of the School of Chemistry of the University of Minnesota, and to Mr. Frank L. Heyer, Jr., of Dakota, Minnesota, for valued assistance in the construction of this furnace.

The temperature gradient was determined by means of two thermocouples. One was in its permanent position, as shown in the cut, while the other was moved, in 1 cm. stages, over the space occupied by the longest boat. These thermocouples were calibrated against one certified by the U. S. Bureau of Standards. Over the range tested a maximum variation of 7° was found, and except at the very ends of the longest boat the temperature range was not over 2° greater or less than the temperature found by adding 4° to the reading of the regular thermocouple. Therefore all temperatures recorded in this paper were obtained by adding 4° to the observed temperature. All temperatures were read with a potentiometer indicator.

Experimental Part

Composition of the Oxide of Praseodymium after Ignition in Air.—In a previous communication[2c] it has been shown that the formula for praseodymium oxide obtained by ignition in air at ordinary pressures agrees very closely with Pr_6O_{11}. This oxide had been slowly cooled in the furnace before being transferred to a desiccator. Later experiments confirmed the correctness of this formula for the slowly cooled oxide, but a question arose as to the effect of varying the conditions of cooling. The following set of experiments was planned to throw light on this point.

3.4636 g. of purest praseodymium sesquioxide was employed. This had been prepared by igniting the oxalate in a large porcelain boat and then reducing with hydrogen at about 900° to constant weight. To guard against the possible presence of weighable amounts of sulfur, as basic sulfate, the sample was treated with steam and hydrogen, and again reduced in dry hydrogen. No change in weight was observed. In these hydrogen reductions the gas was allowed to pass during the cooling until a temperature of about 50° was reached, after which purified air was substituted for the hydrogen. While the purified air continued to flow, the Pyrex tube, A in Fig. 1, was attached to the combustion tube, and the boat was pulled into it. The tube was stoppered and carried to the balance. Purified air was again passed through the tube, the gate, D in Fig. 1, was raised and the tube was slipped into place. The air current was then disconnected from the tube A, and passed into the balance case through the hole back of the right pan. With the stopper in the back end of the tube now removed, the purified air passed in the reverse direction through this tube, and this enabled the boat to be pushed onto the balance pan without the introduction of any unpurified air. After shutting off the air and stoppering the Pyrex tube, a brief pause was allowed for subsiding of air currents, and the boat was then weighed. The same technique was used in all weighings of such oxides as showed a tendency to absorb moisture. Controls with samples of ignited calcium oxide, mixed with a little calcium chloride, proved this method ideally suited to the handling of hygroscopic and carbon dioxide susceptible substances.

In Table I are shown the results of several variables. It will be readily understood that with the furnace slightly tilted, both ends of the tube being open, a current of air would be induced during the cooling, so that conditions would be more favorable for re-oxidation. When the cooling conditions are spoken of as "rapid" in the table it means that the boat at its maximum temperature was pushed to the cool end of the tube outside the furnace. A great many experiments, carried out with smaller quantities of the oxides, gave results agreeing closely with those shown in the table. Tabulation of these runs is omitted for economy of space. In the interest of later discussion the results in this table are placed in the order of decreasing yields.

It will be seen that the slowly cooled runs give the highest values. Under conditions of rapid cooling in a level furnace we find the minimum values. In the last run of this series a hinged furnace was used, so the tube could be lifted from the heat, stoppered and cooled very rapidly in diminished oxygen pressure. It seems justifiable to conclude that the rate of cooling and the supply of oxygen during the cooling period are the main factors in determining the composition of the oxide.

That the oxide heated over long periods of time at relatively low temperatures gives oxygen ratios higher than Pr_6O_{11} was found in an attempt to determine roughly the rate of decomposition of the dioxide. A sample

TABLE I

RESULTS OF SEVERAL VARIABLES

Heating time	Temp., °C.	Cooling conditions	Tilt	Mole % of PrO_2[a]
20 min.	700	To 25° in pure air in furnace	Level	66.9
5	700	To 160° in furnace	7°	66.7
1 hr.	700–725	To 200° in furnace	7°	66.6
1.5	840–860	To 450° in furnace	Level	66.3
1	700–725	Rapid	7°	64.5
2	900–915	Rapid	7°	64.0
2	850	Rapid	7°	63.9
0.5	850	Rapid	7°	63.4
1	850–875	Rapid	3.5	63.4
1.5	900–925	Rapid	Level	61.0
15 min.	950	Tube stoppered and lifted from furnace	...	55.7

[a] CALCULATIONS.—In most papers dealing with the higher oxides of praseodymium the compositions have been indicated in terms of "excess oxygen." Thus PrO_2 contains 4.64% oxygen in excess over Pr_2O_3. This method is somewhat unsatisfactory because the percentages of "excess oxygen" in the higher oxides are so small that even a slight difference in this percentage actually represents a considerable difference in the composition, and concordance of analytical figures with "theory" gives one the impression of much greater purity than is actually the case. Much of the past work on these oxides, when viewed in the light of a 100% basis, is not convincing. It is for this reason that we have used the largest possible samples, and adopted the manipulative refinements described in this paper. In our tabulations and discussions results are expressed in terms of molecular percentages of praseodymium dioxide formed. For example 98 mole % of PrO_2 means that oxidation of the sesquioxide has occurred to such a degree that the empirical composition of the resulting oxide could be expressed by saying that for every 98 molecules of PrO_2 formed, 1 molecule of Pr_2O_3 remains unoxidized. Pr_6O_{11} would correspond to 66.67 mole % of PrO_2, and if the actual percentage purity of a sample in terms of molecules of Pr_6O_{11}, considered as a definite compound, is desired, it can be obtained by simply multiplying the mole % of PrO_2 by 1.5.

of about 93 mole % of PrO_2 heated for five hours in a current of pure air at 375° yielded a composition of 83.6%. Further heating for thirteen hours at 385–395° changed the composition to 70.7%. The heating was continued for periods of thirteen, twenty-one and twenty-two hours at the same temperature and in each of these determinations a constant value of 68.1% was found. Attempting to approach this constant value from the lower side, a sample of 64.5 mole % of PrO_2 was heated in a gentle air current at 385–395° for periods of seven, twenty-four and six hours, and compositions of 68.0, 68.4 and 68.4% were found. This sample was then heated in the open furnace, tilted at an angle of 7°, without forced air current, for twenty hours at 460–495°, and again for twenty hours at 480–510°, and identical values of 67.7% were obtained.

In the work on pressure oxidation to be described later it was frequently necessary to prepare samples of known weight of Pr_2O_3 by hydrogen reduction. The reduced oxide was then re-oxidized in air at 900–950°

for twenty minutes, in the tilted tube furnace and rapidly cooled. Consistent values of 64.1–64.3 mole % of PrO_2 were always obtained, and this regardless of whether we started with pure Pr_2O_3 or almost pure PrO_2.

Thus it is seen that the composition of the air-ignited oxide of praseodymium can be made to vary with the conditions of ignition and cooling—especially are the conditions of cooling important—but with any specified set of conditions reasonably concordant results are found.

Preparation of Praseodymium Dioxide by Pressure Oxidation.—From the evidence of work thus far done it was thought likely that a quantitative yield of praseodymium dioxide could be obtained by heating and cooling in an atmosphere of pure oxygen at very high pressure. Preliminary tests in the first pressure furnace constructed gave apparent yields of 100.6 to 100.7 mole % of PrO_2 by heating for twenty hours at 350° in pure oxygen at a pressure of 195 lb./sq. in. Fearing that the high values might be due to adsorption of oxygen during the cooling under high pressure, the furnace was thoroughly evacuated at high temperature, then filled with oxygen and cooled to room temperature. An oxide sample of constant weight was introduced, allowed to stand for five hours at a pressure of 215 lb. of oxygen and weighed. An increase of only 0.2 mg. was found. The excess in yield over 100% was not large, but with the highly refined manipulations employed it could not be considered as allowable experimental error. Moreover, a slight odor had been noticed in the exhaust oxygen, and it was thought that the error might be due to absorption of volatile organic matter from the decomposition of the cement used. This led to the construction of the new furnace, substituting dental cement for the litharge-glycerin mixture. The work was started anew, and the pressure oxidation results obtained up to that time were discarded.

To determine the effects of the variables, time, temperature and pressure, series of runs were made in which two of the factors were held constant while the third was varied. Each pressure oxidation was followed by a quickly-cooled air ignition in the tilted furnace, which gave uniform

TABLE II

THE EFFECT OF TEMPERATURE

Pressure, 215 lb./sq. in. (±5 lb.). Time, 5.25 hours. Temp. control ±2°. 1.3394 g. of Pr_2O_3.

Temp., °C.	Mole % of PrO_2	Temp., °C.	Mole % of PrO_2	Temp., °C.	Mole % of PrO_2
205	64.9	306	76.2	405	98.7
204	64.9	306	77.1	405	98.7
230	67.0	329	84.5	430	80.2
230	66.6	329	86.5	430	81.7
255	68.6	350	97.8	453	76.6
255	68.2	352	97.2	451	76.9
278	70.9	384	98.0	509	76.6
278	70.4	386	97.8	585	74.5

compositions corresponding to 64.1–64.3 mole % of PrO_2. In all reports true pressures are given, that is, gage pressures plus 15 lb./sq. in. At the end of each series the sample was reduced in hydrogen and weighed as sesquioxide, to make certain that no manipulative loss had occurred.

The results in Table II are graphically shown in Fig. 3. The sharp drop in yield beyond 405° suggests that at temperatures above that point the dissociation pressure of the dioxide exceeds 215 lb. The curve would undoubtedly drop to a minimum much lower than that shown at temperatures 440–585° if the true conditions existing during the entire run could be shown. It is impossible to cool the furnace instantaneously, and thus preserve the stage of oxidation which exists at any instant. It was found that from temperatures around 500° a nearly uniform rate of cooling of about 10° per minute held for the first twenty minutes. It seems reasonable to expect that a certain amount of re-oxidation occurs in passing through the temperature range most favorable to a high rate of oxidation, 400–325°. This point was, in fact, proved by introducing the air-ignited oxide (64.2 mole % of PrO_2) into the furnace at temperatures of 506, 504, 454 and 448°, letting in oxygen as rapidly as possible up to 215 lb. pressure, and then immediately shutting off the heating current. These four runs showed, respectively, 75.0, 75.5, 75.4 and 75.6%, values which lie only about 1% lower than those obtained in five and one-fourth hours at the same temperatures.

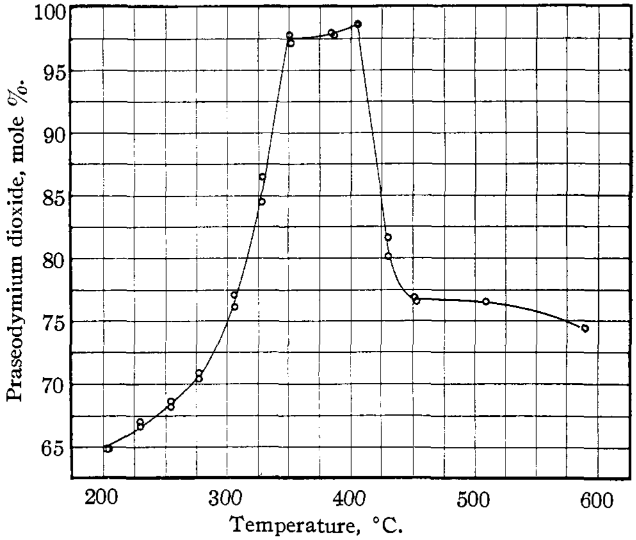

Fig. 3.—Effect of temperature on the formation of praseodymium dioxide; time of each heat, $5^1/_4$ hrs.; oxygen pressure, 215 lb./sq. in.

The effect of varying the time of heating, at the optimum temperature, and at three different pressures, is shown in Table III.

TABLE III
THE EFFECT OF TIME
Temp., 378 ± 3°

215 lb./sq. in.				115 lb./sq. in.		65 lb./sq. in.	
Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %
0.75	77.4	3.75	97.1	0.75	71.0	1.5	67.9
0.75	77.2	5.25	98.0	1.5	73.2	3	68.6
1.5	85.8	5.25	98.0	2.25	76.7	4.5	68.0
1.5	85.8	8	99.1 (356°)	3	79.4	6	68.4
2.25	95.1	11.5	99.2 (370°)	5	95.7	13	68.9
2.25	94.3	12	99.1 (375°)	5	95.0		
3	96.3	15	99.2 (355°)	10	97.0		
3	97.4						

The values in this table are shown graphically in Fig. 4, Curves A, B and C showing values for pressures of 65, 115 and 215 lb., respectively.

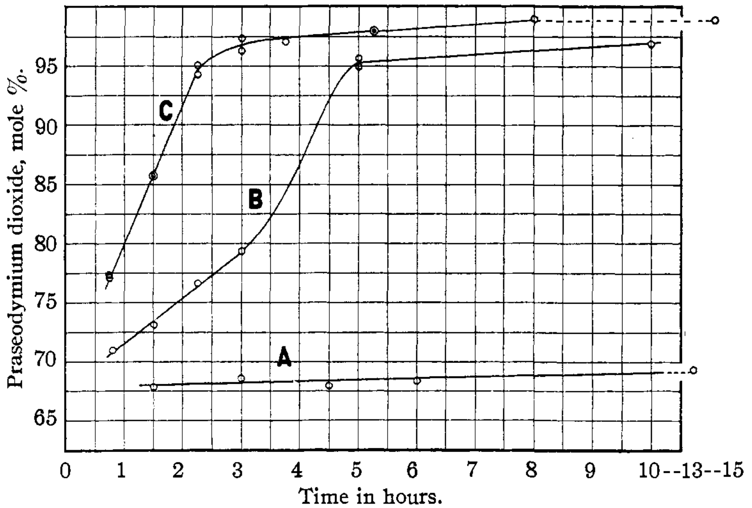

Fig. 4.—Effect of heating time on formation of praseodymium dioxide at pressures of A, 65 lb.; B, 115 lb.; and C, 215 lb. of O_2/sq. in.

It seemed impossible to increase the yield beyond 99.2% of PrO_2. (At figures near 100% the molecular percentage and the weight percentage are almost synonymous.) To be certain of the completeness of the hydrogen reductions upon which the calculations are based, four successive hydrogen reductions were made, and they showed splendid concordance. Then, after ignition in air, another hydrogen reduction of two hours' duration showed perfect agreement with the former values. It seems unreasonable, then, to question the completeness of the reduction. Nevertheless, if one wished to dispute this point, an argument could be made of the fact that the maximum oxidation shows as good concordance as the maximum reduction, and perhaps we have obtained pure dioxide, but never pure sesquioxide. This, however, is less likely.

In a final attempt to get a perfect yield, a larger sample of the sesquioxide (over 3.5 g.) was taken to minimize experimental errors and subjected to pressures up to 400 lb., with temperatures varying from 345 to 405°, approaching this range from the higher as well as from the lower side. Increased pressure showed more rapid oxidation, 99.2% being obtained in three and five-tenths hours at 365 lb. and 353°, and 98% in thirty-five minutes at 390 lb. and 400°, but the final result of continued heating could not be made to exceed 99.2% of praseodymium dioxide.

Effect of Ceria on the Formation of Higher Oxides of Praseodymium.—The catalytic effect of small amounts of ceria has been held responsible by some investigators for the contradictory results obtained in the study of the higher oxides of praseodymium.

A mixture of 98% praseodymium sesquioxide and 2% ceric oxide was prepared by precipitating as oxalate a nitrate solution containing 1.0637 g. of Pr_2O_3 and 0.0213 g. of CeO_2. Hydrogen reduction of the mixed oxides gave 1.0852 g. (calculated value, on the assumption that ceria is not reduced, 1.0850 g.). Ignition in air followed by rapid cooling in the tilted furnace yielded 64.0 mole % of PrO_2. This was the result of four runs, all of which agreed within 0.1 mg. The composition of the oxide obtained by ignition in air seems unaffected by the presence of small amounts of ceria.

This sample was next subjected to pressure oxidation. The results of these runs are shown in Table IV.

Table IV

Results of Pressure Oxidation

Hours of heating	1.5	1.5	0.75	2.25
Lb. O_2/sq. in.	65	115	115	115
Temp., °C.	376–380	376–380	381–386	381–386
Mol. % of PrO_2	83.7	96.1	92.2	95.3

Experiments under practically similar conditions with ceria-free praseodymia showed, in the order of the runs above given, 67.9, 73.2, 71.0 and 76.6%. Thus it is seen that ceria causes an abnormally high degree of oxidation when the oxidation is accomplished under pressure.

The Attempt to Prepare Higher Oxides of Other Rare-Earth Elements.—Pressure oxidation of the sesquioxides of lanthanum, neodymium, samarium, gadolinium, erbium and ytterbium was investigated. Since it is universally recognized that the oxides of these elements are of the type R_2O_3, and cannot be reduced by hydrogen at temperatures ordinarily employed, it was considered unnecessary to include hydrogen reductions in these runs.

The ignition, cooling and weighing of the sesquioxides were carried out in purified air, with all the precautions previously described, since some of these oxides gain weight very rapidly on exposure to ordinary air. The attempts to produce oxides of type higher than R_2O_3 failed with all these elements, so tabulation of the runs may be omitted. Suffice it to say that in no case, with samples varying from 0.5 to 1.4 g., were increases greater than 0.3–0.4 mg. found, that is, increases of 0.03–0.06%, with the exception of erbium, in which an increase of 0.1% was registered. Since, however, we could not be certain of the complete absence of terbium, which admittedly forms a higher oxide, from this sample, we could not accept this slight gain in weight as evidence of any tendency toward higher oxide formation. The effective temperature ranges were covered, and pressures up to 405 lb. of oxygen were employed.

The interest attaching to the element terbium in its higher oxides, and the difficulty in getting enough of this element in a high state of purity, cause us to withhold our data obtained on a small sample of not established purity. It is hoped that this investigation will be finished later.

Discussion

Equilibrium which gives an oxide corresponding approximately to the formula Pr_6O_{11} seems to be rather rapidly attained, so that cooling from higher temperatures to ranges below 400° in an ordinary electric furnace produces this oxide from one of lower oxygen content, provided a sufficient supply of oxygen be present. The results in Table I, calculated to the basis of "mole % of Pr_6O_{11}" give, in the order there used, 100.3, 100.0, 100.0, 99.4, 96.7, 96.1, 95.8, 95.1, 95.1, 91.4 and 83.5%. These figures, considered with the experimental conditions described in the table, show clearly that there is a dissociation of this oxide above 700° (and probably somewhat below this temperature), but that re-oxidation occurs in cooling to below 400°. Meyer, and Prandtl and Huttner, both state that Pr_6O_{11} is formed by heating at any temperatures between 500 and 900°, and assuming that the oxides were slowly cooled in the presence of plenty of air, this is just what our results would lead one to expect. But that a composition of higher oxygen constant than Pr_6O_{11} can be obtained, evidently in equilibrium, at temperatures around 390° we have shown by getting a constant composition of 68.1–68.3 mole % of PrO_2 when approaching from both sides, that is, from initial compositions of about 64 and 93%. A composition corresponding to 67.7 mole % of PrO_2 (which is 1% higher than theoretical for Pr_6O_{11}) seems to be in equilibrium at about 500°, since on successive heatings of twenty hours each at this temperature no change in composition was shown. It is probable, however, that in ordinary slow cooling insufficient time is allowed for the establishment of this equilibrium and therefore the composition corresponding to Pr_6O_{11} is found.

In the preparation of praseodymium dioxide by heating in oxygen we can offer no definite explanation of our failure to reach a purity higher than 99.2%. Curve C, of Fig. 4, shows that the complete oxidation of the last few per cent. of the oxide requires considerable time, and yet the results in Table III indicate that equilibrium had been reached at about 99.2%. It is unlikely that the dissociation pressure of this oxide exceeds 400 lb./sq. in. at the temperatures investigated. This would seem incompatible with our curve in Fig. 3, which shows that the pressure exceeds 215 lb. only when the temperature is raised above 405°. At 378° the longer the heating the higher the yield of PrO_2 at a pressure of 115 lb., while at 65 lb. pressure we get almost the same figure (around 68%) at 378° whether we heat for one hour or thirteen hours. This suggests almost complete dissociation of the dioxide at this temperature in pure oxygen at 65 lb. pressure, and Prandtl and Huttner found complete dissociation of the dioxide in inert gases, in oxygen and in air at atmospheric pressure at temperatures above 350°. Thus our results show clearly, as do also those of Prandtl and Huttner, that praseodymium oxide could not have been formed, as was claimed by Brauner and by Meyer, at 400° at atmospheric pressure.

The experiments with lanthanum, neodymium, gadolinium, erbium and ytterbium would surely have shown a tendency toward higher oxide formation if such tendency exists; failure to obtain positive results with these elements leads us to challenge the placing of any of these elements in a periodic group other than the third.

Summary

1. It has been shown that the composition of the oxide of praseodymium obtained by ignition in air varies with the conditions of ignition and cooling, but with a given set of conditions reasonably constant results are obtained.

2. Praseodymium dioxide of 99.2% purity has been prepared by heating lower oxides in pure oxygen at high pressures.

3. Data on the stability of praseodymium dioxide at different temperatures and pressures have been presented.

4. The effect of ceria in promoting higher oxide formation by praseodymium has been shown negligible at ordinary pressures, but quite marked in high concentrations of oxygen.

5. No higher oxides of lanthanum, neodymium, samarium, gadolinium, erbium and ytterbium could be formed.

6. A furnace generally applicable for the study of oxidation under

pressure and a balance and technique for the weighing of very hygroscopic substances have been described.

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A FURTHER TEST OF THE RADIATION HYPOTHESIS

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Introduction

Since its statement by Perrin[2] the Radiation Hypothesis has been subjected to many experimental tests, with results that have been uniformly opposed to it. Its present position has been summarized by Daniels.[3] This recent rapid decline of the Radiation Hypothesis has been accompanied by the production of an improved theory of activation by collision. Christiansen suggested that the number of internal degrees of freedom of the molecule must be taken into account, and this suggestion was adopted by Hinshelwood[4] and by Fowler and Rideal,[5] who worked out a simple theory of what the former has called "quasi-unimolecular" reactions, that is, reactions which are unimolecular at high enough pressures, but whose rate begins to fall off at lower pressures. Several such reactions are known, as well as some whose rates have not been shown to decrease.

The theory of Hinshelwood was extended by Rice and Ramsperger,[6] and a second theory developed which was in better agreement with the facts; this differed from the former one only in assigning different specific reaction rates to activated molecules of different energy content. A somewhat similar theory, in equally good agreement with experiment, was worked out by the author.[7] Both Rice[8] and the author[9] have since given quantum theories of the effect, also, but without changing much the numerical results obtained. The position of these theories with respect to the experimental facts is that they can account quantitatively for the way in which the rate falls off with decreasing pressure in the decompositions of propionaldehyde, ethyl ether, methyl ether and azo-

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[2] Perrin, *Ann. Physik,* **11,** 5 (1919).

[3] Daniels, *Chem. Rev.,* **5,** 39 (1928).

[4] Hinshelwood, *Proc. Roy. Soc.,* **113A,** 230 (1926).

[5] Fowler and Rideal, *ibid.,* **113A,** 570 (1926).

[6] Rice and Ramsperger, THIS JOURNAL, **49,** 1617 (1927); **50,** 617 (1928).

[7] Kassel, *J. Phys. Chem.,* **32,** 225 (1927).

[8] Rice, *Proc. Nat. Acad. Sci.,* **14,** 113, 118 (1928).

[9] Kassel, *J. Phys. Chem.,* **32,** 1065 (1928).