TABLE IV

EFFECT OF VISCOSITY ON DIFFUSION CURRENT CONSTANTS

$K_2C_3H_2O_4$, M	Relative viscosity (η)	$\eta^{1/2}$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$ (I)	$I \times \eta^{1/2}$
3.0	2.53	1.59	0.80	1.27
2.0	1.98	1.40	1.03	1.45
1.5	1.64	1.28	1.14	1.47
1.0	1.35	1.16	1.25	1.45
0.70	1.25	1.12	1.36	1.52
.40	1.10	1.05	1.42	1.49
.10[a]	1.04	1.02	1.44	1.47
.05[a]	1.04	1.02	1.44	1.47

[a] Ionic strength adjusted to 0.5 with $NaClO_4$.

In the present case, for example, the diffusion current is more than 15% lower in 1 M potassium malonate solutions than in 0.1 M solutions.

Succinate Solutions.—Previous experimenters[14,17,20] agree that any complexes formed between iron and succinate ions are much weaker than those involving oxalate or malonate ions. Franke[17] reports the dissociation constant of the disuccinatoferrate(II) ion to be approximately 13 on the basis of solubility studies. Hydroxosuccinato complexes have been claimed to exist on the basis of preparative studies[11,21] and also on the basis of breaks in potentiometric titration curves.[13]

Polarographic studies were attempted with solutions ranging from pH 5.5 to 9.5 and from 0.1 to 4.0 M potassium succinate. Of the more than thirty solutions studied, the reversibility test could be applied to less than half the resulting polarograms. At the higher pH values all or most of the iron(III) precipitated from solution, either preventing the appearance of a wave or causing the wave to be too small for analysis. At lower pH values, where no precipitation occurred, many of the waves followed so closely after the anodic mercury dissolution wave that residual current corrections could not be made accurately. In the cases where the reversibility test was applied, the slopes of the plots of $E_{d.e.}$ *vs.* log $(i_d - i)/i$ showed considerable variation, ranging from 0.05 to 0.085. Double waves, indicating the presence of two complexes in sluggish equilibrium, were observed in a few cases. Because of the failure to establish with certainty the reversibility of the reductions occurring in succinate solutions, detailed presentation and interpretation of the data are not warranted at this time. However, the data obtained, such as they are, indicate the dissociation constant for the iron(III) complex to be on the order of 10^{-9}, and that of the iron(II) complex to be about unity. This latter value is of a similar order of magnitude as that reported by Franke.

It is apparent that the succinato (7-ring) complexes are considerably weaker than the malonato (6-ring) and oxalato (5-ring) complexes. Furthermore, succinic acid is a rather weak acid, so that in acidic solutions below pH 4 virtually no $C_4H_4O_4^{--}$ ions are present in solution. At higher pH values at which the $C_4H_4O_4^{--}$ concentration becomes appreciable, the large and weakly bound succinate groups tend to be replaced by OH^- ions causing partial or complete hydrolysis of the iron(III). This situation explains why several workers[14,20] have reported no noticeable complex formation occurring between iron and succinate ions.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Higher Oxides of Terbium and Praseodymium from High Pressure Molecular Oxygen Treatment

BY WILBUR SIMON[1] AND LEROY EYRING

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Terbium and praseodymium oxides have been treated with molecular oxygen of pressures up to 282 atmospheres at temperatures as high as 450°. The compositions of the higher oxides thus produced were determined by weight changes on reduction to the sesquioxides with H_2 and CO, and by iodometric titration. X-Ray diffraction patterns were observed for some of the phases produced. It was found that when the reaction vessel was desiccated carefully all the methods of analyses were in agreement. Treatment of the lower oxides of terbium and praseodymium at 282 atmospheres oxygen pressure at 400° yielded $TbO_{1.86}$ and $PrO_{2.00}$, respectively.

Introduction

The higher oxides of terbium and praseodymium are interesting examples of non-stoichiometric compounds. An investigation of these oxide systems in equilibrium with oxygen up to one atmosphere pressure has been completed,[2-4] and an equilibrium study of the region up to 10 atmospheres is underway. Below one atmosphere of oxygen pressure the oxides have compositions in the range $TbO_{1.50}$ to $TbO_{1.81}$ and $PrO_{1.50}$ to $PrO_{1.83}$.

Higher oxides of terbium have been known for a long time, but only a few investigations have been made on their exact compositions. Prandtl and Rieder[5] found that air oxidized samples had an average composition of about $TbO_{1.76}$, and samples treated with 30 atmospheres of oxygen at 340° had the composition $TbO_{1.83}$. TbO_2 has been re-

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ported[6] on the basis of the lattice constant of an atomic oxygen treated sample.

Many investigations[7-13] have been made of the PrO_x system using a variety of methods. In the broadest sense there now seems to be agreement that the upper limit of oxygen composition for the PrO_x system is PrO_2, and that under analogous treatment terbium is less highly oxidized.

This research was undertaken to establish the upper limits of compositions of the higher terbium and praseodymium oxides at oxygen pressures greater than had been previously used, and to develop a method of producing larger quantities of the higher oxides.

Experimental Method

The general procedure was to reduce samples of praseodymium or terbium oxides to Pr_2O_3 or Tb_2O_3 with hydrogen. It was assumed that the sesquioxides were the final products when constant weight was achieved. X-Ray examination and previous work justified this assumption. The reduced samples of Pr_2O_3 or Tb_2O_3 were subjected to a variety of pressures of oxygen at different temperatures and their compositions determined by various methods.

Weight increase determinations established the composition of the oxide after oxidation. Other methods of analyses confirmed the validity of this procedure.

The Reduction Systems.—Reduction of the higher oxides was regularly achieved by flowing purified hydrogen, at atmospheric pressure, over the sample which was heated at 600° for a period of 1.5 to six hours. Commercial hydrogen was purified by successively passing the gas through a catalytic deoxidizer, a column of concentrated sulfuric acid and a U-tube packed with Ascarite and Drierite or preferably a U-tube cooled with liquid nitrogen.

Alternatively the oxides were reduced with carbon monoxide which had been purified by passage through sodium hydroxide, pyrogallol, concentrated sulfuric acid, and finally Ascarite and Drierite. The carbon monoxide was passed over the hot oxide and the excess CO together with the reaction products were passed over magnesium perchlorate and into a Pregl absorption tube which absorbed the CO_2. The Pregl tube was weighed[14] to determine the oxygen removal from the sample.

In reduction with CO care must be exercised to prevent the formation of carbonates. This method if properly developed should provide a convenient procedure for reduction and analysis.

The Oxidation Apparatus.—Two 50-ml. autoclaves were constructed of "316 stainless steel" and "Inconel X" by the Parr Instrument Co. The head of each was equipped with a needle valve and a safety rupture disk, and was fitted with a replaceable calibrated bourdon gage with a range suitable to the pressures of interest in the particular experiment. A thermocouple recess at the bottom of the reactor makes possible the control of the wire wound tube furnace in which the autoclave is placed during the reaction. Furnace control was achieved either by voltage regulation or by a modulated pulse time control mechanism built by Minneapolis Honeywell Co. Bombs of these materials held up very well over long reaction periods. Thin dark oxide films on the inner surfaces appeared to retard further oxidation.

A quartz or Pyrex container was constructed to hold a barium oxide desiccant in the top (cooler part) and the sample crucible in the bottom of the autoclave. The sample crucible was constructed of alundum with which the rare earth oxide is completely unreactive.

Materials.—The PrO_x was obtained 99.9% pure from E. C. Botti. The TbO_x was obtained from Johnson, Matthey and Company, Limited, of London as greater than 98% pure.

Analytical Procedures.—The sesquioxides were assumed to be the products obtained when any higher oxides were reduced to constant weight with hydrogen. X-Ray diffraction patterns agreed with those in the literature for Pr_2O_3 and Tb_2O_3.

The compositions of the higher oxides were determined by weight increase measurements and by iodometric titration of active oxygen.[15] As suggested before, CO reduction of the higher oxides could also be used; however, this method was not fully developed in this study.

Results and Conclusions

Reproducible results were obtained when great care was exercised in the desiccation of the autoclave. Without careful desiccation, the products were generally light tan in color and showed irregular but high weight gains. Analysis of these showed the presence of water and a low content of active oxygen. Perhaps these relatively large weight changes when small amounts of water are present have been responsible for some reports of oxides higher than PrO_2.[5]

It was established that when sufficient precautions were taken weight increase determinations agreed with iodometric measurements of active oxygen. The results of these experiments are shown in Table I. Samples of $PrO_{1.50}$ weighing 150–300 mg. and samples of $TbO_{1.50}$ weighing 130–150 mg. were used in all experiments reported in this study.

TABLE I

COMPARISON OF ANALYTICAL PROCEDURES DETERMINATION OF ACTIVE OXYGEN IN PRASEODYMIUM OXIDES

Oxidation time, hr.	Pressure, atm.	Temp., °C.	% wt. gain Wt. uptake	% wt. gain Iodometric titration
12.5	201	400	4.11	4.11
17	293	400	4.11	4.11
16.5	286	400	4.10	4.09
12	282	400	4.85	4.85

The first three experiments were made on a sample of unknown purity which obviously had some unoxidizable impurity, probably other rare earths. The maximum oxygen uptake of this sample seems to have been 4.11% over Pr_2O_3. The standard deviation of analyses of these three runs is ±0.008. The limit of error in the 95% confidence belt is 0.02%. The last experiment was made on the pure Botti sample and corresponds to the calculated uptake of oxygen to form PrO_2. This phase was examined by X-ray diffraction and was found to have the fluorite structure with $a = 5.395 \pm 0.001$ Å. in excellent agreement with the results of McCullough.[11]

The results of runs in which oxides were treated for periods of six hours or more (sometimes as long as several days) are shown in Fig. 1. These results are not to be considered as equilibrium data since the autoclave is cooled slowly to room temperature and oxygen is undoubtedly absorbed in this process. The pressures and temperatures indicated are those of the long soak period and the composi-

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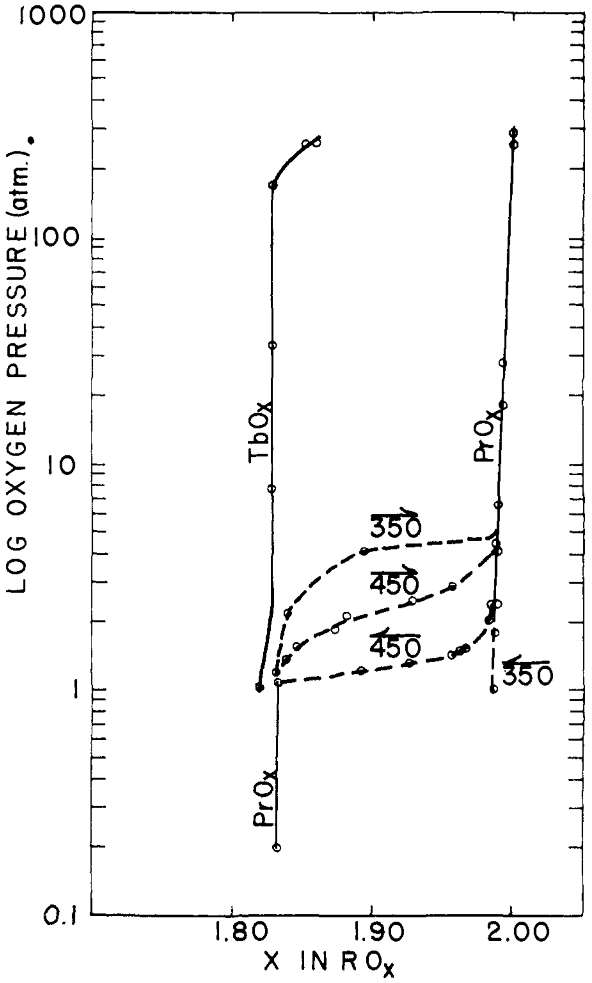

Fig. 1.—Pressure–composition diagram: oxygen–TbO_x, PrO_x systems.

tions are those corresponding to the final cold product determined by weight increase determinations.

It will be observed that samples of composition PrO_2 are obtained only at very high pressures, but that samples treated at 350° and five atmospheres are oxidized almost all the way to PrO_2.

At pressures below five atmospheres and 450° the lack of reproducibility of the points on oxidation and reduction implies that the samples are not really at equilibrium during the soak period at these temperatures.

Terbium oxidizes to a lesser degree than praseodymium at moderate to high oxygen pressures. For example, at 282 atmospheres and 400° the two oxides obtained are $TbO_{1.86}$ and $PrO_{2.00}$. One run with terbium designed to take advantage of any slow uptake of oxygen at lower temperatures was cooled from 400° to room temperature over a period of five days. The final composition was $TbO_{1.86}$.

Some experiments not shown in Fig. 1 are tabulated in Table II. It might be noted that the precise composition of $TbO_{1.75}$, which has long been reported as the brown product obtained when terbium oxides are ignited in air and cooled to room temperature, is not easily realized.

TABLE II

EXPERIMENTS ON TERBIUM OXIDE

Treatment, hr.	Temp., °C.	Pressure, atm.	Compn. (x in TbO_x)	Remarks
12	400	1	1.82	Removed to desiccator while still hot
24	300	1	1.83	Cooled rapidly
14	600	1	1.81	Cooled very rapidly
4	700	1	1.75	N_2 admitted while hot then cooled very rapidly
6	600	0.2	1.80	Cooled slowly
5	900	0.2	1.73	Cooled slowly to 150°, desiccated
5	900	0.2	1.73	Cooled slowly to 200°, desiccated
120	400–25	252–160	1.86	Cooled slowly over 5 days

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

The Iron(II) Chloride–Iron(II) Bromide System[1]

BY RICHARD O. MACLAREN AND N. W. GREGORY

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The arrangement of layers of halogen atoms in mixtures of $FeCl_2$(CCP) and $FeBr_2$(HCP) annealed to 400° has been studied by X-ray powder pattern analysis. Coexistence of CCP and HCP phases with the same composition is observed between 40 and 80 mole per cent. chloride. Solid solutions prepared by mixing the pure components and by halogen exchange reaction of the solid phases with HCl and HBr were found to have the same structural characteristics and to be nearly ideal.

Crystals of $FeCl_2$ and $FeBr_2$ have layer structures with the halogen atoms cubic close packed (CCP) in $FeCl_2$ ($CdCl_2$ type, $R\bar{3}m$) and hexagonal close packed (HCP) in $FeBr_2$ ($Cd(OH)_2$ type, $C\bar{3}m$).[2] These structures are also characteristic of $CdBr_2$ and CdI_2. An intermediate phase in the $CdBr_2$–CdI_2 system, with bulk composition near CdIBr, has been reported by Hägg and Linden[3] to have a unique packing with a layer repeat unit ABCBCABABCAC-. We have made a study of intermediate phases in the $FeCl_2$–$FeBr_2$ system. The halogen exchange equilibrium between the solid iron halide phases and HCl and HBr has been investigated at 400°. An X-ray powder pattern study of solid solutions formed in this way and of those obtained by heating various mixtures of the two simple

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(1) Presented at the Northwest Regional Meeting of the American Chemical Society at Richland, Washington, June 11, 1954.

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