Zinc chloride also was prepared from the elements. Since $ZnCl_2$ cannot be separated from metal by sublimation, the salt was heated extensively with excess chlorine. It was then sublimed at 500°, and melted into fragile containers containing 3 to 5 g. each. The resulting salt evolved no hydrogen when contacted with metal; considerable amounts of this gas, presumably from dissolved water and HCl, were obtained when commercial $ZnCl_2$ was used after one vacuum sublimation.

Zinc iodide was prepared in a V-shaped Vycor tube from metal and excess, vacuum-sublimed iodine, heating the metal to 700° and the iodine to 200°. The product was transferred in air, triply sublimed after removal of the I_2, and similarly stored in 2 to 3-g. batches.

Owing to thermal decomposition, CdI_2 cannot be vacuum sublimed without appreciable contamination of the product with free metal. Hence it was prepared directly from the elements in a sealed tube and the excess I_2 and traces of HI condensed in a side arm at $-190°$ and sealed off. The salt was then sublimed at 450° in the closed tube. For equilibration a 10 to 15-g. sample was weighed in air and then melted *in vacuo* (without decomposition) before the metal was introduced under helium.

For the Ga–$GaBr_2$ system, $GaBr_3$ was prepared from the metal and excess, P_2O_5-dried bromine, sublimed and sealed in ampoules. The $GaBr_2$ was then formed as the initial product during the equilibration with a weighed excess of metal.

Transport Studies.—Observations on the stabilities of gaseous subhalides were carried out in the manner already described for tin and lead.[10] Transport of antimony was obtained when SbI_3 was distilled at $<10^{-2}$ mm. over metal heated as low as 300°. Metal alone would not sublime at this temperature, as expected from a calculated vapor pressure of *ca.* 10^{-10} atm.[26] Similarly, $BiCl_3$ caused transport of Bi, and GaX_2 of Ga at 400°. Studies of this type with lead are, however, limited by the vapor pressure of the metal to temperatures below about 575°.[10] With PbI_2, where the natural color of the solid salt prevents visual detection of metal at less than about 0.1 mole %, transport of lesser amounts either directly or *via* a subhalide does occur below 500°, as detected by direct solubility measurements with salt sublimed from a metal-saturated sample.

Magnetic Susceptibility Observations.—A qualitative Gouy method was used to establish the diamagnetism of metal-containing melts of SbI_3, $ZnCl_2$, GaX_2 and $BiCl_3$. The salts, containing less metal than necessary for saturation at the temperature used, were sealed in small fused silica tubes equipped with evacuated jackets to lessen the rate of cooling. These were lowered from the furnace to between the pole pieces of a magnet with an inhomogeneous field of maximum intensity of about 12000 gauss. A deflection out of the field, indistinguishable from the pure molten salt, was always observed when the magnet was turned on. Experiments with dilute aqueous solutions of paramagnetic salts indicated that the method should be quite capable of detecting paramagnetism in the systems studied if such species had been formed in the expected amounts.

(26) Ref. 17, p. 31.

AMES, IOWA

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

Praseodymium Oxides. IV. A Study of the Region $PrO_{1.83}$–$PrO_{2.00}$[1]

BY C. L. SIEGLAFF AND L. EYRING

RECEIVED JANUARY 19, 1957

This is a study of the phase relationships of the higher praseodymium oxides. X-Ray powder diagrams of quenched, analyzed samples were taken to determine the phases present. A two-phase system was found for the region $PrO_{1.83}$–$PrO_{2.00}$ at preparation temperatures below 350° and oxygen pressures less than ten atmospheres. Lattice constants are given for the various phases found.

Introduction

Several investigations of the praseodymium oxides beyond Pr_2O_3 have been reported recently.[2–8] The oxide system below Pr_6O_{11} has been extensively studied, but in the region Pr_6O_{11} to PrO_2 there is apparent disagreement as to the phases present. Through the use of X-ray diffraction techniques on samples prepared under equilibrium conditions a study of this region has been carried out.

Experimental Methods

Materials.—The Pr_6O_{11} used in these experiments was obtained from Professor F. H. Spedding, Iowa State College, Ames, Iowa, as 99.9+% pure Pr_6O_{11} with no other rare earth cations present in detectable amounts. The oxygen used in the preparation of quenched samples was commercial tank oxygen.

Apparatus for the Preparation of Quenched Samples.—The constant volume apparatus used in preparing the samples below ten atm. oxygen pressure was similar in principle to the one described previously.[3] Since the measurements were made at relatively high pressures, the system was constructed of metal instead of glass. The reaction vessel was an "Inconel X" cylinder bored and fitted with a flanged platinum liner. The brass valves used in the system were designed to have a very small internal free space and were constructed in a manner such that the volume was reproducible in either the open or closed positions.

The pressure was measured by a Wallace and Tiernan, Model No. FA 145, 0-5080 mm. dial manometer. In order to maintain constant volume conditions the manometer had to be isolated from the sorption system, since the manometer worked on an expanding capsule principle. The isolation of the manometer was accomplished by means of a sensitive, specially designed small volume differential pressure gage operating as a null instrument.

The maximum uncertainty in the composition, as measured by the pressure change, is estimated at 0.4%. Weighing of the samples before and after the oxidation-quenching procedure gave a check of the method since there was no appreciable change in oxygen content when the samples were quenched.

Samples prepared at high temperatures and high oxygen pressures were treated in an "Inconel X" autoclave. The procedure and a similar apparatus have been previously described.[3]

X-Ray diagrams were taken in a 114.6 mm. diameter camera using exposure times of about 12 hours.

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(1) Taken from a thesis by C. L. Sieglaff for the Ph.D. Degree. State University of Iowa, Iowa City, Iowa. Support for this work was given by the Atomic Energy Commission.

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(7) R. E. Ferguson, E. Daniel Guth and LeRoy Eyring, THIS JOURNAL, **76**, 3890 (1954).

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TABLE I

PRASEODYMIUM OXIDES ($PrO_{1.833}$–$PrO_{2.000}$)

Composition (O/Pr)	Temp. (°C.)	Oxygen pressure (atm.)	Lattice constant		Quenching time (min.)
			Major phase	Minor phase	
1.996	350	5.41	5.3932 ± 0.0009		30
1.909	350	4.25	5.3919 ± .0008	5.4694 ± 0.0007	30
1.847	350	3.29	5.465 ± .004		30
1.919	350	3.02	5.3918 ± .0001	5.471 ± 0.001	30
1.833	450	0.2	5.467 ± .002		Cooled slowly
1.895	470	27	$PrO_{2.00}$	$PrO_{1.83}$	10
1.855	550	34	$PrO_{1.83}$	$PrO_{2.00}$	10
1.933	600	109.00	5.399 ± 0.002		10
1.868	720	72	5.468 ± .005		10
2.01	720	92	5.392 ± .001	5.469 ± 0.002	Cooled slowly, pressure
1.833	760	112	$PrO_{1.83}$		10
1.839	760	224	5.467 ± 0.001		5
1.956	760	140	$PrO_{1.83}$	$PrO_{2.00}$	Quenched, pressure
1.997	450	231	5.3938 ± 0.0003		Cooled slowly, pressure

Results and Discussion

Table I shows the results of the X-ray analysis on quenched samples. All cell dimensions are reported in Å. units based on the wave lengths Cu K_1 1.5405 Å. and Cu K_2 1.5443 Å. The values for the cell dimensions reported in Table I are calculated by an analytical extrapolation of the back reflection data.[9]

Oxidation of a Pr_6O_{11} sample at 350° and an oxygen pressure of 4.25 atm. results in two crystalline oxide phases with lattice constants of 5.3919 ± 0.0008 Å. and 5.4694 ± 0.0007 Å. The phases are Pr_6O_{11} and PrO_2. A sample which was prepared by oxidation to PrO_2, and then reduced to a composition intermediate to Pr_6O_{11} and PrO_2, showed two phases, Pr_6O_{11} and PrO_2 with lattice constants of 5.3918 ± 0.0001 Å. and 5.471 ± 0.001 Å. One experiment, listed third in the table, gave only one phase, Pr_6O_{11}. This sample was only 12% oxidized which would give at best a very weak minor phase. Since the praseodymium oxides are highly absorbant it is not surprising that a minor phase did not appear.

Oxidation of Pr_6O_{11} with pressures up to 331 atm. and temperatures up to 760° yielded PrO_2 and/or $PrO_{1.83}$. No evidence of an intermediate phase was found. These high temperature-high pressure samples were prepared with questionable quenching techniques, since no check could be made of the sample composition before and after quenching. It is possible that an intermediate phase was present and changed into two phases during quenching.

A high temperature camera capable of keeping the sample under 300 atm. oxygen pressure near 1000° is needed to be certain that no phase changes occur when the sample is quenched. All that can be said is that at pressures less than ten atmospheres there was no appreciable composition change upon quenching.

From their studies, Gruen, *et al.*,[4] and Martin[5] concluded that a single phase inhabited the region $PrO_{1.83}$–$PrO_{2.00}$, whereas McCullough[2] observed a miscibility gap in this range. Also the extensive studies of mixed rare earth oxides by McCullough[10] and others,[11,12] indicated complete solid solution in this range.

It should be pointed out that in the study of the praseodymium system reported by Ferguson, *et al.*,[7] there were at least three regions of continuous non-stoichiometric composition which tended toward separation into two phases. Although these diphasic regions were not observed from X-ray studies, they were inferred from the nature of the $(P, X)_T$ isotherms. As the oxygen content increased, the apparent critical transition temperature decreased. Also, the dissociation pressure at the critical temperature increased. An extrapolation of this trend to the region above $PrO_{1.83}$ indicates a critical temperature of less than 585° and a dissociation pressure above one atmosphere should be expected.

Gruen, *et al.*,[4] using atomic oxygen to treat the praseodymium oxides, reported a reaction temperature of 450°. Similar experiments carried out in the present study showed that the surface of the oxide sample was heated to incandescence by the recombination of oxygen and reaction at the surface. Therefore, the temperature reported by Gruen, *et al.*, might have been that of the bulk of the material, not the surface temperature. It is then probable that the true reaction temperature was considerably higher than 450°.

The one mixed oxide study carried out at low temperatures was the Nd–Pr system studied by McCullough.[2] It was reported that at 300° one phase inhabited the region $RO_{1.83}$–$RO_{2.00}$. It is possible that the substitution of Nd^{+3} for Pr^{+3} lowers the critical temperature.

The existence of a solubility loop between similar phases is not unique. Grønvold and others[13-15] have shown that the uranium oxide system in the region UO_2–U_4O_9 is monophasic at low temperatures (equilibrium here is questioned) changing to a diphasic region as the temperature is raised to 250°. At approximately 350° the system again be-

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comes monophasic.[15] The phases present in this region are anion excess fluorite structures with lattice constants of 5.4704 and 5.4411 Å. for UO_2 and U_4O_9, respectively.[15]

It is apparent, then, that there is a solubility loop in the fluorite region between $PrO_{1.83}$ and $PrO_{2.00}$ below a temperature of at least 350° with a probable transition to a homogeneous system at elevated temperatures. This observation based on the present study apparently explains much of the work of others previously thought to be contradictory. It also appears to be a reasonable extension of the known facts of the PrO_x system, as determined by equilibrium dissociation pressure measurements, and is not at variance with observations on related oxide systems including many of the mixed oxides.

It is not possible from the present study to fix the transition temperature exactly, but it must be above 350°. From the extension of the lower oxide studies and the Nd–Pr system an upper limit of approximately 585° would be expected.

Reasonably complete studies of the oxide systems of cerium and praseodymium and preliminary studies on the oxides of terbium[7,8,16,17] have now been reported. It is of interest to compare the phase relationships' of these lanthanide oxides. Each oxide system changes from a body-centered cubic to a rhombohedral to a face-centered cubic phase as the oxygen content is increased. Similar stable compositions exist in each system, with the major difference being the lack of an intermediate face-centered cubic phase in the cerium system. A given region of any of these systems can be either diphasic or monophasic depending upon the temperature and pressure of the preparation.

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IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Species of Molybdenum(VI) in Hydrochloric Acid[1]

BY H. M. NEUMANN[2] AND NANCY C. COOK

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Ultraviolet spectrophotometry has been applied in a study of the species of Mo(VI) present in hydrochloric acid solutions. Compounds of Mo(VI) containing molybdenum and chlorine in the ratios 1:2, 1:3 and 1:4 have been prepared and their spectra determined in ether solutions. Although all three types display a maximum at 226 mμ, each has a second maximum at longer wave lengths that is characteristic of the particular Mo:Cl ratio. These results have been applied to the analysis of the spectra of solutions of Mo(VI) in hydrochloric acid. The species containing two chlorines is the most important in these solutions, its maximum amount occurring in 6 *M* HCl. At greater acidities a species containing three chlorines becomes important. There is no evidence for species containing a larger number of chlorines. The species containing two chlorines is apparently the one extracted by ethers and bound by anion-exchange resins.

Although molybdenum is most commonly encountered as molybdenum(VI), the aqueous chemistry of this oxidation state is, to a large extent, unknown. The greatest difficulties in working out the details of molybdenum(VI) chemistry arise from the fact that in acidic solution polymerization occurs to form polymolybdates. By using an acid whose anion could become involved in complex formation, one is more likely to find the molybdenum(VI) present in monomeric form, and hence have some chance of identifying the species actually present. The work reported here is based upon the use of hydrochloric acid as the medium and ultraviolet absorption spectrophotometry as the means of studying the composition of the various solutions. This seemed a promising method since any chloro complexes would be expected to have absorption maxima in the ultraviolet region. In addition, several compounds of Mo(VI), containing various numbers of chlorine atoms, have been reported in the literature, and it seemed likely that a comparison of their spectra with those of solutions of Mo(VI) in hydrochloric acid would give information about the species of Mo(VI) present in the acid solutions.

The ultraviolet spectra of the compounds themselves are of interest, since at the present time there is little apparent correlation between the spectra and structure of halo complexes. In part, this is due to insufficient data, so that any additional data from known compounds, as is possible in the molybdenum(VI) case, may ultimately lead to some correlations.

Experimental

Analytical Methods.—Determinations for molybdenum in macro concentration were performed by the method described by Kolthoff and Sandell.[3] The chloride determinations employed the method suggested by Michael and Murphy[4] for chloride in the presence of molybdenum. The determination of the total molybdenum(VI) in ether solutions when the molybdenum concentration was of the order of 10^{-4} *M* was accomplished by completely transferring all the Mo(VI) into an aqueous 6 *M* HCl solution by evaporating a measured aliquot of the ether solution while in contact with the 6 *M* HCl solution, boiling to remove all the ether, and then diluting with additional 6 *M* HCl to a fixed volume. The absorption spectrum of the solution was then measured, and compared with the spectra of solutions of known concentrations in 6 *M* HCl.

Measurements of Absorption Spectra.—All absorption spectra were measured with a Beckman Model DU spectrophotometer using matched, fused silica cells having a light path of 1 cm. The cells were maintained at a constant temperature of 25° by means of a water jacket. The spectra of hydrochloric acid solutions were obtained from 212 to 350

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[1] Taken in part from a thesis submitted by Nancy C. Cook in partial fulfillment of the requirements for the M.S. degree. Presented in part at the Dallas meeting of the American Chemical Society, April, 1956.

[2] School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

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