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The Stoichiometry of Praseodymium Oxide¹

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The variation in composition of praseodymium oxide has been studied in the range 0.001 to 150 mm. and at temperatures between 400 and 1000°, using a vacuum microbalance. A set of stable compositions which may be represented by the "homologous series" $m\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$ ($0 \leq m \leq 8$) or $\text{Pr}_n\text{O}_{2n-2}$ ($4 \leq n \leq 12$) were encountered. Between 700 and 1000°, it is necessary to exceed a critical pressure which increases from 0.1 to 15 mm. to effect a change from hexagonal Pr_2O_3 to rhombohedral $\text{PrO}_{1.714}$. Enthalpy and entropy changes were calculated for this transition. The experimental results are interpreted in terms of electronic defects which accompany stoichiometry changes. It is pointed out that non-stoichiometric compounds should in general be associated with low entropies of formation.

Introduction

The praseodymium-oxygen system represents an interesting example of a binary inorganic solid which exhibits wide changes in stoichiometry. Stable phases occur over virtually the entire composition range between Pr_2O_3 and PrO_2 . Comprehensive reviews dealing with the physical and chemical properties of praseodymium oxide are available.³

The most reliable studies of the stoichiometry of the praseodymium oxides were made by Ferguson, Guth, and Eyring.⁴ Using conventional, volumetric techniques, they obtained isotherms of sample composition *vs.* pressure at a series of temperatures in the range 400–1050°. On the basis of their results, these authors reported a whole series of single non-stoichiometric and of diphasic composition ranges.

The volumetric procedure does not readily lend itself to precision measurements below 10 mm.; this region was, therefore, not explored to any great extent. Thus, it appeared of interest to complete the study of the PrO_x system by examining composition changes which occur in the low pressure range.

Experimental

The present studies were undertaken with a quartz-beam microbalance with a sensitivity of 0.05 $\mu\text{g.}$ and a reproducibility of 0.1 $\mu\text{g.}$; the design, construction, and operating characteristics of this instrument are described elsewhere.⁵ The balance was placed in a vacuum line and the sample suspended *via* long quartz fibers into a tube surrounded by a furnace. A counter-weighting system, consisting of an enclosed alnico needle, was attached to the other side and a dummy bulb suspended by nearly identical fibers into a matching leg and furnace. Changes in mass were compensated by proportionally altering the current flowing

through a solenoid surrounding the alnico needle. Corrections were applied for thermomolecular gas flow and for buoyancy as described elsewhere.⁵ The thermomolecular perturbations were rather marked in the region of 0.001 to 0.5 mm.; balance compensation settings in this pressure region were subject to greater experimental error than the others. Pressure readings were taken with a McLeod gage or U-tube manometer.

The praseodymium oxide powder was ion-exchanged material with a purity of at least 99.99%. The samples were first heated in air to eliminate the readily volatile impurities, then transferred to the vacuum line and heated under high vacuum at 940° for 15 hr. The final product was a pale green powder which in the subsequent stoichiometry calculations was assumed to have the composition Pr_2O_3 .⁶ After cooling under high vacuum to the desired operating temperature, a null reading was made; then small increments of oxygen gas were admitted to the vacuum line. The system was permitted to equilibrate for periods ranging from one to several hours, depending on the region of the isotherm under study. Equilibrium was considered to have been reached when no change in compensation current was required over a period of 1 hr. In the majority of cases, measurements made after a 10-min. period were the same as those made after the lapse of 15 hr. under identical conditions.

Oxygen was prepared by thermal decomposition of dried KMnO_4 . The first few milliliters were discarded; thereafter, the oxygen was passed through a Dry Ice trap and collected in storage flasks.

Sample temperatures were measured by use of chromel-alumel thermocouples, cemented into the walls of the tube furnace. They were calibrated with a master thermocouple which in turn had been standardized against the freezing points of Pb, Sn, Zn, Sb, Ag, and NaCl. The master thermocouple was placed in the position of the sample during the calibrating runs.

Stable Stoichiometries

Isotherms of composition, expressed as x in PrO_x , *vs.* oxygen pressure are shown in Fig. 1–4. Extensive tabulations of the data are available.^{3b} In general, the precision of the experimental points may be represented by circles whose diameter is roughly twice the thickness of the curves. To save space, the steeply rising portions for the isotherms in the ranges $1.5 \leq x \leq 1.72$ and $1.50 \leq x \leq 1.80$ were omitted from Fig. 1 and 2.

The majority of isotherms are characterized by the presence of plateaus which represent stable, non-stoichiometric compositions. In some instances, these

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(2) Lincoln Laboratory, Massachusetts Institute of Technology, Lexington 73, Mass.

(3) (a) J. M. Honig, "Literature Review on Properties of Praseodymium and Cerium Oxides," AFOSR Report TN-58-57, Astia Report No. AD 148 098, January, 1958; (b) P. A. Faeth, Ph.D. Thesis, Purdue University, June, 1961; (c) L. Eyring and N. C. Baenziger, *J. Appl. Phys.*, **33**, 428 (1962).

(4) R. E. Ferguson, E. D. Guth, and L. Eyring, *J. Am. Chem. Soc.*, **76**, 3890 (1954).

(5) A. W. Czanderna and J. M. Honig, *Anal. Chem.*, **29**, 1206 (1957).

(6) This composition was checked independently by an analytic determination of Pr^{+3} after dissolving an aliquot in nitric acid.

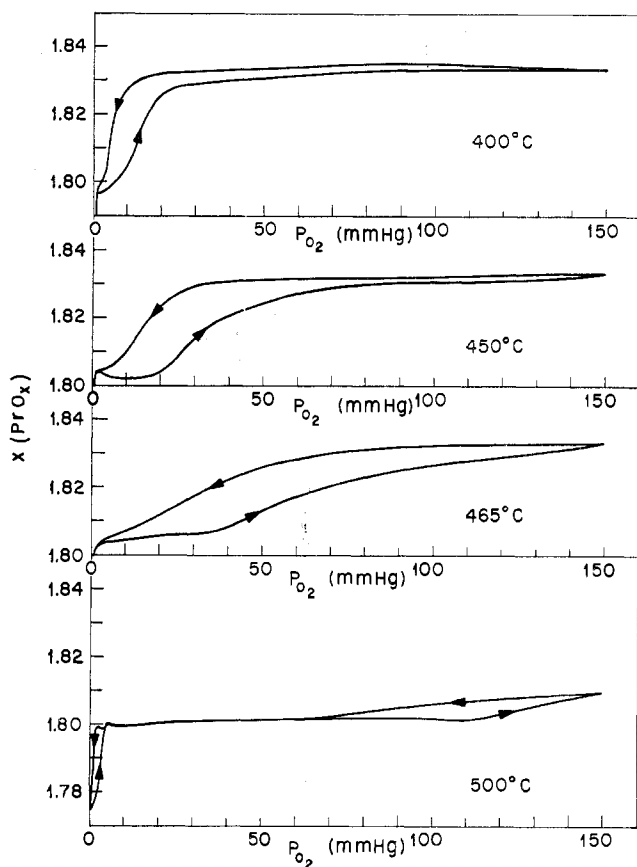


Fig. 1.—Isotherms for the composition of praseodymia *vs.* partial oxygen pressure in the range 400–500°. The steeply rising portions of the isotherms below 2 mm. have been omitted.

plateaus are interconnected *via* nearly vertical steps, which presumably represent biphasic regions; in other cases, they are connected by sloping isotherms which indicate bivariant domains, *i.e.*, single phases exhibiting relatively large stoichiometry ranges.

Values of the x in the formula PrO_x that correspond to stable stoichiometries are entered in column 1 of Table I. The remaining columns in that table show that the stable compositions may be represented by the formulas $m\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$, $\text{Pr}_{4+m}\text{O}_{6+2m}$, or $\text{Pr}_n\text{O}_{2n-2}$. The first designation is not meant to imply that compounds of intermediate compositions are mixtures of Pr_2O_3 and PrO_2 . However, it is noteworthy that the stable stoichiometries can be represented as integral combinations involving the end members in the series. The formulation $\text{Pr}_n\text{O}_{2n-2}$ conforms to the homologous series concept which has been used by Wadsley^{7a} and by Magnéli and co-workers^{7b} in the interpretation of the structure of oxides where the cation can assume several valence states. Portions of the curves in Fig. 1–4 which deviate appreciably from horizontal or vertical indicate single-phase material whose oxygen solubility range is very large.

Three biphasic regions were encountered in the following ranges: (a) $1.504 < x < 1.713$ for $890 > T > 695^\circ$; (b) $1.500 < x < 1.800$ for $500 > T > 400^\circ$; (c) $1.718 < x < 1.776$ for $T \approx 600^\circ$. While only three

(7) (a) A. D. Wadsley, *Rev. Pure Appl. Chem.*, **5**, 165 (1955); (b) S. Ander-son, A. Sundholm, and A. Magnéli, *Acta Chem. Scand.*, **13**, 989 (1959).

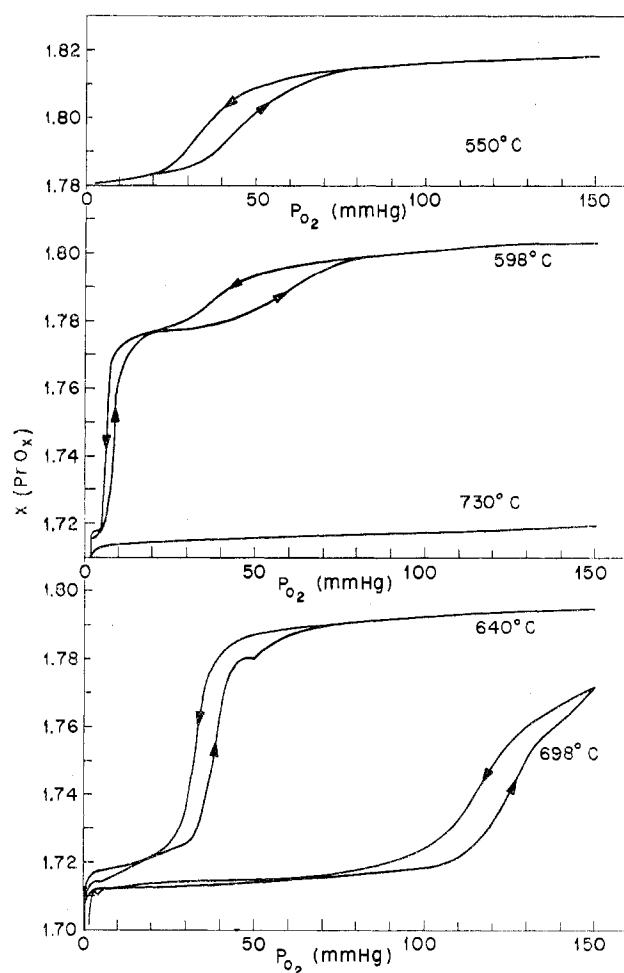


Fig. 2.—Isotherms for the composition of praseodymia *vs.* partial oxygen pressure in the range 550–730°. The steeply rising portions of the isotherms below 2 mm. have been omitted.

such regions could definitely be identified, the isotherms of Fig. 1–4 suggest the possible existence of others which might be encountered under different operating conditions. Careful examination of the data shows incipient biphasic regions covering the stoichiometry ranges $x = 1.67$ – 1.70 , 1.70 – 1.71 , 1.78 – 1.80 , and 1.80 – 1.83 . This suggests that, under suitable conditions of temperature and oxygen pressure, discontinuous transitions between all of the various stoichiometries listed in Table I might be achieved.

TABLE I
A POSSIBLE SERIES OF RATIOS OF Pr^{+4} TO Pr^{+3}

Exptl. regions of stability	Indicative compn. ratio ^a	Theor. x value	Simple ratio $\text{PrO}_2/\text{Pr}_2\text{O}_3$	Reduced ratio
1.50	Pr_2O_3	1.500	0:1	0
1.62	$\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.600	0.5:1	1
1.67	$2\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.667	1:1	2
1.71	$3\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.714	1.5:1	3
Not found ^b	$4\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.750	2:1	4
1.78	$5\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.778	2.5:1	5
1.80	$6\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.800	3:1	6
1.82	$7\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.818	3.5:1	7
1.833	$8\text{PrO}_2 \cdot 2\text{Pr}_2\text{O}_3$	1.833	4:1	8

^a The symbolism used here is not to be interpreted as indicating a physical mixture of PrO_2 and Pr_2O_3 . ^b See, however, U. E. Kuntz and L. Eyring in "Kinetics of High Temperature Processes," W. D. Kingery, Ed., John Wiley and Sons, New York, N. Y., 1959, Chapter 8.

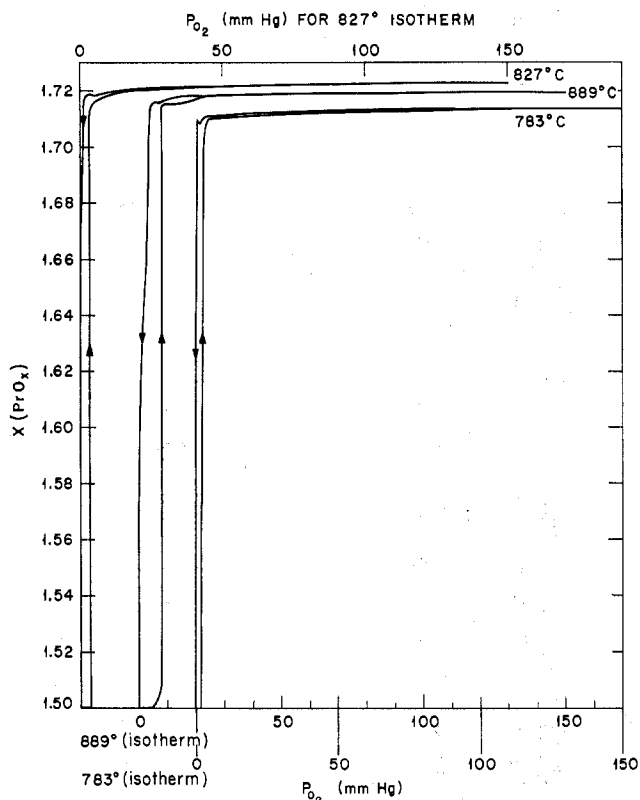


Fig. 3.—Isotherms for the composition of praseodymia vs. partial oxygen pressure in the range 783–889°. The increasing degree of hysteresis with rising temperature is noteworthy.

A preliminary X-ray study⁸ on quenched samples has shown that PrO_x does indeed undergo phase changes in the vicinity of the x values shown in Table I. Accordingly, each listed composition is likely to represent a different phase and structure.

On the whole, the agreement between our work and that of Eyring and co-workers is very satisfactory, both as regards the experiment and interpretation. The isotherms of Fig. 1–4 interleave reasonably well with those in ref. 4. Where minor discrepancies arise, they probably can be traced to difficulties in measuring the sample temperatures. There is no disagreement regarding the general trend of the isotherms with temperature. Because of the availability^{8b} of measurements in the 0–10 mm. pressure range, we could establish the existence of biphasic regions (a) and (b) mentioned earlier, which had been reported as incipient by Eyring and co-workers. We agree with the earlier workers regarding both the remaining number of incipient biphasic regions and the stoichiometry ranges in which they are likely to be located.

In Fig. 5 is shown the 150-mm. isobar over the 300–900° range. Measurements obtained with the microbalance⁹ are indicated by open circles and triangles, those read from Fig. 1–4 are entered as squares, and those taken from ref. 4, as closed circles. This graph is of interest since it is representative of the compositions which are obtained by heating praseodymium oxide in air. The various sets of results are

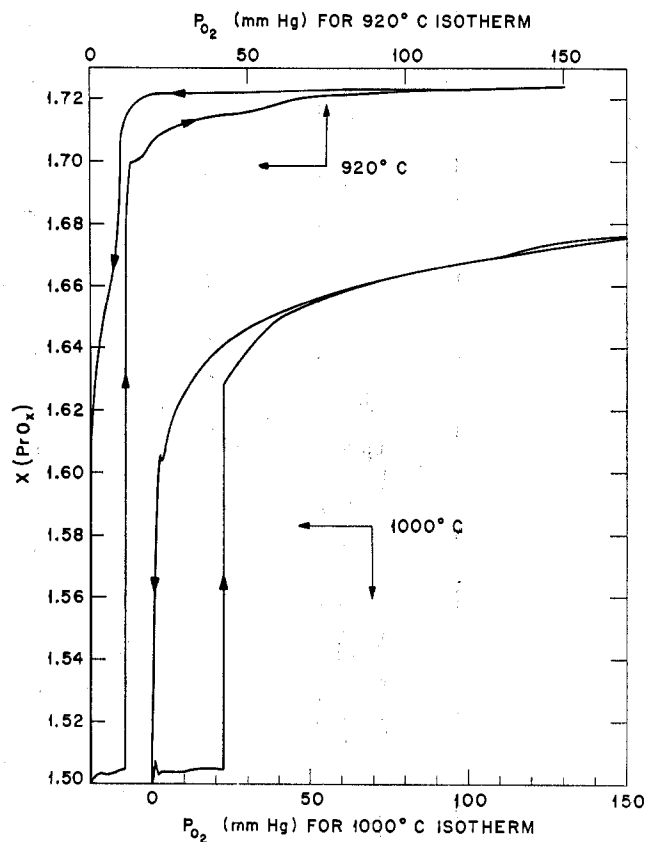


Fig. 4.—Isotherms for the composition of praseodymia vs. partial oxygen pressure in the range 920–1000°. The increasing degree of hysteresis with rising temperature is noteworthy.

in excellent agreement. It is noteworthy that in the literature the compound having the composition Pr_6O_{11} ($x = 1.833$) usually is cited. While this is certainly a stable phase, both the gravimetric and volumetric work show that the intermediate composition $x = 1.714$, in which Pr^{+3} and Pr^{+4} occur in equimolar (equielectronic) amounts according to Table I, also is very stable.

It is of great interest that virtually all isotherms show evidence of hysteresis. This phenomenon will be made the subject of a separate study in another paper. However, a few guiding remarks are essential to the present discussion: The loops are most marked in the bivariant regions of the isotherms and practically non-existent in regions of phase stability. These loops cannot be ascribed to kinetic effects: as will be more fully documented in a subsequent publication, the hysteresis effects for starting materials with the same composition and structure are completely reproducible, and the loops show no tendency to shrink or collapse when more time is taken to traverse the isotherms. Moreover, raising the temperature usually has the effect of increasing the size of the loops. No hysteresis effects have been reported in ref. 4; apparently this is due to the fact that these workers traced out isotherms in the forward and reverse directions only at 527 and 1050°. It so happens that the loops in these two cases are either small or else occur at the low pressure end which is out of reach of precision volumetric determinations. However, in earlier data released by Ferguson,

(8) C. N. R. Rao, P. A. Faeth, and J. M. Honig, unpublished.

(9) A. W. Czanderna, Ph.D. Thesis, Purdue University, 1958.

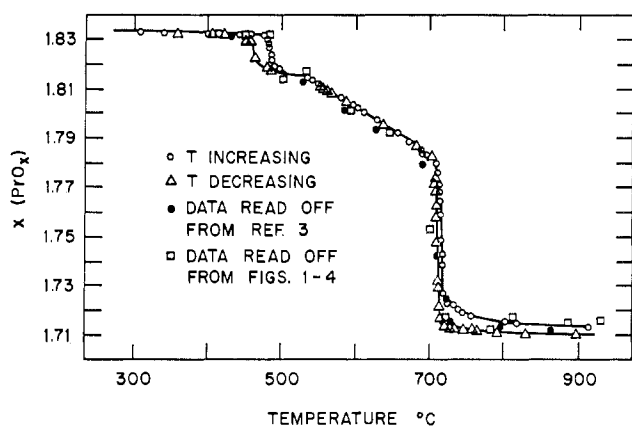


Fig. 5.—The composition of praseodymia as a function of temperature at $p_{O_2} = 150$ mm.

Guth, and Eyring¹⁰ hysteresis effects similar to ours are detectable.

The hysteresis phenomenon is of great importance in the preparation of quenched samples for X-ray analysis or other purposes. Under conditions where hysteresis is marked, the final sample composition will depend on the thermal history of the sample. For this reason, many of the stability limits cited in the literature in conjunction with X-ray analyses on quenched samples are in doubt.

Low Pressure Region of the Isotherms

A phenomenon related to hysteresis is the initial uptake of oxygen gas by Pr_2O_3 above 600° . Examination of the isotherms in Fig. 3 and 4 shows that Pr_2O_3 , prepared by overnight heating under high vacuum, suffers little change in composition until a critical pressure, p_C , is reached. At that point an extremely rapid and very pronounced uptake of oxygen occurs. This phenomenon is reminiscent of cooperative processes; roughly similar effects have been reported by Smyth and Roberts¹¹ in the $Cu_2O-CuO-O_2$ system.

If, on reaching the plateau at $x = 1.714$ the gas pressure is diminished, one ultimately returns to the starting material, Pr_2O_3 , but the return loop differs very considerably from the forward loop. This effect cannot be ascribed to kinetic effects because p_C increases with increasing temperature. Furthermore, the absorption of oxygen at the critical pressure p_C is very rapid, and the evolution of oxygen on the return loop follows the general pattern mentioned in the Experimental section.

In the absence of X-ray data taken concurrently with the gravimetric measurements, the interpretation of this hysteresis effect remains uncertain. An ultimate explanation must be consistent with the fact that Pr_2O_3 , as prepared by overnight heating under vacuum at 940° , is in the hexagonal configuration,^{12,13} which

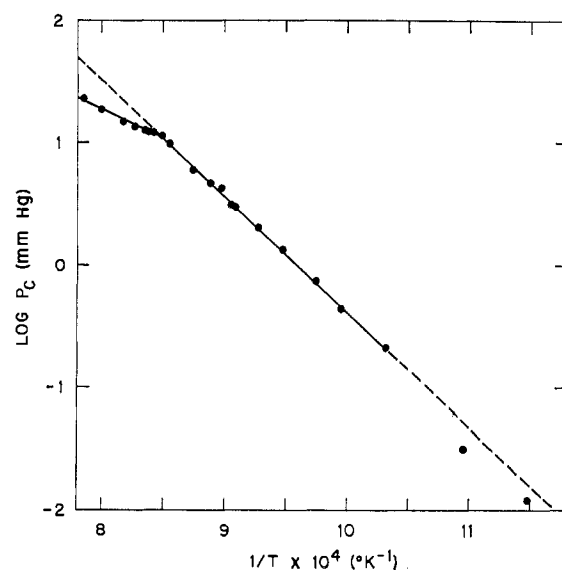


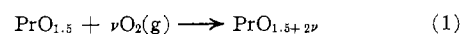
Fig. 6.—Plot of critical pressure vs. reciprocal temperature.

exhibits only a limited variation in stoichiometry. $PrO_{1.714}$ is rhombohedral,³⁰ whereas the composition range $1.70 \gtrsim x \gtrsim 1.63$, which is traversed gradually on the return loop, is inhabited by the bcc structure of roughly constant lattice parameter.

A plot of $\log p_C$ vs. $1/T$ is shown in Fig. 6. One may distinguish between two linear regions separated by an abrupt change in slope. The greater slope extends over a temperature range from 600 to 900° in which the sample composition on completion of the transition remains near $x_C = 1.714$. Above 900° , x_C drops with rising temperature, and this effect presumably is responsible for the change in slope of Fig. 6, as detailed later. Below 600° , the graph may again exhibit an increase in slope, but this is uncertain since the measured p_C values are subject to considerable experimental error in this range.

Discussion

The transitions described above proceed at a constant pressure p_C for a fixed temperature and therefore are subject to the following thermodynamic treatment¹⁴: For a heterogeneous system, the free energy change associated with the reaction



is given by

$$\Delta F = \Delta F^0 + kT \sum_i \nu_i \ln a_i \quad (2)$$

where $\Delta F^0 \equiv \sum_i \nu_i \mu_i^0 = -kT \sum_i \nu_i \ln a_i^{eq}$ is the free

energy change for eq. 1 under standard state conditions, ν_i the stoichiometry number of species i in eq. 1, and a_i and a_i^{eq} are the corresponding activities of each species for the process occurring at pressure p_C and under equilibrium conditions, respectively. This relation applies whether or not the process occurs at equilibrium. Writing $\Delta F = \Delta H - T\Delta S$, one may reformulate (2) as in eq. 3.

(14) F. H. McDougall, "Thermodynamics and Chemistry," John Wiley and Sons, New York, N. Y., 1939.

(10) R. E. Ferguson, E. D. Guth, and L. Eyring, Doc. No. 4204 ADI, Auxiliary Publications Project, Library of Congress, Washington, D. C.

(11) F. H. Smyth and H. S. Roberts, *J. Am. Chem. Soc.*, **42**, 2582 (1920).

(12) A. Iandelli, *Gazz. chim. ital.*, **77**, 312 (1947).

(13) L. Eyring, H. R. Lohr, and B. B. Cunningham, *J. Am. Chem. Soc.*, **74**, 1186 (1952).

$$\log p_c = \frac{\Delta S - \Delta S^0}{2.303\nu R} + \frac{1}{\nu} \log \frac{a_{1.714}}{a_{1.5}} - \left(\frac{\Delta H - \Delta H^0}{2.303\nu R} \right) \frac{1}{T} \quad (3)$$

Providing that $\Delta S - \Delta S^0$, $\Delta H - \Delta H^0$, and the activity ratio in (3) remain sensibly independent of temperature, the slope of the 600–900° portion in Fig. 6 (for which $\nu = 0.107$) yields a value for $(\Delta H^0 - \Delta H)/2.303\nu R$ and the intercept is given by the first two terms on the right of eq. 3. In this way, one obtains

$$\begin{aligned} \Delta H - \Delta H^0 &= +(4.64 \pm 0.08) \text{ kcal./mole of Pr} \\ &= +(43.4 \pm 0.4) \text{ kcal./mole of O}_2 \end{aligned} \quad (4)$$

$$\begin{aligned} (\Delta S - \Delta S^0) + 2.303R \log \frac{a_{1.714}}{a_{1.5}} &= \\ &+ (3.05 \pm 0.05) \text{ cal./deg.-mole of Pr} \end{aligned} \quad (5a)$$

$$\begin{aligned} \Delta S - \Delta S^0 + \frac{2.303R}{0.107} \log \frac{a_{1.714}}{a_{1.5}} &= \\ &+ (28.5 \pm 0.5) \text{ cal./deg.-mole of O}_2 \end{aligned} \quad (5b)$$

Since $a_{1.714}$ and $a_{1.5}$ represent the activities of the pure solids, no serious error is made in setting $a_{1.714} \approx a_{1.5} \approx 1$, as a first approximation, thereby neglecting the logarithmic terms in (5).

Standard enthalpies of formation have been cited by Stubblefield, Eick, and Eyring¹⁵ from measurements of the heats of solution of PrO_x in nitric acid; their data yield a value of $\Delta H^0 = -(6.1 \pm 1.6)$ kcal./mole of Pr for reaction 1 with $\nu = 0.107$ under standard conditions. Since the variation of ΔH^0 with x ($= 1.5 + 2\nu$) is linear,¹⁵ one also can utilize data cited by Kuznetsov and Rezukhina¹⁶ for Pr_6O_{11} to calculate a value of $\Delta H^0 = -(5.6 \pm 0.4)$ kcal./mole of Pr for reaction 1 with $\nu = 0.107$. Similar interpolations carried out on older data concerning the heats of formation of Pr_2O_3 and PrO_2 , as assembled in the Bureau of Standards tabulation,¹⁷ yield a value of $\Delta H^0 = -5.1 \pm 2.0$ kcal./mole of Pr for reaction 1 with $\nu = 0.107$. Using the figure $\Delta H^0 \approx -5.6$ kcal./mole of Pr as a rough average, it is seen that for reaction 1 with $\nu = 0.107$, $\Delta H \approx -1$ kcal./mole of Pr.

If ΔS and ΔS^0 are taken to be roughly independent of x , then the change in slope in Fig. 6 may be associated with the alteration in ΔH^0 as x_c diminishes with increasing temperatures above 900°. Data pertaining to reaction 1 at 1000° are available for $x_c = 1.630$; setting $\nu = 0.065$ one obtains

$$\begin{aligned} \Delta H - \Delta H^0 &= +(3.31 \pm 0.16) \text{ kcal./mole of Pr} \\ &= -(51.0 \pm 0.8) \text{ kcal./mole of O}_2 \end{aligned} \quad (6)$$

According to Kuznetsov and Rezukhina¹⁶ the standard entropy change for reaction 1 with $\nu = 0.167$ at 298°K. is $\Delta S^0 = -25.35$ e.u./mole of O_2 . Adopting this value, ignoring the logarithmic term in (5) as well as the small dependence of ΔS^0 on x and T , one finds that $\Delta S = +3.1$ e.u./mole of O_2 .

From these admittedly crude estimates, it is seen that the ΔH and ΔS values for the conversion of $\text{PrO}_{1.5}$ to $\text{PrO}_{1.714}$ do not differ very much from the quantities

ΔH^0 and ΔS^0 for the reaction under standard conditions.

The value for $|\Delta S^0|$ cited in ref. 16 is anomalously small; this fact may be brought out in one of two ways: (a) According to standard methods of statistical mechanics,¹⁴ the entropy change corresponding to the removal of one mole of oxygen from the gas phase under standard conditions is $\Delta S^0 = -49$ e.u. In the majority of cases the observed ΔS^0 values for the oxidation of metals lie in the range -42 to -44 e.u. per mole of O_2 ,¹⁸ which suggests that under normal circumstances the incorporation of oxygen in a solid during the oxidation process entails an entropy increase of roughly 5 to 7 e.u. (b) The average *differential* molar standard entropy change for the reaction $(2/\delta)\text{CeO}_x + \text{O}_2 \rightarrow (2/\delta)\text{CeO}_{x+\delta}$ as determined in the range 700–1010° using wüstite as electrolyte¹⁹ is $\Delta S^0 = -49.6$ e.u./mole of O_2 and is independent of x in the range $1.58 < x < 1.71$. One would not expect this quantity to be significantly different for PrO_x .

In an attempt to explain the anomalously small $|\Delta S^0|$ value cited in ref. 16 for reaction 1 with $\nu = 0.167$, one must take account of the following factors: (i) Reaction 1 is accompanied by a phase transition, with a concomitant entropy change. (ii) Not all of the oxygen ions in $\text{PrO}_{1.714}$ may be stationary. If there is a random hopping of anions to adjacent vacancies, the entropy of the system is increased over that of a lattice in which all constituents are immobile, and ΔS^0 for reaction 1 is correspondingly reduced. Some support for this hypothesis is gained from the fact that the mobility of oxygen through PrO_x is sufficiently high so that stoichiometry changes can be brought about at temperatures as low as 300°. (iii) The incorporation of oxygen in the lattice involves the destruction of lattice vacancies.³⁰ This causes a change in the configurational entropy that can be estimated to be roughly -6 e.u./mole of O_2 , since in cubic $\text{PrO}_{1.5}$ there exist 0.5 mole of anion vacancies and 1.5 moles of O^{-2} per mole of Pr, whereas in $\text{PrO}_{1.714}$, regarded as $3\text{PrO}_2 \cdot 4\text{PrO}_{1.5}$, there exist 2 moles of vacancies and 12 moles of O^{-2} per 7 moles of Pr. (iv) The incorporation of oxygen is accompanied by drastic changes in the electrical properties of praseodymia,²⁰ which is indicative of severe perturbations in the electronic structure of the solid. There is no electronic disorder in $\text{PrO}_{1.5}$; if $\text{PrO}_{1.714}$ is again considered to be $3\text{PrO}_2 \cdot 4\text{PrO}_{1.5}$, and if, as is likely,^{3b,20} this represents a random distribution of 3 moles of Pr^{+4} and 4 moles of Pr^{+3} among 7 moles of cation sites, then the corresponding configurational entropy change is 13 e.u./mole of O_2 .

The importance of (iii) and (iv) on the ΔS^0 values is brought out by the following experimental facts: (a) The standard entropies of formation¹⁸ in the range -42 to -44 e.u./mole of O_2 refer to the formation of

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(16) A. Kuznetsov and T. N. Rezukhina, *Zh. Fiz. Khim.*, **36**, 1304 (1962).

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