5. *Rare-earth Metal Oxides. Part I. The Direct Oxidation of Praseodymium and Terbium Sesquioxides.*

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Repetition of work by Prandtl and Rieder gave no evidence for the existence of quinquevalent praseodymium. Sesquioxides and dioxides form solid solutions, and dioxide formation by praseodymium and terbium is promoted by admixture with sesquioxides of metals with larger apparent ionic radii, provided C-type sesquioxide structure be maintained. Otherwise the shrinkage in lattice size on dioxide formation, by causing stronger mutual oxygen repulsion, inhibits quantitative dioxide formation. A-Type sesquioxides, being unable to form solid solutions with praseodymium dioxide, inhibit its formation. Praseodymium monoxide mixed with thoria may be prepared by high-temperature reduction.

ALTHOUGH several of the rare-earth metals have been reported to form oxides in which they show a valency higher than three, the evidence except in the cases of cerium, praseodymium and terbium is very unsatisfactory. These three have been commonly supposed to yield quadrivalent oxides, but even this has been called in question by Prandtl and his co-workers, in the case of praseodymium, and a valency of five postulated; the author cannot, however, confirm their experimental findings.

The dioxides of the rare earths where formed belong to the face-centred cubic (fluorite) type of crystal structure. Only cerium, however, has a definite ionic quadrivalency, and cerium dioxide is an almost colourless material. On the other hand, praseodymium and terbium, which form no quadrivalent ions in solution, give dark-coloured higher oxides. This may be attributed to a valency equilibrium or a partial ionic bonding. The rare-earth sesquioxides show only colours arising from the incomplete N-shell level characteristic of each of the elements. They mostly have a cubic crystal lattice of 32 metal atoms per unit cell built up on the pattern of the calcium atoms in 8 fluorite cells, each metal atom being surrounded by 6 oxygen atoms occupying approximately 6 of the 8 cube corner positions of the fluorine atoms in the fluorite cell. Highly distorted octahedra of oxygen are thus formed, which are of two types according to whether the vacant cube positions are on face or solid diagonals (Pauling and Schappell, *Z. Kryst.*, 1930, **75**, 128). This close resemblance in structure between dioxide and sesquioxide permits of solid solution between the two. The C-type sesquioxide lattice is in fact a subtraction lattice of fluorite type with slight modification. It is stable over an ionic radius ratio range $R_M/R_O = 0.53$—0.86. The upper limit is reached about Sm_2O_3 in the rare-earth series, and for larger ratios (0.86—0.92) found in La_2O_3 and other early members of the series a hexagonal layer A-type of lattice is formed. However, Lohberg (*Z. physikal. Chem.*, 1935, B, **28**, 402) finds that even La_2O_3 can give indications of C-type; and Nd_2O_3 and Pr_2O_3 (Bommer, *Z. anorg. Chem.*, 1939, **241**, 272) can give definite C-type oxides. Equilibria rather than sharp transitions between the forms appear to be general. Only oxides capable of forming A-type lattice appear to slake and give true hydroxides.

The oxygenation of terbium and praseodymium in presence of other rare-earth metal oxides, and with thorium dioxide, has now been investigated. Work on similar lines has been done by Prandtl and Rieder (*Z. anorg. Chem.*, 1938, **238**, 225). Their results, however, are at some variance with those now reported, the most serious discrepancy being their recording of experiments which they took to be evidence of quinquevalence for praseodymium. Repetition of part of the work which led to this conclusion failed to afford any evidence for a valency greater than four, although rather higher oxygenation had been found than they record when conditions give a value under four. The results for yttrium–praseodymium oxides heated at 350° under different pressures are compared in Table I.

TABLE I.

Ratios of O : Pr_2O_3 taken up by Pr_2O_3 in admixture with Y_2O_3.

	Gas and pressure (atm.).					
	Air, 1.		Oxygen, 1.		Oxygen, 3.	Oxygen, 15.
Ratio Y_2O_3/Pr_2O_3.	M.*	P. and R.	M.	P. and R.	M.	P. and R.
2	0.92	0.86	0.96	1.09	—	1.14
5	—	1.00	—	1.24	1.00	1.57
7	—	1.11	—	1.61	1.00	1.71
9 or 10	—	1.03	—	1.41	1.00	1.80

(A value 1.00 represents quantitative production of PrO_2.)

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Yttrium oxide after heating in hydrogen, for some reason not accounted for, was found by the author to be quite abnormally hygroscopic, and Prandtl and Rieder mention no adequate precautions against absorption of atmospheric moisture. They used the same sample of oxide repeatedly. Any exposure to air would result in an accumulation of water, for, from the work of Weiser and Milligan (*J. Physical Chem.*, 1938, **42**, 673), it is evident that a temperature of 550° is necessary to desiccate Y_2O_3. It will be seen that in dilute solution in yttrium oxide PrO_2 is formed quantitatively, but there is no evidence for a higher oxide.

All Prandtl and Rieder's results, except the above, can be interpreted with the aid of our knowledge of crystal structures. Praseodymium oxide obtained by ignition in air under a wide range of conditions is Pr_6O_{11}. In the presence of lanthanum oxide, Prandtl and Rieder found that with small amounts of lanthanum (up to

$3Pr_2O_3 + 2La_2O_3$) there is an increase in the degree of oxygenation of the praseodymium, but larger amounts of lanthanum cause a rapid fall. With neodymium the results were similar, but the fall was less. With samarium and gadolinium, the initial rise was again encountered but there was no subsequent fall, perhaps indeed a further small rise. These results may be interpreted as follows. The oxygenation of the praseodymium–lanthanum oxide mixture depended upon the maintenance of the C-type fluorite-type oxide. At first, on admixture of lanthanum, formation of $4PrO_2,Pr_2O_3$ (*i.e.*, Pr_6O_{11}) gave way to $4PrO_2,La_2O_3$, with consequent rise in total oxygenation and maintenance of a cubic lattice, but with larger quantities of lanthanum the hexagonal A-type lattice appeared which could only take up praseodymium in a tervalent state. Finally, with $9La_2O_3 + Pr_2O_3$ the A-type lattice predominated and dioxide formation practically ceased. Owing to the greater stability of C-Nd_2O_3 the effect was less marked in this case. With Sm_2O_3 and Gd_2O_3, there being no tendency to form A-oxide, no fall occurred. Results recorded later show that these oxides readily allow of quantitative $PrO_2\bullet$formation.

The influence of cerium on the formation of PrO_2 has occasioned diverse observations. Cerium compounds decompose at temperatures so much below those of other rare-earth salts that cerium dioxide probably forms comparatively large aggregates in oxide mixtures and complete solid solution is not brought about except with intense and prolonged ignition. For example, in Debray's nitrate fusion process for separating cerium, cerium dioxide can be precipitated with very little other rare earth in solid solution, because cerium dioxide will form at 250° by oxidation and decomposition of cerous nitrate, whereas other tervalent nitrates will not decompose much below 400° (see Part II, following paper).

A series of measurements of the gain in weight of mixtures of praseodymium and of terbium oxides with twice their equivalent quantities of other earths has been made, and is shown in Table II. This ratio was selected as being likely best to demonstrate the influence of the diluent earth on the quadrivalent earth, and to give close to maximum oxygenation in all cases.

TABLE II.

Degree of oxidation to dioxide of praseodymium and terbium in admixture with 2 atomic proportions of other elements, in air and in oxygen at 350° or 330°.

Metal, M.	Ionic radius, A.	Wt. of mixed reduced oxides. $Pr_2O_3 + 4ThO_2$, g.	Increase for $Pr_2O_3 \longrightarrow PrO_2$. Calc., mg.	Found in 1 atm. of air, mg.	air, %.	oxygen, mg.	oxygen, %.	Wt. of mixed reduced oxides. $Tb_2O_3 + 4ThO_2$, g.	Increase for $Tb_2O_3 \longrightarrow TbO_4$. Calc., mg.	Found in 1 atm. of air, mg.	air, %.	oxygen, mg.	oxygen, %.
Th	1·10	1·3435	15·5	—	—	15·4	100	1·0866	12·2	—	—	8·7	71
		$Pr_2O_3 + 2M_2O_3$.						$Tb_2O_3 + 2M_2O_3$.					
La	1·22	0·9286	15·2	9·2	60	9·9	65	—	—	—	—	—	—
Pr^IV	1·00	—	—	—	—	—	—						
Pr^III	1·16	—	—	—	67 *	—	78 †						
Nd	1·15	0·9441	15·4	14·3	93	15·2	99	0·8295	12·8	11·4	89	12·0	94
Sm	1·13	1·0020	15·2	15·3	100	15·3	100	—	—	—	—	—	—
Gd	1·11	0·9443	14·4	14·2	99	14·4	100	0·8625	12·8	11·1	87	11·2	88
Tb^IV	0·89	—	—	—	—	—	—	—	—	—	—	—	—
Tb^III	1·09	—	—	—	—	—	—	—	—	50 *	—	67 †
Y	1·06	0·8009	15·6	14·3	92	14·9	96	0·6475	12·7	9·6	73 23 †	10·6	84 77 †
Yb	1·00	1·0813	15·5	11·9	77	13·3	86	0·8411	12·0	6·7	56	8·0	67

* Established products.   † Prandtl and Rieder's findings.

It is found in both instances that with increase in apparent ionic radius of the admixed element there is an increase in dioxide formation provided C-type structure be maintained. The influence of A-oxide gives poor oxygenation of praseodymium admixed with lanthanum. Some A-influence is also found with neodymium. Samarium, gadolinium and thorium allow full oxygenation of praseodymium. In the case of terbium the quadrivalent tendency is less strong than with praseodymium. The slight tendency of neodymium to form A-oxide will be lessened in presence of terbium, but increased in that of praseodymium as the latter is itself A-forming. Thus neodymium oxide is the most favourable medium for the peroxidation of terbium, but not for praseodymium. Thorium and gadolinium have very similar ionic radii but thorium is a less favourable peroxidising medium than the latter. This is attributable to the lower resistance offered to the introduction of further oxygen by the less oxygen-saturated lattice of the gadolinium oxide. The lattice size is normally the resultant of the electrostatic attraction of opposite charges and the repulsions of like charges. In non-stocheiometric oxides these forces must be in unstable equilibrium. This arises through a valency equilibrium readily displaceable towards ionic or co-ordinate. In general, positive ions decrease in size on passing to higher valency states. This is seen in the case of the terbium oxides. The sesquioxide unit cube has $\alpha = 10\cdot70$, but Tb_4O_7 has $\alpha = 5\cdot20$ or $10\cdot40$ A. Thus, exercise of a higher ionic valency by terbium is countered by repulsive forces between oxygen atoms, and in air, oxidation above Tb_4O_7 does not occur, and oxygen gas pressure has a large effect on the state of equilibrium. It follows also that if the lattice size can be prevented from contracting on peroxidation, oxygenation will become greater. This is what has in fact been found experimentally. The promotion of higher oxide formation is facilitated in lattices of large size and not, as might at first sight appear probable, by lattices of dimensions to fit most correctly the quadrivalent ion. The

electron field of the metal holds 8 oxygen atoms better at a distance than close to. The bonds have become more covalent in character.

An interesting observation was made when heating thorium and praseodymium oxides. On reduction in hydrogen the black oxide formed a yellow-green powder, which on reoxidation gave the theoretical increase in weight for the change $Pr_2O_3 \longrightarrow 2PrO_2$. Strong ignition in hydrogen, however, caused the green powder to lose further weight and again become black. The increase in weight on reoxidation was then found to be double the previous, and it appears that PrO was formed at the high temperature. Similar experiments with thorium–terbium and thorium–neodymium oxides failed to give evidence of TbO or NdO. The author has shown (*J.*, 1942, 398) that praseodymium possesses an appreciable degree of bivalency. It appears probable that the cubic form of PrO_2 was retained on reduction in solid solution with ThO_2, and was thus capable of undergoing further reduction not possible with pure hexagonal Pr_2O_3. The oxides PrO_2, ThO_2, and BaO all have cubic oxides of similar lattice size.

EXPERIMENTAL.

Rare-earth mixtures were prepared by precipitating oxalates from the requisite quantities of mixed nitrate solutions and igniting them. This did not prove satisfactory with thorium mixtures, however, and for these, hydroxide precipitation was used. Each oxide mixture was then ignited at a bright red heat in a porcelain boat in a silica tube for $\frac{1}{2}$—1 hour, then transferred to a Pyrex tube and heated in a stream of dry hydrogen at 600—700° behind another boat filled with cerium dioxide. The cerium dioxide was partly reduced in the back half of the boat, but traces of oxygen kept the front half from reducing. The traces of water vapour resulting, however, did not appear to cause weighable errors in the oxides. The praseodymium or terbium dioxides in the mixtures underwent reduction. The boat when cool was placed in a small weighing tube with minimum exposure to air. Subsequently it was heated in another tube in air or oxygen for $1\frac{1}{2}$—2 hours at 350° for praseodymium mixtures, and 330—340° for terbium mixtures. The air was passed over soda–lime, sulphuric acid, and phosphoric oxide before use. The increase in weight was then determined.

Yttrium oxide was found to be very hygroscopic, and a blank experiment at 3 atm. pressure of oxygen gave an increase of 0·4 mg. on 1·4 g. of oxide. The rate of increase of the same sample in its boat on exposure to air in the balance case was 6 mg. in the first 5 minutes. In the five experiments with Pr–Y mixtures conducted at 3 atm. of oxygen pressure, 6·83 g. of oxides, calculated to gain 52·3 mg. by the transformation $Pr_2O_3 \longrightarrow 2PrO_2$, gave an increase of 53·8 mg., or after application of the blank correction 51·8 mg., showing as close a correspondence to theory as could be expected. The pressure was obtained by blowing off cylinder oxygen under a head of mercury. Other oxides except that of neodymium are hygroscopic, and blank corrections were not necessary. All the results obtained, once the technique had been proved satisfactory, are recorded in Table II, with the exception of one giving a value of 105% for praseodymium dioxide in neodymium oxide in oxygen. The high value was undoubtedly due to the hygroscopic nature of the neodymium oxide and insufficiently short atmospheric exposure during transfers. A third experiment exactly confirmed the recorded result.

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