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On the Phase Interval $PrO_{1.50}$ to $PrO_{1.71}$ in the Praseodymium Oxide–Oxygen System

RHÉAL P. TURCOTTE, JOYCE M. WARMKESSEL, RICHARD J. D. TILLEY AND LEROY EYRING

Department of Chemistry, Arizona State University,
Tempe, Arizona 85281

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Phase relationships and phase transitions in the composition region $PrO_{1.50}$–$PrO_{1.71}$ have been studied by X-ray diffraction analysis on quenched samples and *in situ* at high temperatures. An interpretation of the results are given in terms of a metastable set of phases including C-form Pr_2O_3 below 910°C and a stable set including A-form Pr_2O_3 above that temperature.

Besides these two polymorphic sesquioxides and the oxygen-rich end member, Pr_7O_{12}, a widely nonstoichiometric phase and a phase of approximate composition $PrO_{1.67}$ have been identified. Thermal expansion measurements have been made on C-form Pr_2O_3 and Pr_7O_{12}.

Hysteresis is clearly indicated by the high-temperature X-ray studies. These results are contrasted with those of recently published high-temperature emf studies in this composition region.

Introduction

The phase diagram for the PrO_x system over much of its composition range has been described in detail by Hyde et al. (*1*). Two genuinely nonstoichiometric phases (σ with $1.5 \leqslant x \simeq 1.714$ and α with $1.714 \simeq x \leqslant 2.0$ for x in PrO_x) were seen to be interrupted by a homologous series (Pr_nO_{2n-2}) of ordered phases of relatively narrow composition width at lower pressures and temperatures. The region $1.5 \leqslant x \leqslant 1.714$ is bounded on the left by the cubic C-form sesquioxide (when reduction occurs at lower temperatures) or the hexagonal A-form (at higher temperatures) and on the right by the rhombohedral ι phase ($PrO_{1.714}$ up to ~1050°C) and the oxygen-rich boundary of σ phase (at higher temperatures).

In the sesquioxide–ι region, the thermogravimetric technique is far less powerful in revealing phase relationships than in the higher composition region because of the difficulties of obtaining and measuring the low partial pressures of O_2 (10^{-6}–10^{-3} Torr) and of the occurrence of slow equilibrium at lower temperatures and pressures. The irreversible cubic to hexagonal transition for the sesquioxide at temperatures as low as 600°C is a further complication, especially as the A-form is resistant to oxidation, requiring elevated oxygen pressures for conversion to more oxidized phases (*1–3*).

Because of the complexity and obscurity of the several phases inhabiting this region, a detailed X-ray examination was considered necessary. The results presented here are derived from several limited studies, each of which is able to clarify partially the structural types occurring in the phase interval between $PrO_{1.50}$ and $PrO_{1.714}$. The first part of these studies consists of X-ray analysis of the products of interrupted reduction of higher oxides and of oxides which were annealed in sealed quartz ampoules and then quenched to room temperature. Because of the acknowledged uncertainties in quenching these oxides it is necessary to examine them *in situ* using high-temperature X-ray diffraction techniques if equilibrium information is desired. These latter studies form the second part of the experiments. The results of this work are in agreement with previous structural studies, but also indicate that more complex phases are likely to exist within this lower region of the Pr–O phase diagram. A recent determination by Lott et al. (*4*) of the thermodynamic properties of oxides in this region, made by high-temperature emf measurements, is in contrast to this body of largely self-consistent experimental data. The interpretation of their results differs sharply with the results of the present study and those of previous workers. These differences are discussed below in the light of the present results.

Experimental Part

Materials. Unless otherwise noted the praseodymium oxide used in the experiments was 99.999% pure (with respect to other rare earths) as supplied by the American Potash and Chemical Corporation, Lindsay Division. The lower purity material (99.9%) used in some experiments is believed not to yield different results in these experiments since the principal impurities totalling typically about 0.1% are not rare earths. Temperature measurement was made by means of a Pt–Pt–10% Rh thermocouple which was calibrated in the Nonius camera by thermal expansion measurements.

Interrupted Reductions of Higher Oxides. Two series of experiments were conducted in which higher oxides were reduced in hydrogen or argon atmospheres. The products were cooled rapidly and X-ray diffraction patterns obtained to clarify the nature of intermediate phases in the composition region of present concern.

Samples of $PrO_{1.833}$ (99.9%) contained in platinum boats were heated in flowing hydrogen or argon. The boats were placed in a Vycor tube of 1 in. diameter which was heated by a concentric Kanthal wound furnace. The hydrogen was "ultrapure," paladium diffused, with a quoted purity of 99.9998% and a dew point of –90°F. The argon was "special purity 99.998%" with 2 ppm oxygen and a dew point of –117°F. At the conclusion of the reduction the furnace was turned off and the Vycor tube was cooled rapidly by a rush of cool air blown through the cylindrical annular space between the tube and furnace. When the reduced sample was at room temperature it was removed for gravimetric analysis and X-ray analysis using a Hägg–Guinier focusing camera.

Anneal–Quench Experiments at Constant Composition. An anneal–quench X-ray examination was made to establish the composition-lattice parameter relationship required for the analyses of the high-temperature equilibrium studies. The desired compositions were prepared by mixing $PrO_{1.500}$ (C-form) and $PrO_{1.833}$ in the required proportions. The C-form starting material was prepared by hydrogen reduction of a higher oxide in an alumina boat at about 600°C. The $PrO_{1.833}$ was prepared by heating the oxide for several hours at 900°C in flowing air from which water and CO_2 had been removed; the temperature was then reduced to 600°C for one day. The mixtures were sealed in quartz ampoules under vacuum and annealed at the desired temperature for 24–28 hr, a period of time found sufficient to ensure homogeneity. After annealing, the quenched compositions were checked gravimetrically by reducing an aliquot to A-form sesquioxide and calculating the original composition from the weight loss. X-Ray analyses were made on the annealed samples using a Hägg–Guinier focusing camera.

High-Temperature X-Ray Measurements. Most of these were accomplished by means of a Nonius Guinier–Lenné high-temperature camera system. The temperature of the specimen could be controlled or changed at any desired rate between 0.15 and 6°C per minute. The furnace cavity of the camera was connected to an atmosphere control system utilizing an oil diffusion pump and liquid nitrogen trap for producing high vacuum or a Granville–Phillips leak valve driven with a micrometer screw to control the oxygen pressure or rate of pressure change over the sample. Thoria was used as an internal standard in all experiments. Rand's (*5*) thermal expansion data for thoria were used in the analysis of the results. The lattice parameter as a function of temperature is given by

$$a = 5.59507 + 4.5135 \times 10^{-5}\, t + 6.5552 \times 10^{-9}\, t^2.$$

All data were reduced by computer methods to give refined lattice parameters and curves were fit by least-squares analyses. The error at the 95% confidence level was ±0.003 Å or better for the 11 Å-bcc cell characteristic of the nonstoichiometric σ phase. Because three sets of data were required for determination of a single composition at high temperatures, the resulting uncertainty in composition was approximately ±0.015 in x.

Although total pressures were maintained constant by the leak valve in the low pressure region, reproducible and accurate measurement of O_2 partial pressure was not obtained, due to outgassing of the ceramic components in the furnace. Where pressures are denoted this problem was negligible. A few isobaric studies were made on a high-temperature diffractometer previously described (*6*).

Thermal Expansion Measurements. The Nonius X-ray camera system was used to obtain thermal expansion parameters. Three different samples of $PrO_{1.5}$ were utilized. One was prepared by H_2 reduction at 600°C and the other two by vacuum reduction *in situ* at about 725°C for 24 hr. The vacuum reduction produced a trace of A-form $PrO_{1.5}$. Oxygen pressure during the runs never exceeded 3×10^{-6} Torr.

Results and Discussion

Interrupted Reduction of Higher Oxides. Table I summarizes these results. When hydrogen was used

TABLE I

INTERRUPTED REDUCTIONS OF $PrO_{1.83}$

Temperature (°C)	Time of treatment (min)	Final composition (x in PrO_x)	Phases present (X-ray)	a of new bcc phase (σ_b) (Å)
		Hydrogen reduction[a]		
310	360	1.74	ι + other	
400	60	1.77	ι + other	
480	660	1.50	C form	
633	60	1.50	C + A (trace)	
680	660	1.50	C + A	
720	60	1.50	C + A	
786	100	1.50	C + A	
845	90	1.50	C (trace) + A	
		Argon reduction[b]		
600	60	1.78	ι + other	
705	60	1.74	ι + other	
801	70	1.71	ι	
826	100	1.70	ι + other	
870	350	1.61	$\sigma_b + \sigma_a$	11.097
870	660	1.59	$\sigma_b + \sigma_a$	
872	60	1.64	$\sigma_b + \sigma_a$	11.072
886	60	1.69	$\sigma_b + \sigma_a$	
890	60	1.67	$\iota + \sigma_b$	
920	630	1.55	$\sigma_b + \sigma_a$	11.110
925	300	1.58	$\sigma_b + \sigma_a$	
936	80	1.62	σ_b (only)	11.086
984	40	1.60	$\sigma_b + \sigma_a$	

[a] All products are green, except the first two which were mixed black and green.

[b] All products are black.

as the flow gas, the reaction was rapid and produced intermediate oxides only at temperatures of 400°C and below. No compositions between the ι phase and the sesquioxide were prepared. These experiments show that in all complete reductions of $PrO_{1.833}$ the C-form sesquioxide is first formed, with subsequent transformation to the A-form.

When argon was used to reduce the oxygen activity in the gas phase, the solid lost oxygen at a much slower rate and samples of composition between the ι and sesquioxide phases were easily obtained. In several of these preparations a new fcc phase with a lattice parameter significantly smaller than that of the C-form sesquioxide was present. The relative amount of this new phase increased as one approached the overall composition $PrO_{1.62}$, where the lattice parameter is $a = 11.086$Å. The value of a depended on which other phase was present, indicating substantial variability of composition.

Reduction in argon on a recording thermobalance using the apparatus described previously (*1*) revealed no special significance for the composition $PrO_{1.62}$. The shape of the curves were similar to runs made at 50 Torr of oxygen, which may well have been the oxygen pressure within the oxide powder bed.

The results of these experiments differ from those obtained at temperature (to be discussed below) in suggesting a single phase at $PrO_{1.62}$ rather than at $PrO_{1.66}$. This discrepancy probably is to be explained by a lack of an effective quench in the cooling procedure.

Anneal–Quench and Thermal Expansion Measurements. The results of the anneal–quench experiments are given in Table II. In addition to confirming the two-phased ($\sigma_a + \sigma_b$) region, they establish the relationship between cell edge and composition required for interpretation of the high-temperature data. These data are expressed as a least-squares fit to a quadratic equation where x = O/Pr ratio and a = bcc lattice parameter,

$$x = -452.3731 + 83.55472a - 3.842904a^2 (\pm 0.007).$$

Within the σ region, stoichiometry was determined from the high-temperature X-ray data by first correcting for thermal expansion and then applying the $x = f(a)$ information given by this curve. In order to deduce compositions in this fashion, the assumption was made that the coefficient of thermal expansion was independent of composition, as was observed in the PrO_x α region (*7*). In further justification of this assumption, the coefficients of thermal expansion given by Burnham and Eyring (*6*) for the ordered phases do not show any trends but have a value of ~9.7×10^{-6} at ~450°C for the pseudocubic cell.

During the course of the work, it became apparent that an earlier (*6*) thermal expansion measurement on C-form $PrO_{1.500}$ was probably not carried out at oxygen partial pressures which were low enough to maintain stoichiometry. A redetermination for this phase as well as for the $PrO_{1.714}$ phase was made as discussed elsewhere (*8*). The data for $PrO_{1.500}$ indicated a possible discontinuity at 270°C which, however, was not confirmed by a series of quench experiments (*8*). The points may be fit nearly equally well to two curves or to a single straight line, but for a number of reasons the former was used in interpreting the results of this work. In any case, the effect on stoichiometries is slight (<0.01 in x) and only for $t < 270$°C. The $PrO_{1.714}$ lattice parameters obtained for both single-phase and biphasic material were slightly higher when σ phase was present. The thermal expansion data for rhombo-

TABLE II

X-RAY ANALYSIS OF ANNEALED SAMPLES

Average composition (O/Pr ratio)	Annealing temperature (°C)	Lattice parameter, phase I (Å ± .003)	Estimated composition, phase I (O/Pr ratio)	Lattice parameter, phase II (Å ± .003)	Estimated composition, phase II (O/Pr ratio)
1.53	570	11.134 ± .003 Å	1.53	—	—
1.53	405	11.144	1.516	11.102 ± .003 Å	1.596
1.53	390	11.152	1.50	11.100	1.593
1.536	605	11.132	1.536	—	—
1.536	550	11.141	1.51	Trace bcc	—
1.54	600	11.134	1.54	—	—
1.56	580	11.120	1.558	—	—
1.56	405	11.142	1.518	11.108	1.58
1.56	390	11.152	1.50	11.096	1.60
1.568	605	11.123	1.57	—	—
1.568	550	11.140	1.51	11.085	1.60
1.58	600	11.107	1.58	—	—
1.58	490	11.109	1.58	—	—
1.58	450	11.108	1.58	—	—
1.58	425	11.132	1.538	11.097	1.60
1.60	530	11.100	1.595	—	—
1.60	430	11.100	1.595	—	—
1.60	390	11.098	1.598	—	—
1.62	605	11.086 ± .003 Å	1.62	—	—
1.62	550	11.086	1.62	Trace rhomb.	1.71
1.67	605	Rhombohedral	1.714	—	—
1.67	550	Rhombohedral	1.714	Trace bcc	—

hedral $PrO_{1.714}$ (single phase) and C-type $PrO_{1.500}$ were fit to the following least-squares curves:

$PrO_{1.500}$ $18°C < t < 270°C$ (11 points), $a = 11.1454 + 7.301 \times 10^{-5} t + 0.891 \times 10^{-3} t^2 \pm 0.002$;

$PrO_{1.500}$ $270°C < t < 725°C$ (9 points), $\mathrm{a} = 11.1526 + 7.051 \times 10^{-5} t + 1.866 \times 10^{-3} t^2 \pm 0.002$;

$PrO_{1.714}$ $18°C < t < 1013°C$ (16 points), $a = 6.7390 + 5.5414 \times 10^{-5} t + 2.259 \times 10^{-3} t^2 \pm 0.001$ and $\alpha = 99.31 \pm 0.03$.

The Phase Relationships. A phase diagram compatible with all the results is given in Fig. 1. When C-form $PrO_{1.500}$ is the low composition limit (rather than A-form $PrO_{1.500}$), the diagram is composed of one broadly nonstoichiometric single-phased region (σ) and two biphasic fields, ($\sigma_a + \sigma_b$) and ($\sigma + \iota$). These regions are indicated by dashed lines.

The critical temperature (380°C) defining the two-phased bcc region ($\sigma_a + \sigma_b$) was obtained by employing the continuous recording capability of the Nonius camera. The exposure was taken with temperature decreasing at a rate of 2.3°C/hr starting from 435°C. The O_2 pressure was nominally 4×10^{-5} Torr and the disproportionation gave nearly equal amounts of the two phases. A continuous film was also exposed with increasing temperature starting with a two-phased mixture having 30% reduced σ_a at 334°C. The conversion to single-phased σ was not distinct, but there was some indication of line broadening, particularly for σ_a beginning at about 400°C. The intensity also began decreasing at this point, but the transition was very slow, with a merging of reflections that was not completed until a temperature of approximately 550°C was reached.

It might be pointed out here that the σ phase retains bcc symmetry across its entire range of stoichiometry. In progressing to higher O/M ratios, the only changes observed in the X-ray patterns are a slight reduction in the intensity of the bcc superstructure lines and a decreasing lattice parameter. The unit cell may be considered as composed of eight fluorite (MO_2 symmetry) cells from which oxygen has been removed in an ordered fashion along small cell body diagonals. There is no evidence

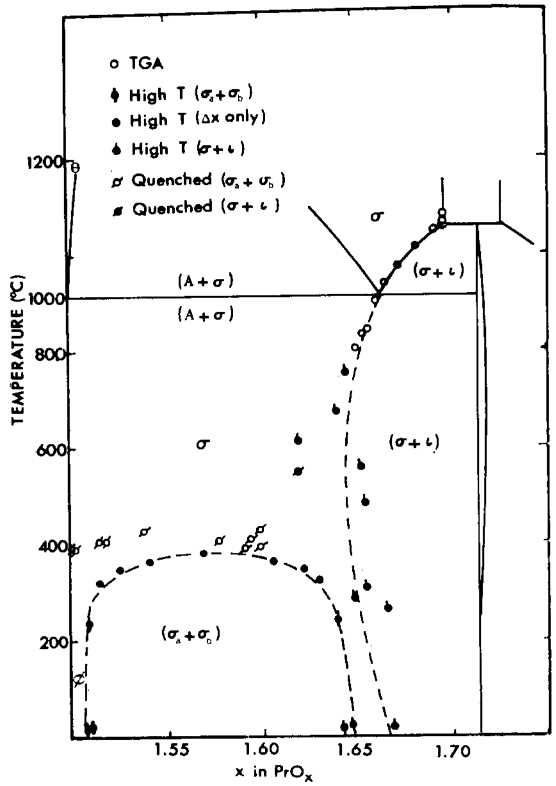

FIG. 1. Stable and metastable phase relationships in the region $1.5 < x < 1.72$.

at this point for anything but random occupation of the "vacant" sites in this cell across the σ field.

The $(\sigma + \iota)$ boundary was determined by nine points taken at temperature and one from the quench study. Although one of the high-temperature points and the quench result suggest a possible discontinuity in the boundary, this was not further explored. In fact these points do not lie very far outside the limits of experimental error of the curve.

The phase relationships described by solid lines in Fig. 1 are believed to represent the thermodynamically stable case in which the A-form sesquioxide is the low composition phase at $x = 1.500$. The data which have forced a consideration of the phase behavior from two viewpoints (i.e., stable and metastable) depending on whether the A- or C-form sesquioxide is the low composition boundary are discussed below.

High-Temperature X-Ray Diffraction. The isothermal tensimetric studies of reactions in this region by Ferguson et al. (*9*), Faeth et al. (*2*) and by Kordis and Eyring (*10*) are seen to reveal the following general behavior. Isotherms at 900°C and below show A-form sesquioxide to oxidize rapidly (after a minimum break pressure is reached) to a composition in the region of $PrO_{1.71}$. At 920°C and above the oxidation rate following the break pressure slows markedly at compositions significantly below $PrO_{1.71}$ and then oxidation continues slowly. At temperatures between 946 and 998°C the curves indicate an incipient diphasic behavior between $PrO_{-1.66}$ and $PrO_{-1.70}$ but at temperatures of 1050 and 1100°C, this diphasic character is replaced by a continuous gradual approach to $PrO_{1.7}$. In all cases hysteresis is observed and the curves on reduction lie significantly below the curves in oxidation. These results are compatible with those obtained using an isobaric technique as has been previously discussed (*1*).

Isothermal High-Temperature X-Ray Results. The results of the isothermal high-temperature X-ray studies using the Nonius camera are summarized in Fig. 2. The mode of operation was continuous film drive with continuous oxygen pressure increase at 875, 950, 1025, 1050 and 1075°C. By this technique the diffraction lines of the sample were recorded as each phase was formed both in oxidation and reduction. The banded dual bars indicate the phases seen in the pressure range shown both in oxidation (right side) and reduction (left side) at each temperature. The general features are consistent with the isotherms reviewed above. In each case the A-form was stable until a certain break pressure was reached. At 875°C, the break was from A-form to ι, and at 950°C and above it was seen to be from A-form to σ (Faeth's (*2*) break pressures are indicated by circles). The pressure width of the σ field increases with temperature as shown by the dashed lines marking the break pressure and the $\sigma \rightarrow \iota$ transition.

In all cases the hysteresis on the reduction cycle is obvious and is seen to result from a different reaction sequence. Whereas the oxidation was $A \rightarrow \sigma \rightarrow \iota$ above 910°C, the reduction cycle was $\iota \rightarrow \sigma \rightarrow C \rightarrow A$ at all temperatures. The C-form is unstable at all temperatures and ultimate pressures of the apparatus and decays to the A-form with approximately a 50-hr half life at 875°C, approximately a 16-hr half life at 950°C and thereafter, with rapidly decreasing periods as the temperature of the isotherm rises.

The 1050°C isotherm should be commented on. Whereas the X-ray diffraction patterns for all other runs were sharp, having clear superstructure lines, at 1050°C the pattern was marked by extreme fuzziness. Broad superstructure lines characteristic of the ι phase were also clearly visible. The pattern appears to be a fuzzy superposition of the σ and ι patterns. The lattice parameter of the σ phase formed

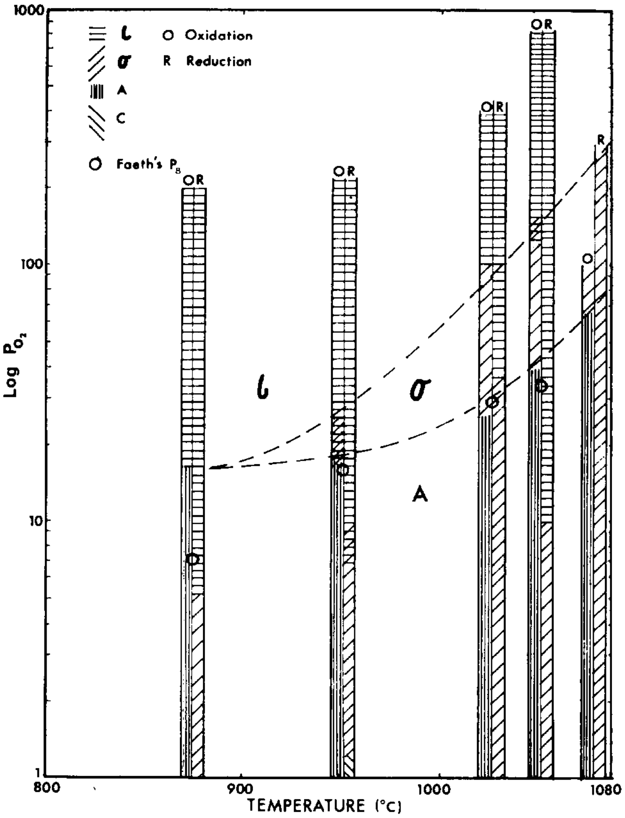

FIG. 2. Phase relationships in the sesquioxide–ι region from high-temperature X-ray diffraction measurements.

in reduction at about 90 Torr increases continuously and markedly as the pressure is decreased. The A-type sesquioxide begins to grow in at 1 Torr and reaches 90% 25 hr later when the pressure is 2×10^{-3} Torr. The behavior is distinctly different at these higher temperatures where the σ phase simply reduces smoothly whereas at 950°C there is a clear discontinuity where σ decomposes to C-form. The X-ray diagram of the sample at 1050°C in vacuum is A-form.

Isobaric High-Temperature X-Ray Runs. Two reactions on the high-temperature diffractometer were studied at 0.1 Torr O_2 in order to clarify the $PrO_{1.5}$ (A) $\rightleftarrows$ $PrO_{1.714}$ oxidation–reduction paths. At this pressure, reduction occurs at about 800°C and oxidation at temperatures in excess of 400°C. As discussed by Hyde et al. (*1*) under these conditions no other phases than the A-form sesquioxide and ι should be observed as oxidation or reduction occurs. In fact, oxidation from $PrO_{1.5}$ (A-form) was observed over a 2-hr period at 463°C to proceed directly to $PrO_{1.714}$ with no trace of the cubic oxide. It might be noted that oxidation proceeds quickly beyond $PrO_{1.714}$ even with a trace of A-form remaining. The reduction to sesquioxide from ι at this pressure was, however, not by the same pathway, but proceeded through a cubic phase (σ). Even after 24 hr at 1075°C, conversion to A-form $PrO_{1.5}$ was incomplete.

It is clear from both the isothermal and isobaric high-temperature X-ray studies that the reaction sequence is different in oxidation and reduction. In oxidation the A-form takes up oxygen to form ι directly below 910°C but oxidizes via a σ phase at higher temperatures to ι or σι. In reduction the higher oxides decompose via the topotactically related and sometimes thermodynamically unstable σ and C-form. The C-form undergoes the displacive transformation to A-form at low pressures at all temperatures of these high-temperature experiments.

General Discussion

In interpreting the results of these experiments, we are confronted with information leaving some basic questions not clearly answered. There is ample evidence that the A-form sesquioxide is the stable form for the sesquioxide over much if not all of the temperature range investigated. Each new study of the C- to A-form transformation seems to yield a lower transition temperature and we have observed a small percentage of the hexagonal form in a sample of C-form oxide after 6-days heating at 550°C (in vacuum). It is expected that the transformation is kinetically unlikely when oxygen mobility becomes extremely low, i.e., below 400°C, but this cannot be considered as thermodynamically significant.

It is, therefore, necessary to consider two-phase diagrams in this region, one being metastable. We believe then that the true equilibrium diagram in this composition region is essentially that given previously (*1*) and shown as solid lines in Fig. 1. In this case the A-form oxide is taken as the true low composition boundary over the complete temperature axis. In the range $1.50 \leqslant x \leqslant 1.714$ below 910°C, a simple two-phase region is seen to exist, with A-form sesquioxide defining one boundary and the $PrO_{1.714}$ the other.

The data compiled from excursions from high composition are interpreted as relevant to the metastable case in which ι is one boundary and the C-form sesquioxide defines the low composition boundary. Between these, the phase diagram consists of one nonstoichiometric region (σ) and two diphasic regions ($\sigma_a + \sigma_b$ and $\sigma + \iota$) as shown by dashed lines in Fig. 1. The experiments were not sufficiently accurate to elucidate the $PrO_{1.50-1.52}$ and $PrO_{1.65-1.67}$ regions which appear to be single-phased. For this reason we have refrained from using a notation which fixes $\sigma_a =$ C-form Pr_2O_3 or $\sigma_b = \sigma$ when present in the two phase ($\sigma + \iota$) region. It is interesting that the upper limit of composition for the $PrO_{1.65-1.67}$ boundary is equivalent to the phase of composition $PrO_{1.667}$ which belongs to the homologous series, Pr_nO_{2n-2} for $n = 6$.

Despite the difficulty of interpreting unequivocally certain results, the body of evidence is in agreement with the experiments reported here. In contrast to this, Lott et al. (*4*) have recently published some results of their high-temperature solid-state galvanic cell study of the PrO_x system in the composition region $0 \leqslant x \leqslant 1.714$. Their interpretation of these experiments is quite at variance with the results reported in this paper. Specifically they failed to detect the polymorphic C- to A-form transition in the sesquioxide and they also missed the σ, σ_a, and σ_b phases.

The reason for their not detecting the C- to A-form transition may well be due to the transformation of any C-form sesquioxide to A-form when their loaded apparatus was heated to 1000°C to effect the seal by the fusion of the powdered glass. The C–A-form transition is irreversible so their measurements then would indeed be on the A-form only. This preparative heating of the cell would also lead to uncertainty in the composition of the sample to be studied, which is so sensitive to temperature and oxygen pressure. There is no indication that X-ray or other analyses were made on the cell charges before or after their preparation and measurement.

No explanation can be advanced as to why their preparations would not result in the formation of the σ phases, since essentially the same preparative methods were used in this research where clear evidence of the variable σ phase and of the gap yielding σ_a and σ_b were obtained. The high-temperature X-ray work and the tensimetric measurements also confirm these observations. The A-form sesquioxide was indeed observed to transform directly to the ι phase at temperatures below 910°C as indicated above, but if an intermediate composition (even if it were two-phased) were heated above that temperature it would encounter the region of stability of the σ phase.

The $\Delta_R G^\circ$ vs. T plot (Fig. 5 of Lott et al.) shows a large and changing curvature which could perhaps better be represented by two curves intersecting at about 900°C which is the temperature region where some disturbance might well be seen due to phase transitions in the stabilization of the σ phase (Fig. 1). One would need to see the data at several compositions and look for systematic changes in the curvature in this region to verify such transformations.

If the free energy data of Lott et al (*4*) are plotted together with the phase transformation data of Hyde et al. (*1*), as shown in Fig. 3, it is observed that the points below 900°C form a very good extension of the $\sigma - \iota$ phase transition; above this temperature the points lie in the single-phase σ region. This would suggest from the phase diagram (Fig. 1) that their specimen composition must be approximately $PrO_{1.66}$ at about 900°C.

These emf results are very interesting and important but by themselves seem to give little hint of the complexity of the system in this region. It would be very helpful to have X-ray diffraction results confirming the phases present. In particular, as stated above, the technique of sealing the samples at high temperatures is likely to lead to structural changes in the oxide which cannot be regarded either as reversible or even totally reproducible.

The studies described here underline the fact that it is essential to obtain as complete a record of structural changes as is possible in studying non-

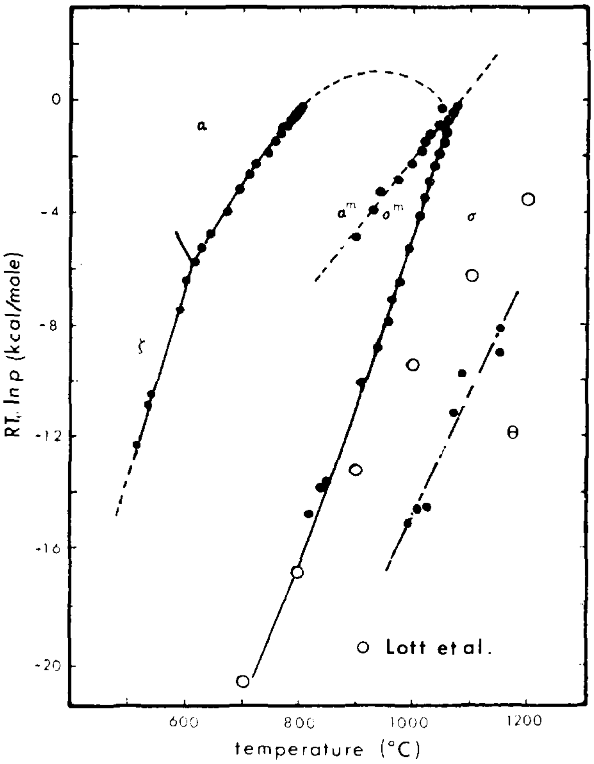

FIG. 3. Comparison of the partial molar free energy of oxygen in PrO_x for phase transitions in the sesquioxide–ι region from tensimetric and emf measurements.

stoichiometric systems before the thermodynamic or kinetic data can be interpreted unequivocally. The experiments outlined above are an attempt to obtain structural information on equilibrium species, and the lack of coordination between all the results reflects the way in which this system changes structurally under very small and subtle changes in the conditions imposed upon it. The importance that structure plays upon the kinetics and path of reaction is shown by the isothermal and isobaric high-temperature X-ray studies. It is apparent that if two ordered or structurally distinct phases are formed at the ends of an oxidation–reduction cycle then considerations which may loosely be described as topotactic may well govern the reaction paths and hence the intermediate phases located in the system. Further structural studies on as fine a scale as possible are needed before the anomalies in this and related systems can be finally explained.

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