tric. It is doubtful that the temperature differences of the crystals can account for these increments in the value for the dielectric constant.

The method holds great promise in that the accuracy seems to be limited only by the measuring devices. In addition, it is very simple in application and difficult experimental controls are kept at a minimum. The method is applicable to the measurement of isotropic crystalline material which cannot be grown to appreciable single-crystal size as well as to single crystals.

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

Praseodymium Oxides. I. Phase Study by Dissociation Pressure Measurements

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A phase study of the praseodymium oxide system in the composition range Pr_2O_3 to Pr_6O_{11} has been made by an equilibrium dissociation pressure method involving the construction of isothermal (equilibrium oxygen pressure *vs.* composition of oxide) curves. The pressure–composition diagram is interpreted as indicating the existence of four separate non-stoichiometric regions in the range Pr_2O_3 to Pr_6O_{11}, and the existence of five stable phases, or regions of stability, in the same range. Conditions for the existence of the various phases are discussed qualitatively in terms of the theory of non-stoichiometric compounds.

Some interesting investigations of the praseodymium oxides beyond Pr_2O_3 have recently been made.[2-6] The results are on some points apparently contradictory and on others quite puzzling, due to difficulties in the interpretation of the data obtained. In particular: (1) there is disagreement as to whether the composition Pr_6O_{11} ($PrO_{1.83}$) represents a point within a non-stoichiometric range of composition or an isolated point in the PrO_x phase diagram; (2) although there is much evidence for the existence of separate non-stoichiometric ranges between $PrO_{1.5}$ and PrO_2, the nature and extent of these regions have not been established. For example, Asprey's dissociation pressure *vs.* temperature diagram[6] shows eight changes in slope in the composition range $PrO_{1.5}$–$PrO_{1.83}$.

Since it appeared, from the work referred to above, that the PrO_x system might afford a striking example of the existence of non-stoichiometric phases, it was thought that a further study of the range $PrO_{1.5}$–$PrO_{1.83}$ might prove interesting. The $(P,X)_T$ method was selected as one likely to give unambiguous information. This method has the further advantage that the experimental technique can be adopted to cover conveniently a wide composition range.

Experimental Method

Apparatus and Calibration.—An apparatus similar to one which has been used for precise low temperature adsorption studies[7] met the requirements (a) of accurate determination of oxide composition by oxygen absorption measurements on small samples and (b) of measurement at constant volume to simplify calibration and to increase the precision of the data. The apparatus (Fig. 1) consisted mainly of a zero-reference manometer, a water-jacketed gas buret, and a quartz sample tube with small dead space containing the alundum sample crucible. The sample tube was surrounded by a close-fitting furnace which could be regulated to ±0.2° at 1000°.

The various parts of the system were carefully calibrated with mercury in the usual way and by P,T measurements using pure oxygen. The sample tube dead space, without sample, was determined, after the rest of the system had been calibrated, at several furnace temperatures between 400 and 1000°. The data yielded a smooth curve from which interpolations could be made. A correction was made for the volume occupied by the sample. Since this was only about 0.025 ml., the change in sample volume with oxidation was assumed to be negligible.

With simple precautions, considerable precision was easily obtained with the apparatus. Errors due to adsorption of oxygen on the walls, possible slight reaction with impurities in the alundum crucible, etc., were apparently reproducible and corrections for these effects were implicit in the method of calibration, the conditions for which were the same as for the absorption experiments except that the sample was omitted.

The compositions calculated are probably accurate to ±0.0007 near $PrO_{1.83}$ and to about ±0.0002 near $PrO_{1.60}$. Pressures were read (corrected) to ±0.05 mm.

Materials and Procedure.—The praseodymium oxide used, "greater than 99.9% pure Pr_6O_{11}," was obtained from F. H. Spedding of Iowa State College at Ames. After reduction by hydrogen at 650° to Pr_2O_3, a sample was weighed to the nearest 10 μg. (dry atmosphere) into the sample crucible. The weight was redetermined after reduction *in vacuo* for 15 hours at 1000°.

The oxygen for both the calibration of the apparatus and for the absorption experiments was prepared by heating outgassed potassium permanganate.

Before each series of equilibrium measurements, the sample was evacuated using an oil diffusion pump at 1000° for 8 to 12 hours. Between each series of measurements, the sample was left overnight *in vacuo* at 1000°. This procedure ensures that Pr_2O_3 with the same past history is used for each series of measurements, since this annealing process undoubtedly allows recrystallization of the oxide in its equilibrium form.

The equilibrium points were obtained by adding a carefully measured quantity of oxygen to the part of the system containing the sample, allowing time for equilibration, and then determining the final dissociation pressure of the oxide. More oxygen was then added, etc. In this way a series of $(P,X)_T$ points at increasing X was obtained, oxide composition being calculated from the oxygen absorption. Where convenient, the procedure was revised by reducing the oxygen pressure and measuring the oxygen given off by the oxide. The time required for equilibration varied from 5 minutes to 2 hours, and was shorter, generally, at the higher com-

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(1) National Bureau of Standards, Washington, D. C. Part of the data reported here were included in a dissertation submitted by R. E. Ferguson to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. D. McCullough, THIS JOURNAL, **72**, 1386 (1950).

(3) W. Simon, Ph.D. Thesis, University of Iowa, 1951.

(4) D. M. Gruen, W. C. Koehler and J. J. Katz, THIS JOURNAL, **73**, 1475 (1951).

(5) R. L. Martin, *Nature*, **165**, 202 (1950).

(6) L. B. Asprey, Ph.D. Thesis, University of California, 1949.

(7) W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glassblowing and Laboratory Techniques," Instruments Publishing Company, 1949, Ch. XII.

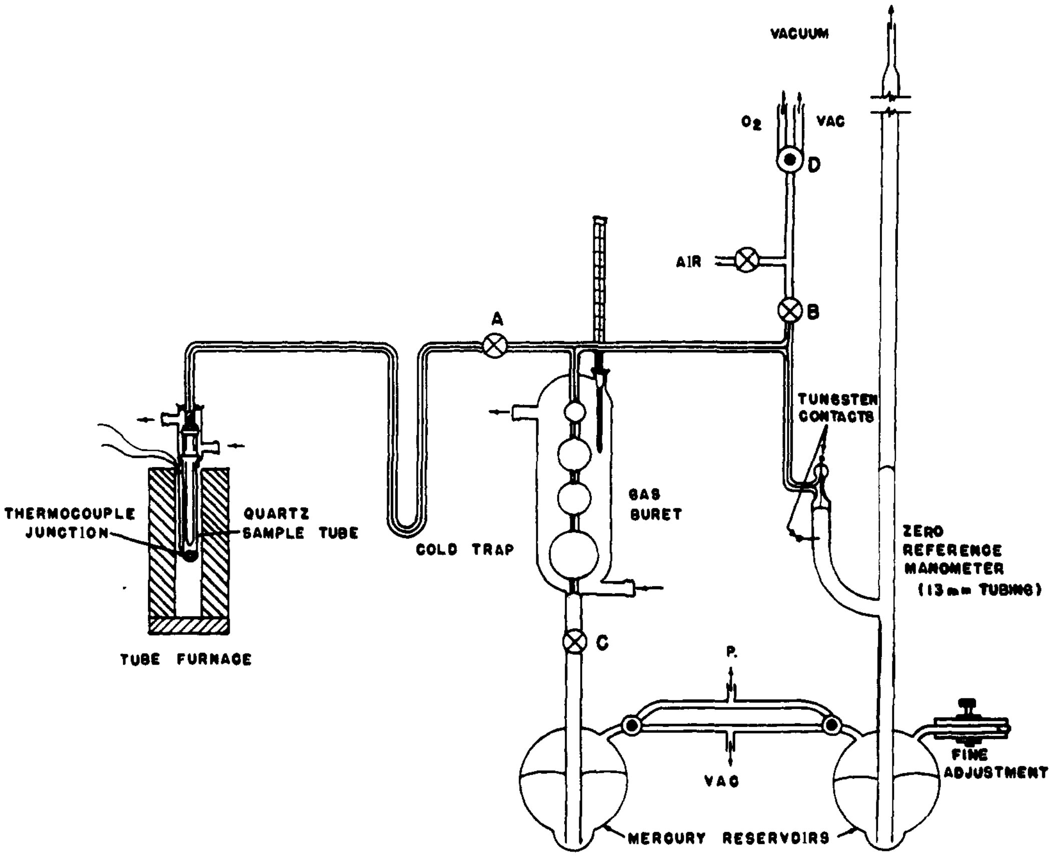

Fig. 1.—Absorption system.

positions, notwithstanding the lowering of temperature necessary to reach compositions near $PrO_{1.83}$.

Since, in a series of measurements in which Pr_2O_3 is oxidized by successive small additions of oxygen, errors might accumulate and become appreciable at higher pressures, a check on this point was made in the following way. For each isotherm, one or two $(P,X)_T$ points in the 300 to 600 mm. pressure region were determined directly by one or two additions of oxygen to the vacuum annealed Pr_2O_3 sample, and the points so obtained were compared with those which had been determined by the method of small successive additions. In all cases the points so determined agreed with those previously obtained to within the experimental error of the "one-shot" determination.

No one of the isotherms was calculated from a single series of measurements. For example, it was found convenient to obtain a well-scattered series of points in a first series of additions, to plot these points, and to examine the isotherm for interesting regions. A second and sometimes a third run was then made in order to fill out the curve in detail. Depending upon convenience, the second or third runs were made either by addition or removal of oxygen.

Due to the procedures described above, each isotherm was checked and rechecked as a matter of course during the collection of the data, and agreement within the experimental error stated was obtained with two different samples.

Criteria for Equilibrium.—Commonly, in the study of solid–gas equilibria, there is some uncertainty as to whether equilibrium points are obtained.[8] Low reaction rates, a marked difference in the rates of the forward and reverse reactions, etc., may make difficult the application of the fundamental requirement of reversibility.

In the system discussed here, the rates of oxidation and reduction in the region $PrO_{1.62}$-$PrO_{1.83}$ were such that the gross reversibility of the reaction taking place could be established by tracing out the isotherms in the forward and reverse directions. Only two isotherms, the 527 and 1050° curves in Fig. 2 were so retraced over most of their range. (The 527° curve was selected as a test case because it may be assumed that if, at this relatively low temperature, the reactions occurring are reversible, then the same should be true of similar reactions at higher temperatures.) Nevertheless, nearly all of the reactions represented by lines of steep slope in Fig. 2 were checked by retracing the isotherms.

A second criterion for reversibility could be applied to each point on the diagram. The furnace temperature regulator was set so that the temperature oscillated approximately 0.6° about the mean, with a period of 3 to 4 minutes. At equilibrium, the dissociation pressure of the solid could be seen to oscillate with sample temperature. The effect was much greater than that due to the change in gas density with temperature. The pressure oscillation was observed at all points where it could be expected to occur.

One important consideration remains. It has been suggested[8,9] that the peculiar form of the isotherms obtained in several studies of $(P,X)_T$ equilibria may be due to the existence of false equilibria; that is, that the equilibrium observed is one between $X_2(g)$ and a surface layer, perhaps only a few atomic radii deep, surrounding each particle of the solid. This is likely to be the case especially at low temperatures (less than one-half the absolute melting point of the solid), where diffusion in the solid may be slow. False equilibria might also arise from the formation of a solid phase which possesses high surface energy due to imperfect crystallization, or which exists in a metastable form. Both of these possibilities must be considered if equilibrium measurements are made at temperatures at which diffusion in the solid phase is not known certainly to be rapid.

The criteria for equilibrium applied in this study suffice to show that some sort of equilibrium exists, but throw no light upon the nature of the equilibrium observed. There is no way to ensure, experimentally, that "true" equilibrium conditions are obtained, since it is necessary, in order to study an appreciable composition range, to go to lower temperatures so that the dissociation pressures can be measured conveniently. However, the possibility of surface equilibrium, we believe, can be rejected on simple grounds. At 402°, Pr_2O_3, treated as described in the section on pro-

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[8] J. S. Anderson, *Ann. Rep.. Chem. Soc. London*, **43**, 104 (1946).

[9] J. S. Anderson, *Proc. Roy. Soc. (London)*, **A185**, 69 (1946).

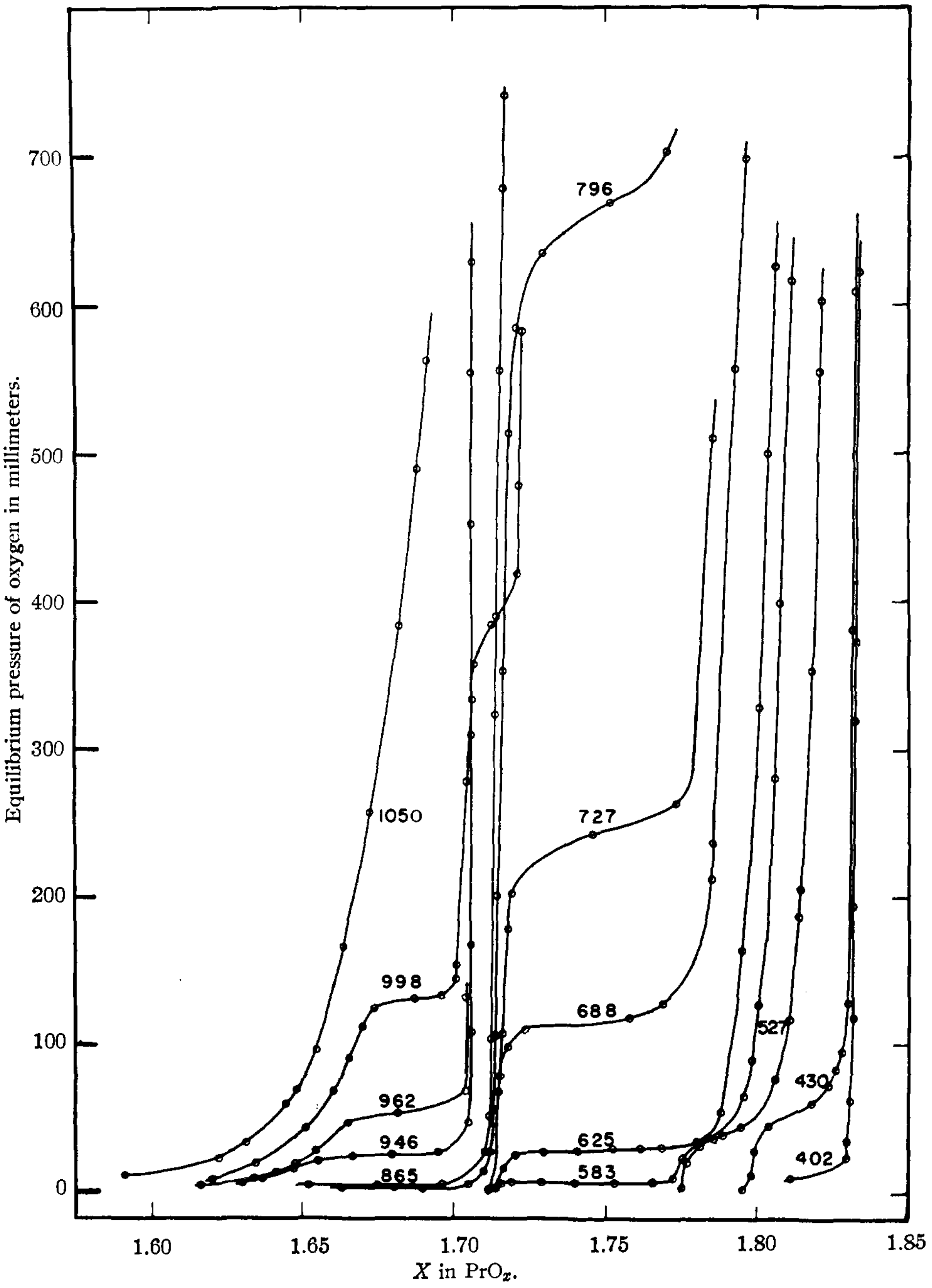

Fig. 2.—Composition of praseodymium oxide.

cedure above, is oxidized to Pr_6O_{11} in a few minutes under an oxygen atmosphere sufficient to give a final pressure of 150 mm. This phase, so produced, has the same composition as the homogeneous product obtained by air ignition. McCullough[2] found that upon annealing this oxide for two weeks at 400° in air (150 mm. oxygen partial pressure) the only effect was a sharpening of the X-ray diffraction lines; the composition and crystal structure did not change. The identity of the composition obtained during the construction of the 402° isotherm and that obtained by McCullough shows that the sample is oxidized all the way through in a short time at 402°. Since the structures (which influence the diffusion rate) of the oxides between $PrO_{1.715}$ and $PrO_{1.83}$ are very similar,[10] it may be assumed that the rate of penetration of the lattice by oxygen at temperatures above 402° is sufficiently great to eliminate the possibility of stable surface layer formation in this compositin range. In the region $PrO_{1.60}$-$PrO_{1.715}$, the isotherms were obtained at temperatures high enough that surface layers are not to be expected on the usual grounds.

The possibility remains that, at temperatures below 700–900°, the solid phases formed may be imperfectly crystallized. Probably the phase of composition $PrO_{1.83}$ obtained by brief treatment with oxygen at 402° is such a phase (*cf.* the effect of annealing described by McCullough). However, the sharpening of the diffraction lines could be due to an increase in particle size as well as to an ordering process in the lattice. Since the magnitude of the effect of "imperfect crystallization" upon the dissociation pressure of a phase is not easily estimated (it may be negligible), and since the presence of the phenomenon is not certain, the isotherms will be discussed as if the effect were absent.

Results and Discussion

Gross Features of the Diagram.—The collection of isotherms in Fig. 2 shows the complexity of the

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[10] Unpublished high temperature X-ray data from this Laboratory.

composition range studied.[11] The range of composition accessible to the apparatus used is limited on the left by a region where oxidation is very slow and probably irreversible, and on the right by the formation of the stable phase Pr_6O_{11}. In this range there appear to be at least five phases of narrow composition range, and four distinct non-stoichiometric regions. Only one clearly diphasic region exists, *under the conditions defined by the isotherms*, in the whole range; it appears in the region $PrO_{1.715}$–$PrO_{1.77}$, at 583°, with an equilibrium pressure of about 6 mm. In this same range, the 625, 688, 727 and 796° isotherms show that the system is bivariant, which means that a single phase is present at these temperatures; the curves do bend toward the horizontal, however, and this may be interpreted as a tendency toward the formation of two phases.[9] There are altogether three rather well-defined incipient diphasic regions of this nature in the range $PrO_{1.62}$–$PrO_{1.83}$, and the 527 and 583° isotherms may show a fourth (in the vicinity of $PrO_{1.79}$), although the relationship of this curve to those on either side is not clear.

There are three compositions, $PrO_{1.715}$, $PrO_{1.802}$ and $PrO_{1.833}$, at which the isotherms rise vertically indicating that these compositions represent stable phases (again, under the special conditions defined by the isotherms) of negligible composition range. These phases can be written Pr_7O_{12}, Pr_5O_9 and Pr_6O_{11}, respectively, although it is doubtful whether any significance should be attributed to the integral ratio formulas.

It should be emphasized at the outset that a collection of isotherms such as that in Fig. 2 cannot show what happens in a composition range under any and all conditions. For example, the range $PrO_{1.62}$–$PrO_{1.66}$, which is clearly monophasic between 963 and 1050°, might be diphasic at 600°. Considering this, and the over-all complexity of the system, it is not difficult to see how apparently contradictory conclusions might be drawn from sets of data collected under differing conditions over the same composition range. An excellent example of a similar situation is that given by the long series of investigations of the UO_X system (1927 to 1950), reviewed by Katz and Rabinowitch.[12]

Detailed Discussion of the $(P,X)_T$ Diagram. 1. The Range $PrO_{1.5}$–$PrO_{1.62}$.—The isotherms plotted in Fig. 2 do not extend into this range. A few points obtained in this region are shown at the end of the table[11]; whether they are equilibrium points is not known. In this region, a temperature above 900° is necessary to raise the dissociation pressure to a value measurable by an ordinary mercury manometer; at such temperatures, Pr_2O_3 (phase I) exists in the hexagonal "A" form. The points obtained by oxidation of this phase seem to indicate an equilibrium pressure of about 9.5 mm. up to $PrO_{1.60}$. The oxidation is slow at an oxygen pressure a few millimeters above the apparent dissociation pressure. For example, in obtaining the point $P = 9.58$ mm., $X = 1.5463$ at 963°, 24 mm. of oxygen was brought into contact with a solid of composition $PrO_{1.5274}$; in 2.5 hours the pressure had dropped to 9.58 mm., where uptake sensibly ceased. The pressure oscillation (described above in the section on equilibrium) began at about 10.5 mm., however, apparently indicating that some sort of rapid, reversible equilibrium exists while another much slower reaction proceeds toward completion. As a further complication, the isotherm at the same temperature falls far below 9 mm. if the equilibrium points are determined by the decomposition of a higher oxide.

It is possible that an explanation of the peculiar phenomenon observed in this range, in terms of structural transitions in the solid, can be devised; however, additional information is required.

2. The Range $PrO_{1.62}$–$PrO_{1.66}$.—A single non-stoichiometric phase, call it phase II, inhabits this region at temperatures near or above 950°. The form of the isotherms indicates that an incipient diphasic system bounds the region on the right. At lower temperatures if the oxygen content is increased beyond $X = 1.66$ the non-stoichiometric phase would probably break up into two phases: the anion-saturated phase II ($PrO_{1.66}$) and a phase of composition $PrO_{1.70}$ (phase III).

Asprey[6] found that $PrO_{1.66}$ is an homogeneous phase with a body-centered cubic lattice. The sample was cooled to room temperature before the X-ray patterns were obtained; hence it is not certain that the phase of this composition has the same structure at 963°. If the structure is actually cubic, it can be inferred that phase II is cubic over its entire range of composition, since $PrO_{1.66}$ is shown by the diagram to be approximately the defect-rich limit of phase II, and since the isotherms show no transition in the range.

3. The Range $PrO_{1.66}$–$PrO_{1.715}$.—The composition range of phase II extends well into this region, at least above about 950°. Near $X = 1.70$, at temperatures above about 950°, the curves rise steeply, indicating a region of stability which will with some trepidation be called phase III.

The 946, 963 and 998° isotherms break over toward $X = 1.715$ at successively higher pressures, indicating an incipient diphasic region in this small range. However, the behavior of the system in this region is difficult to understand. The isotherms determined at lower temperatures (864 and 946°) cross over both the 998 and 963° curves; furthermore, the results of absorption measurements between 130 and 300 mm. at 963° are not reproducible, and in one case a spontaneous reversal of the oxidation was observed, due possibly to the initial formation of a phase, metastable at 963°, which then decomposed.

The anomalous region is bounded on the right by the well-defined phase IV, which has the composition limits $PrO_{1.715}$–$PrO_{1.72}$, and which exists over a considerable temperature range, at least from 583 to 1000°. Asprey's (P,T) diagram shows clearly the existence of this phase. X-Ray diffraction

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[11] The precise data have been deposited as Document number 4204 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[12] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 276-290.

patterns obtained from a sample of $PrO_{1.715}$ indicate that it has a face-centered cubic structure identical to that of Pr_6O_{11} except for lattice constant.[6]

Between the upper composition limit of phase II and the lower limit of phase IV there must be a transition from the body-centered to the face-centered cubic lattice, if the X-ray evidence is unambiguous. It is likely that the incipient diphasic region between $PrO_{1.66}$ and $PrO_{1.70}$ is due to this transition, although the available evidence does not warrant any definite conclusions as to the structure of phase III.

4. **The Range** $PrO_{1.715}$–$PrO_{1.80}$.—Above about 583°, phase IV exists over most of this range. At or below this temperature a true diphasic region appears; the phases present are the defect-rich $PrO_{1.715}$ and a non-stoichiometric phase of range $PrO_{1.78}$–$PrO_{1.802}$, to be referred to as phase V. Whereas the composition of phase IV is almost independent of temperature, that of phase V is apparently dependent upon both temperature and pressure (note the displacement toward the left of the isotherms in the 260–700 mm. region with increasing temperature). Isotherms of form very similar to those in this region of the PrO_X system have been obtained in the study of the UO_X system by Biltz and Muller[13] and are discussed by Anderson[9] in terms of his theory of phase composition limits.

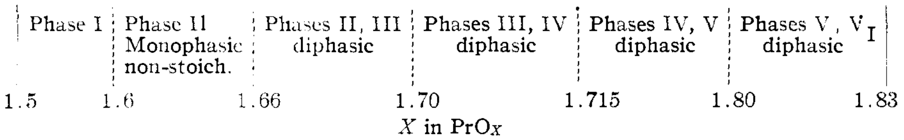
The forms of the 527 and 583° isotherms below $X = 1.80$ are uninterpreted at this writing. They do seem to show a region of stability in the vicinity of $X = 1.78$.

5. **The Range** $PrO_{1.80}$–$PrO_{1.83}$, **and the Composition** Pr_6O_{11}.—This region is also a non-stoichiometric monophasic range under the conditions of the experiments, although, again, the forms of the two isotherms at 430 and 402° suggest that at temperatures somewhere below 400°, a diphasic region might conceivably be encountered, provided that at low temperature the necessary solid state reactions can occur.

More specifically, if the oxidation of $PrO_{1.80}$ to $PrO_{1.83}$ (Pr_6O_{11}, phase VI) could be carried out at, say, 250°, it is likely that Pr_6O_{11} would then appear, on an isotherm at this temperature, as a unique stable phase of constant composition. The 430 and 402° isotherms, on the other hand, indicate very definitely that Pr_6O_{11} is the upper composition limit of a non-stoichiometric phase. To belabor the point: it is also likely that, at high temperature and high pressures of oxygen, an isotherm could be obtained which would show a monophasic region extending from $PrO_{1.80}$, *through* the composition Pr_6O_{11} to some higher composition, perhaps even to PrO_2. And to take an extreme case, the available data suggest the possibility of oxidizing $PrO_{1.62}$ to $PrO_{1.83}$ or PrO_2 along a path such that the system is bivariant over the entire range. These considerations may suffice to explain tentatively many of the divergent results obtained in studies of this system.[14]

A Final Speculation.—Suppose that each region discussed above were investigated separately, under such conditions that the tendencies toward the formation of diphasic systems are realized (that is, suppose that all possible valid inferences from the data in Fig. 2 are utilized).

The diagram obtained might be similar to the following



In this diagram the boundaries would not be sharp, since each phase shown, except perhaps Pr_6O_{11}, could be expected to have a range of composition, the limits of which, for a given phase, would be determined by temperature and oxygen pressure.

Acknowledgment.—The authors express their thanks to the Atomic Energy Commission for their interest and financial support of this study and to Dr. Spedding for making the sample of pure praseodymium oxide available to them.

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(13) W. Biltz and H. Muller, *Z. anorg. Chem.*, **163**, 279 (1927).

(14) It is interesting to note that in the customary preparation of Pr_6O_{11} by ignition in air of Pr_2O_3, $Pr(NO_3)_3$, etc., the Pr_6O_{11} must be formed *after* the solid is removed from the source of heat. The path of oxidation during cooling would be represented on Fig. 2 by a horizontal line at about 150 mm., starting at an isotherm representing the ignition temperature and ending at or near the composition $PrO_{1.83}$.