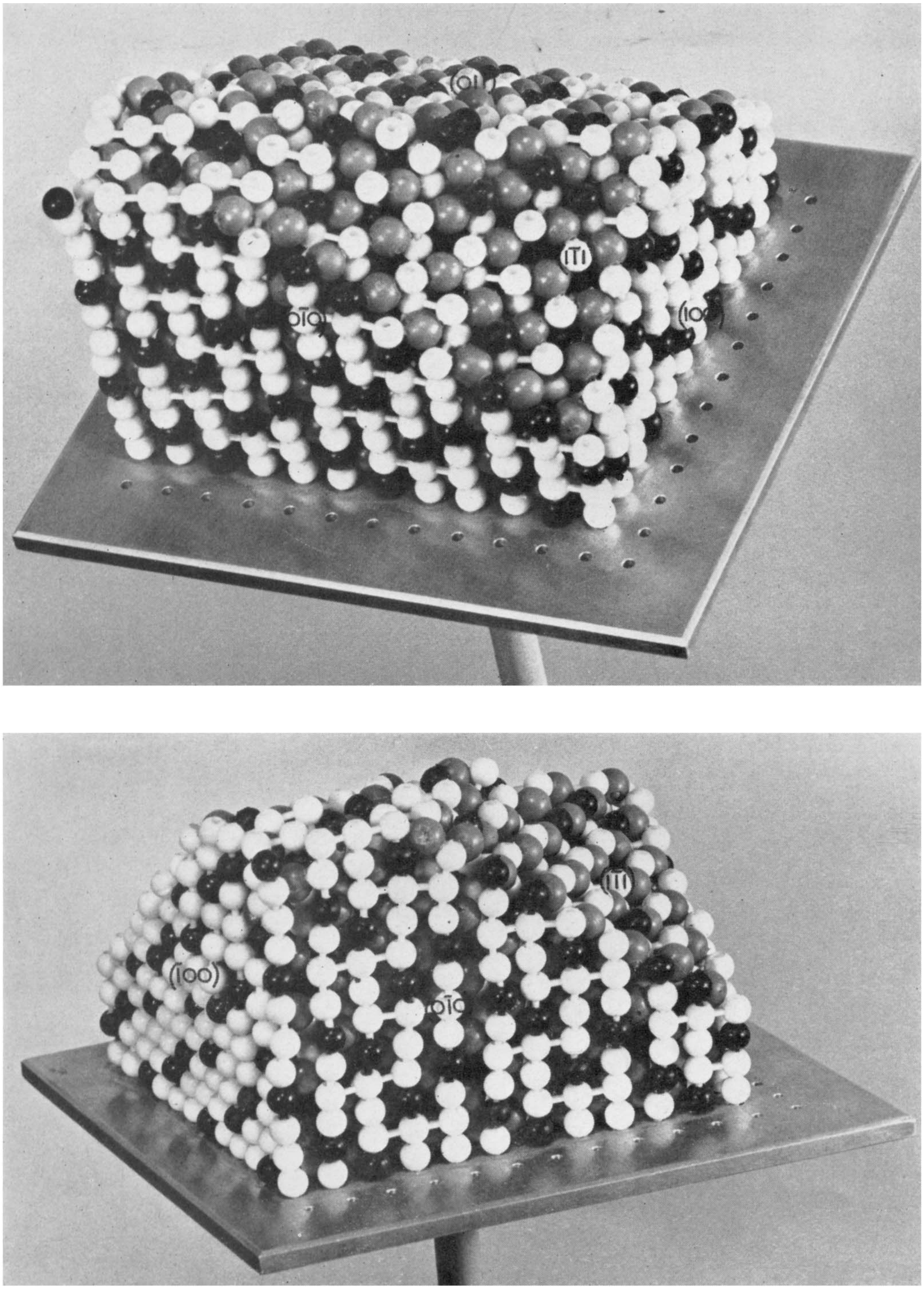
9. *The Oxidation of Praseodymium Oxide. Part I. Chemisorption on Praseodymium Oxide.*

By J. S. Anderson and K. J. Gallagher.

Both type C and type A modifications of $PrO_{1\cdot5}$ chemisorb oxygen at $-196°$ with little or no activation energy. The amount of oxygen chemisorbed per unit surface area is greater on material of type C than on material of type A, and this difference is attributed to the high concentration of anion vacancies in the former. Anion vacancies are inherent in the type C structure but are absent from the type A structure which is close-packed. It is suggested that the extent to which type A $PrO_{1\cdot5}$ chemisorbs oxygen is a measure of the average "defect" co-ordination number of oxygen ions around praseodymium ions on the surface.

Both carbon dioxide and hydrogen are strongly bound by $PrO_{1\cdot5}$ surfaces and are extremely difficult to remove, even at high temperatures. Their presence on the surface diminishes its chemisorptive capacity for oxygen.

Discussion of gas–solid reactions is severely limited by paucity of information about the detailed mechanism of (*a*) the chemisorption step and (*b*) the way in which the reacting species is transferred into the solid phase. In particular, such questions as whether diatomic gases necessarily dissociate during chemisorption, whether O_2^- and O^- occur as intermediate species in the formation of O^{2-} and, if so, at what stage, remain largely unanswered. The answers that may be applicable to reaction on a perfectly bare metal



PLATE

Two views of a model of the type C structure of $PrO_{1\cdot5}$, showing O^{2-} ions (white), Pr^{3+} ions (grey), and anion vacancies (black). The model is intended primarily to show the different distributions of anion vacancies which the type C structure develops on different crystallographic faces. It was more convenient to build a model in which the radius of the cation is larger than that of the anion, but this does not affect the relative positions of the anion vacancies.

surface (cf. Ehrlich[1]) may be inapplicable to reactions of molecular oxygen on the surface of a metallic oxide, where the binding energies of chemisorbed oxygen species necessarily vary greatly from point to point.

Because it is in certain features simpler than most other systems commonly studied, the oxidation of certain lanthanide and actinide oxides was attractive. We have studied the chemisorption of oxygen on praseodymium sesquioxide and the kinetics of the subsequent oxidation; in this paper we report the results for chemisorption.

In the actinide series, the UO_2–O_2 system has been much studied by others. At −183°, uranium dioxide chemisorbs the equivalent of 0·5—0·8 of a physically adsorbed monolayer of oxygen; the activation energy of the process is zero or very small,[2] and the heat of adsorption is large.[3] Above about −180° the chemisorbed oxygen enters the uranium dioxide lattice.[4] In the range −130° to +50° (approximately) the rates of reaction follow a formal logarithmic law and above ~50° the parabolic law for bulk diffusion was obeyed. It appeared to us advantageous to study adsorption by lanthanide oxides. Uranium(V) and uranium(VI) compounds commonly show a strong association with oxygen, giving UO_2^+ or UO_2^{++} structural units, so it was possible that such oxy-ions might affect the oxidation behaviour of uranium dioxide and its solid solutions. Lanthanon sesquioxides with the so-called type C structure have essentially the fluorite structure and form complete ranges of solid solution with the fluorite-type oxides MO_2. A type C oxide containing oxidisable lanthanon cations, *e.g.*, Pr^{3+} or Tb^{3+}, can thus take up oxygen, in the same way as do anion-deficient systems containing uranium(IV), *e.g.*, UO_2–Y_2O_3 solid solutions.[5] In this case, however, there is no possibility of special association between the higher-valent cations and oxygen.

Praseodymium oxide and its mixed crystals thus provide an opportunity to test the general validity of the results deduced for uranium dioxide. Praseodymium gives two limiting oxides, $PrO_{1\cdot5}$ and PrO_2, and a series of oxides of intermediate composition. Praseodymium oxide, as normally prepared by ignition in air, has the composition $PrO_{1\cdot83}$. An oxide PrO_2 can be obtained at very high oxygen pressures[6] and is isostructural with UO_2; $PrO_{1\cdot5}$ possesses the type C or the type A structure typical of the rare earths, depending on whether the reduction from the higher oxide is carried out below or above ~700°, respectively.[7] These will hereafter be denoted by $(PrO_{1\cdot5})_C$ and $(PrO_{1\cdot5})_A$. The type C (bixbyite) structure is very closely related to the fluorite structure, being derived from it by the removal of a quarter of the oxygen ions from certain ordered positions (production of anion vacancies), yielding a space group of lower, though still cubic, symmetry.[8,9] The remaining oxygen ions are only slightly displaced from their fluorite positions, so that a model of the fluorite structure with the appropriate oxygen atoms absent is a very close approximation to the true structure of the type C oxide. Such a simplified structure, in which the black beads mark the vacant oxygen sites, is illustrated in Plate 1. It follows from its relation to the fluorite structure that, in addition to anion vacancies, the type C structure contains the same octahedral interstices as those which accommodate the excess oxygen in the oxidation of UO_2 to UO_{2+x}.

$(PrO_{1\cdot5})_A$, on the other hand, has a close packed structure[10] in which neither interstitial sites nor anion vacancies are available to reacting oxygen ions. The two forms of praseodymium oxide provide a unique opportunity to compare the effect of structural changes alone on the chemisorption. In this paper we discuss the chemisorption on type A

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[1] Ehrlich and Hudda, *J. Chem. Phys.*, 1960, **33**, 1253.
[2] Roberts, *J.*, 1954, 3332.
[3] Ferguson and McConnell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 67.
[4] Anderson, Roberts, and Harper, *J.*, 1955, 3946.
[5] Ferguson and Fogg, *J.*, 1957, 3679.
[6] Simon and Eyring, *J. Amer. Chem. Soc.*, 1954, **76**, 5872.
[7] Iandelli, *Gazzetta*, 1947, **77**, 312.
[8] Pauling and Shappell, *Z. Krist.*, 1930, **75**, *A*, 128.
[9] Dachs, *Z. Krist.*, 1956, **107**, 370.
[10] Pauling, *Z. Krist.*, 1929, **69**, 415.

and type C praseodymium oxide. As is the case with uranium dioxide, chemisorption of oxygen is almost instantaneous at liquid-air temperatures, but in amounts considerably less than for the dioxide UO_2.

EXPERIMENTAL

Preparation of Praseodymium Oxide.—Praseodymium oxide was separated in 6 g. amounts on a large column (100 × 4 cm.) filled with Dowex 50-X8 ion-exchange resin (50—100 mesh). The starting material was a rare-earth oxide mixture from Johnson and Matthey who supplied the following analysis: Pr 77%, La 22·5%, and Nd 0·5%. This was dissolved in dilute hydrochloric acid, adsorbed on the column, and eluted with 0·5% ammonium citrate solution at pH 4·64 and a flow rate of 500 ml./hr. These conditions are similar to those used by Spedding,[11] except that the temperature of the column during elution was maintained at 80° instead of room temperature. Although considerable resolution of the peaks occurs, the bands are not completely separated on this scale even under optimum conditions. The minimum limit of detection of neodymium in praseodymium is about 0·05% by the standard analytical methods. For a more sensitive analysis the isotopic dilution method was used. A small quantity of the radioactive ^{147}Nd was added before the lanthanons were adsorbed on to the column and the eluate was passed through a liquid-flow counter. Praseodymium was collected after the neodymium activity had dropped to a level indistinguishable from the background count. From these fractions the praseodymium was precipitated as the oxalate and the radioactivity of the dried precipitates determined. From the initial activity of the original material (after correction for decay) the neodymium content was estimated to be not more than 10 parts per million in these fractions.

The praseodymium oxalate so obtained was ignited to oxide. This was dissolved in dilute hydrochloric acid and reprecipitated as oxalate by the homogeneous precipitation technique with methyl oxalate (cf. ref. 12).

The pure oxalate samples, except Y3c, were ignited at 930—950° in an open platinum crucible for 20—30 min., during which the furnace was occasionally flushed with air to remove the carbon dioxide produced. On removal from the furnace, samples were immediately placed in a desiccator containing potassium hydroxide pellets as a precaution against poisoning of the freshly ignited PrO oxide surfaces with atmospheric carbon dioxide. The temperature of ignition must be well above 833°, which is the dissociation temperature of the dioxide carbonate ($Pr_2O_2 \cdot CO_3$) at atmospheric pressure (see below).[13] The oxide Y3c, which was ignited at 838°, showed zero chemisorption of oxygen at −196°, indicating that a clean $PrO_{1 \cdot 5}$ surface was by no means obtained. Unfortunately, the high temperature required to ensure complete decomposition of the dioxide carbonate limits the surface area obtainable by this method of producing oxide. Three samples, designated X1, Y2, and Y3, were used. The sequence of reprecipitation as oxalate and reignition to oxide is described by an additional letter, a, b, c, etc. Conditions of ignition of the precipitated oxalate are given in Table 1.

TABLE 1.

Conditions of ignition in the preparation of praseodymium oxide from precipitated praseodymium oxalate.

Sample no.	Sample wt. in bulb (g.)	Ignition of oxalate in air		Sample no.	Sample wt. in bulb (g.)	Ignition of oxalate in air	
		Temp.	Time (min.)			Temp.	Time (min.)
X1a	0·411	900—1000°	15	Y3e	2·375	940°	20
Y3b	2·632	950	30	Y3f	2·287	947	20
Y3c	2·540	838	30	Y3g	2·216	945	15
Y3d	2·441	940	30	Y2b	1·320	910	15

Purification of Gases.—Cylinder hydrogen was used for reduction and dead-space calibration at low temperatures, and was purified by passage through a commercial " Deoxo " unit and a liquid-air trap, over red-hot nickel wire, through two more liquid-air traps the second of which was packed with copper turnings to ensure maximum cooling, and, finally, over glass wool to hold back ice.

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[11] Spedding, *Discuss. Faraday Soc.*, 1949, **7**, 214.

[12] Gordon, Vanselow, and Willard, *Analyt. Chem.*, 1949, **21**, 1323.

[13] Preiss and Rainer, *Z. anorg. Chem.*, 1923, **131**, 287,

Oxygen was prepared by heating crystalline "AnalaR" potassium permanganate and passed through potassium hydroxide pellets and a liquid-air trap, the first gas portions being discarded.

Carbon monoxide, prepared from sulphuric acid and formic acid, passed successively through potassium hydroxide pellets, a liquid-air trap, copper turnings at 500° (which were blistered by repeated oxidation and reduction to increase the surface area), potassium hydroxide pellets, a liquid-air trap, and glass wool on which sodium had been evaporated (to remove traces of oxygen and water vapour [14]).

Spectroscopically pure nitrogen, supplied by the British Oxygen Co., was used as such.

Apparatus and Procedure.—Measurements were carried out in a high-vacuum apparatus similar to that used by Roberts.[2] The dimensions and design of the Vitreosil adsorption bulb in which the specimens were contained are shown in Fig. 1. Pumping of samples was carried out through the wide-bore lead A, which was connected to the pumps by a tube of large diameter, so that the resistance to pumping was almost entirely due to the constriction B and the platinum wire plug (this plug was inserted to prevent oxide from being blown out of the bulb). During the filling of the adsorption bulb the praseodymium oxide powder was exposed to the atmosphere for not longer than 1 hr. The amount of atmospheric carbon dioxide adsorbed by the powder in this time was estimated to be negligible. Dead-space volumes were calibrated by using pure hydrogen. It was shown that hydrogen is not chemisorbed by reduced or oxidised praseodymium oxide below room temperature. At temperatures above room temperature, dead-space volumes were calibrated with pure nitrogen.

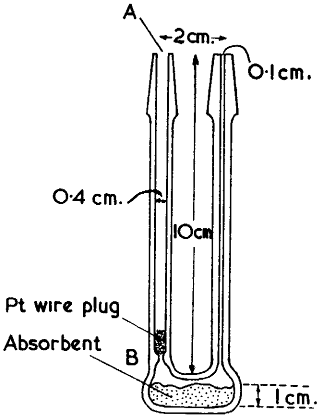

FIG. 1. Adsorption bulb.

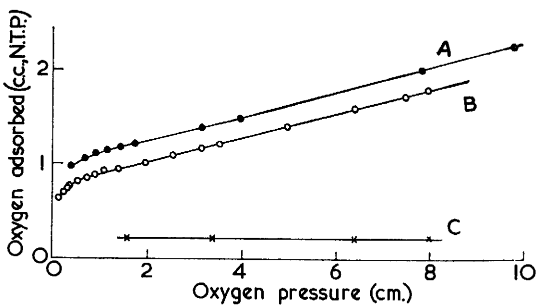

FIG. 2. Oxygen isotherms on (A) reduced and (B) oxidised surfaces of sample no. Y3f of $(PrO_{1\cdot5})_C$ at −196°. The amount of oxygen chemisorbed (plot C) is the difference between curves (A) and (B).

The highly basic rare-earth oxides attack silica at high temperatures, but a test showed no corrosion of the glazed surface of a silica boat containing praseodymium oxide in 1 hr. at 1000°. At the outset of the work a platinum liner was incorporated in the adsorption bulb, but since it added considerably to the experimental difficulties it was abandoned later; nevertheless, the temperature necessary for the different operations in the silica adsorption bulb was kept to a minimum.

An oxide $PrO_{1\cdot83}$ was reduced to $PrO_{1\cdot5}$ by streaming hydrogen at atmospheric pressure, at the rate of 30 c.c./min. for 1 hr., through the bulb at a temperature which depended on whether type A or type C product was required. It was found by *X*-ray diffraction analysis that above ~700° reduction produced type A and below this temperature type C material, in agreement with Iandelli's work.[7] In general, type C oxide was obtained by reduction at 500—600°, and type A at 850—950°. It was found that reduction in very dry hydrogen began at temperatures as low as 200°. The standard period of reduction between adsorption experiments was 1 hr.

In only one experiment was carbon monoxide used to reduce the oxide (see Table 3). Since the carbon dioxide produced would poison the surface by formation of the dioxide carbonate these reductions were carried out in the same temperature range as the ignition. Thus, it

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[14] Storch, *J. Amer. Chem. Soc.*, 1934, **56**, 374.

is not possible to obtain $(PrO_{1\cdot5})_C$ in this way. The method suffers the additional disadvantage that there is apparently some deposition of carbon owing to disproportionation $2CO \longrightarrow C + CO_2$; this was inferred because after reduction with carbon monoxide the oxide was grey, whereas hydrogen gave a white oxide, and because chemisorption was about one-half of that on the hydrogen-reduced oxide under identical conditions (deposited carbon blocks sites for the chemisorption of oxygen[15]). After reduction, the sample was pumped at the temperature of reduction for 1 hr., unless otherwise stated (see Discussion regarding the completeness of desorption of hydrogen). After ½ hour's cooling in liquid nitrogen an oxygen adsorption isotherm was determined at $-196°$. Without removal of the liquid-nitrogen bath, the oxide was then pumped for 1 hr. and a second oxygen adsorption isotherm was determined at $-196°$. Pressures for measuring adsorptions were in the range 5—300 mm. and were read by means of a constant-volume mercury manometer accurate to 0·1 mm.

The monolayer volume of gas adsorbed, V_m, was obtained directly by the point B method. Two such values were checked by the B.E.T. equation. The difference between the straight-line portions of the first and the second isotherm, which is the amount of adsorbed oxygen that cannot be removed by pumping for 1 hr. at $-196°$, was taken as the amount of chemisorption. That the adsorbed oxygen corresponding to the second isotherm consists solely of physically adsorbed gas was shown by the fact that a third isotherm determined after one hour's pumping at $-196°$ was identical with the second. Several experiments were carried out to test whether the difference between the first and the second isotherm could be due to oxygen bound by strong physical forces at $-196°$ and therefore difficult to pump away. These indicated that such was not the case. The experiments were as follows: (*a*) After the second isotherm was measured a sample of $(PrO_{1\cdot5})_C$ was pumped for 7 hr. A third oxygen isotherm was coincident with the second. (*b*) Double oxygen isotherms on $PrO_{1\cdot83}$ with the standard inter-pumping period of 1 hr. were always coincident. Oxygen would not be expected to be more strongly bound physically to surfaces of $(PrO_{1\cdot5})_C$ than to $PrO_{1\cdot83}$. (*c*) After a standard double isotherm determination a sample of $(PrO_{1\cdot5})_C$ was allowed to warm to room temperature. No oxygen was evolved at any stage. After 5 days the oxide was again cooled to $-196°$ and the standard double isotherm procedure was repeated. The first set of isotherms coincided with the second set, indicating that the first strongly bound oxygen had penetrated the solid, leaving a fresh surface which was capable of binding strongly a further and equal amount of oxygen. Neither the absence of desorbed oxygen nor the reproducibility is conclusive, but they make physical forces less tenable as a theory for the origin of the irreversibly adsorbed oxygen on $(PrO_{1\cdot5})_C$.

In the presentation of results, the amount of oxygen chemisorbed is given as a fraction of $V_m(O_2)$, the volume of oxygen required to cover the surface with a complete monolayer of physically adsorbed oxygen molecules, rather than as a fraction of the surface area. This avoids difficulties arising from uncertainties about the area covered by one oxygen molecule. The area covered by an adsorbed argon molecule is generally accepted as very nearly the same as that covered by an oxygen molecule (both are given as 14·6 Å by Livingston[16]). Comparison of $V_m(O_2)$ and $V_m(A)$ is a useful check. Argon and oxygen isotherms, measured on an oxidised surface of a sample of $(PrO_{1\cdot5})_C$ weighing 1·320 g., gave the same value for V_m, namely, 0·39 c.c.

RESULTS

Chemisorption on $(PrO_{1\cdot5})_C$.—Typical oxygen isotherms measured at $-196°$, on "reduced" and "oxidised" surfaces of $(PrO_{1\cdot5})_C$, are shown in Fig. 2. Equilibrium was reached in less than 2 min. at $-196°$. Table 2 lists values of V_0 (in c.c. of oxygen at N.T.P.), the amount of chemisorption of oxygen per g. of sample, for various samples of $(PrO_{1\cdot5})_C$ together with details of treatment where these differ from the standard procedure previously described.

Great difficulty was experienced in degassing the oxide samples after reduction with hydrogen, even at pumping temperatures considerably higher than those at which the reduction had taken place. Consequently $(PrO_{1\cdot5})_C$ was pumped at a high temperature for long periods to free it from some or most of the hydrogen taken up during reduction, and then its chemisorption capacity towards hydrogen was examined. Repeated temperature-cycling between 300° and 500° resulted in a progressive increase in the amount of sorbed hydrogen, measured at 300°. On completion of two cycles, which covered a period of 63 hr., the final total

[15] Roberts, Walter, and Wheeler, *J.*, 1958, 2472.
[16] Livingston, *J. Colloid Sci.*, 1949, **4**, 447.

TABLE 2.

Adsorption of oxygen on $(PrO_{1·5})_C$ at −196°.*

Sample no./	Reduction †		Pumping after reduction		V_m (O_2)	V_o	
Expt. no.	Temp.	Period (min.)	Temp.	Period (min.)	(c.c./g.)	(c.c./g.)	V_o/V_m
X1a/1	800°	75	800°	60	0·268	0·019	0·07 ± 0·02
2	800	60	800	60	0·251	0·117	0·47 ± 0·04
3	800	60	800	60	0·234	0·117	0·50 ± 0·04

The sample was oxidised to $PrO_{1·83}$ before reduction in the next experiment (No. 4). Also a P_2O_5 drying tube was introduced in the H_2 purification train.

Sample no./ Expt. no.	Reduction Temp.	Reduction Period (min.)	Pumping Temp.	Pumping Period (min.)	V_m (O_2) (c.c./g.)	V_o (c.c./g.)	V_o/V_m
4	700	60	700	60	0·302	0·088	0·29 ± 0·02
5	700	60	700	60	0·277	0·053	0·20 ± 0·02

Subsequent experiments were carried out with the P_2O_5 drying tube removed, but additional and more efficient liquid-air traps were inserted in the H_2 purification train.

Sample no./ Expt. no.	Reduction Temp.	Reduction Period (min.)	Pumping Temp.	Pumping Period (min.)	V_m (O_2) (c.c./g.)	V_o (c.c./g.)	V_o/V_m
Y3b/1	450	60	450	60	0·304	0·000	0·00 ± 0·01
2	450	60	450	60	0·312	0·038	0·12 ± 0·01
Y3c/1	458	300	458	60	0·575	0·000	0·00 ± 0·01
Y3d/1	460	60	460	60	0·426	0·051	0·13 ± 0·01
2	507	60	507	60	0·393	0·111	0·28 ± 0·01
3	507	60	507	60	0·385	0·139	0·36 ± 0·01
4	507	60	507	60	0·402	0·127	0·32 ± 0·01
5	507	60	507	60	0·418	0·107	0·26 ± 0·01
6	507	60	507	120	0·418	0·107	0·26 ± 0·01
7	507	60	507	60	0·418	0·078	0·19 ± 0·01
8	570	60	570	60	0·397	0·148	0·37 ± 0·01
9	500	60	500	60	0·414	0·074	0·18 ± 0·01
10	500	60	500	60	0·414	0·090	0·22 ± 0·01
11	500	60	500	3600	0·352	0·229	0·65 ± 0·01
Y3e/1	500	60	500	180	0·245	0·052	0·21 ± 0·01
Y3f/1	525	150	525	90	0·429	0·000	0·00 ± 0·01

Sample Y3f oxidised and kept for 12 min. at 900—940° in oxygen and then cooled slowly.

Sample no./ Expt. no.	Reduction Temp.	Reduction Period (min.)	Pumping Temp.	Pumping Period (min.)	V_m (O_2) (c.c./g.)	V_o (c.c./g.)	V_o/V_m
2	525	180	525	60			
			then				
			625	60	0·367	0·096	0·26 ± 0·01
3	525	60	625	120	0·402	0·101	0·25 ± 0·01
Y2b/1	500	90	500	60			
			then				
			600	60	0·644	0·000	0·00 ± 0·01
2	500	60	650—700	60	0·576	0·045	0·08 ± 0·01
3	No further reduction		940 ‡	15	0·227	0·061	0·27 ± 0·01

Sample Y2b oxidised to $PrO_{1·83}$ at 500°.

Sample no./ Expt. no.	Reduction Temp.	Reduction Period (min.)	Pumping Temp.	Pumping Period (min.)	V_m (O_2) (c.c./g.)	V_o (c.c./g.)	V_o/V_m
4	500	60	525	60	0·424	0·000	0·00 ± 0·01
5	No further reduction		770 §	60	0·349	0·045	0·13 ± 0·01
6	,,		700 ¶	60	0·299	0·072	0·24 ± 0·01

* Results in chronological order on descent of the Table.

† Reduced with H_2 according to standard procedure described in text.

‡ Before pumping, the oxide was heated in an enclosed system at this temperature, and 0·14 c.c. of gas were evolved. Mass-spectrometric analysis gave the composition: H_2 39·7, CO 29·7, CO_2 30·5%; H_2O was neglected in the analysis. These results are expressed in percentages by volume. Since the rate of the transition, type C ⟶ type A, is extremely slow even at 940°, only negligible amounts of type A could be formed during the period at which the oxide was kept at this temperature.

§ Treated as ‡; 0·08 c.c. of gas was evolved. Mass-spectrometric analysis indicated that over 99% of this consisted of H_2.

¶ Further small quantities of H_2 were evolved on heating in an enclosed system.

TABLE 3.

Adsorption of oxygen on $(PrO_{1·5})_A$ at −196°.

Sample/	Treatment before 1st isotherm		V_m (O_2)	V_o	
Expt. no.	Reduction	Pumping	(c.c./g.)	(c.c./g.)	V_o/V_m
Y3g/1	H_2, 1 hr., 960°	1 hr., 960°	0·158	0·016	0·10 ± 0·01
2	H_2, 1 hr., 870°	1 hr., 870°	0·158	0·020	0·13 ± 0·01
3	CO, 1 hr., 860°	1 hr., 860°, then 3 hr., 910°	0·190	0·009	0·05 ± 0·01

of hydrogen adsorbed by sample Y3e was 0·344 c.c. [= 0·61 $V_m(O_2)$] at 300°/26 cm. (H_2). This sample had been reduced for 2 hr. at 500° and pumped for 90 hr. at 550°. No reversible adsorption of hydrogen (similar to that discovered by Taylor *et al.*[17] on ZnO) was detected over the range $-196°$ to 500°.

In addition to adsorbed hydrogen, evidence of chemisorbed carbon dioxide was found on a sample (Y3b) which had been ignited in air at 910°, a temperature well above that required to decompose the dioxide carbonate. (See footnote ‡ of Table 2.)

Chemisorption on $(PrO_{1\cdot5})_A$.—Table 3 shows the measurements of chemisorption of oxygen on material of type A. As with type C, it was difficult to degas the oxide after reduction.

DISCUSSION

The results in Tables 2 and 3 indicate that both modifications of reduced praseodymium oxide react with oxygen even at $-196°$, at rates sufficiently high for equilibration within a few minutes. Indeed chemisorption is faster than attainment of thermal equilibrium. $PrO_{1\cdot5}$, therefore, resembles UO_2 in this respect. The V_0/V_m values, however, tend to be smaller than on UO_2. The average V_0/V_m value on UO_2 samples in Table 1 in Roberts's paper is 0·54; the corresponding figure for $(PrO_{1\cdot5})_C$ is 0·22 or approximately half. The V_0/V_m values of $(PrO_{1\cdot5})_C$ cover a wider range than those of UO_2: 0—0·65V_m for $(PrO_{1\cdot5})_C$ and 0·29—0·86V_m for UO_2. Even on the same sample quite large differences have been observed. These are apparent in Table 2, where the determinations are given in chronological order. In particular, the sequence Y3d/2—7 shows the variation in chemisorption value determined several times without alteration in the conditions (except in one case, indicated). V_0/V_m first increases, from 0·28 to a maximum at 0·36, after which it diminishes to 0·19. Then, in the sequence Y3d/8—9, V_0/V_m increased sharply to 0·37 when the temperature of reduction and pumping was raised from 500° to 570°, but decreased to 0·18 on returning to 500°. The next determination (Y3d/10) was repeated under the same conditions as Y3d/9 and showed a slight increase in chemisorption. In the next determination (Y3d/11), the pumping time was increased from 60 to 3600 minutes and the chemisorption rose to 0·65, the highest recorded in this work.

A likely explanation for the frequent fall in chemisorption in a series is suggested by Roberts's work[18] on the chemisorption of hydrogen on uranium oxide. He found that UO_2 powder adsorbed hydrogen by an activated mechanism in amounts as high as 1·3$V_m(O_2)$ after temperature-cycling and that the presence of this adsorbed hydrogen diminished somewhat the chemisorption of oxygen. He also observed that hydrogen adsorbed during reduction is difficult to remove even at high temperatures. In the present work up to 0·61$V_m(O_2)$ of hydrogen was found to be chemisorbed by $(PrO_{1\cdot5})_C$ after temperature-cycling between 300° and 500° and this gas was also difficult to remove even when the oxide was pumped for a long period. It is interesting that temperature-cycling during pumping assisted the removal of hydrogen. The disadvantage of poisoning by the reducing agent was overcome in the UO_2 work by the use of carbon monoxide for reduction, but this gas is unsuitable for reducing praseodymium oxide to the type C modification because the decomposition temperature of the monocarbonate is higher than the temperature of the transition of type C into type A. For this reason it is not as easy to prove that hydrogen irreversibly adsorbed during reduction was responsible for some of the low oxygen chemisorption values on $(PrO_{1\cdot5})_C$, as it was on UO_2.

Another contribution to a diminution in chemisorption would arise if some sites were blocked by residual water on the surface arising from incomplete desorption during reduction with hydrogen, even at the high temperatures used. The very basic character of $PrO_{1\cdot5}$, compared with UO_2, would favour this possibility.

The more strongly basic character of $PrO_{1\cdot5}$ is undoubtedly the cause of the difficulty of obtaining surfaces free from chemisorbed carbon dioxide. Sample Y2b, although

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[17] Taylor and Strother, *J. Amer. Chem. Soc.*, 1934, **56**, 586; Taylor and Liang, *ibid.*, 1947, **69**, 1306.
[18] Roberts, *J.*, 1955, 3939.

ignited at 910° in air, evolved a gas containing carbon dioxide when heated at 940° in a vacuum (see experiment Y2b/3 in Table 3). Since hydrogen was also present, the presence of all the constituents of the water gas equilibrium, $H_2 + CO_2 \rightleftharpoons CO + H_2O$, would be expected at this temperature and this was confirmed by the mass-spectrometric analysis described in footnote † to Table 2. Previous to this discovery, *i.e.*, during the experiments preceding Y2b/3, it was believed that a temperature of 910° was sufficient to produce praseodymium oxide free from carbon dioxide. Unfortunately, the very high temperatures that are required to ensure clean $(PrO_{1\cdot5})_C$ surfaces inevitably introduce some risk of conversion into the type A modification; although the rate of transition is slow,[19] it is fast enough to preclude prolonged pumping at these temperatures. Even when $(PrO_{1\cdot5})_C$ surfaces free from carbon dioxide were obtained the chemisorption did not always reach the maximum recorded in this work, which suggests persistent retention of hydrogen adsorbed during the reduction stage. It might be expected that the high temperature of pumping required to remove carbon dioxide from the surface would also favour removal of hydrogen. This is not necessarily so. Hydrogen was removed faster at somewhat lower temperature (500—600°), and even more effectively when temperature-cycling was introduced.

Measurements of the chemisorption of oxygen by $(PrO_{1\cdot5})_C$ indicate that surfaces of this oxide chemisorb up to at least $0{\cdot}65V_{\rm m}$, although it is not clear whether this is the maximum. For UO_2 the maximum chemisorption of oxygen was found to be $0{\cdot}86V_{\rm m}$. Factors which might produce differences in chemisorption behaviour between the two oxides are as follows:

(1) Oxidation of UO_2 may be accompanied by a transfer of two electrons per cation ($U^{4+} \longrightarrow U^{6+}$), as compared with a single-electron transfer per cation in $PrO_{1\cdot5}$ ($Pr^{3+} \longrightarrow Pr^{4+}$). Although the two electrons may not be transferred simultaneously (the improbability of simultaneous transfer is discussed by Basolo and Pearson[20]) the number of donor sites involved in the chemisorption of oxygen must be different in the two oxides. Surface cations, however, are not the only source of electrons in the act of chemisorption. Recent work on thorium oxide by Roberts[21] indicates that O^- ions exist on the surface. If this behaviour is universal, it suggests the possibility of further chemisorption by the reaction $2(O^{=})_{\rm surface} + (O_2)_{\rm gas} \longrightarrow 4(O^-)_{\rm surface}$.

(2) There are three different kinds of position (defined as points of minimum potential energy) that chemisorbed oxygen may occupy in $(PrO_{1\cdot5})_C$. Only two of these are available in UO_2. The three types of surface position are as follows: (*a*) Anion vacancies, inherent in the type C structure, and exposed in this surface layer (represented by black spheres in the Plate). Occupation of these completes the fluorite structure of the exterior layers. These are the positions which are utilised in the bulk oxidation of $(PrO_{1\cdot5})_C$ but are not available in UO_2. (*b*) Octahedral interstices, inherent in both type C and fluorite structures. (In the fluorite unit cell of UO_2 these interstices are at $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $0\frac{1}{2}0$ when a uranium atom is taken as the origin.) These are the positions occupied by reacting oxygen in the bulk oxidation of UO_2,[4] but not in $(PrO_{1\cdot5})_C$; * they might, however, be used in oxidation at the surface of $(PrO_{1\cdot5})_C$ where the energy parameters are very different from those of the bulk oxide, although it is to be expected that the vacant anion positions would be occupied first. (*c*) Positions above the surface cations, which are extensions of the oxygen framework of the fluorite lattice of the oxide.

If purely electrostatic forces operate, then the gain in energy from the transfer of an oxygen atom from the gas phase to one or other of these three kinds of sites would be

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* This is deduced from the fact that the fully oxidised form, PrO_2, does not contain oxygen in *b*-type positions.

[19] Douglass and Staritzky, *Analyt. Chem.*, 1956, **28**, 551.
[20] Basolo and Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, New York, 1958, p. 315.
[21] Roberts, personal communication.

expected to decrease in the order (*a*), (*b*), (*c*) and this would give the sequence of occupation in $(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$. In UO_2, occupation would commence with type (*b*), followed by type (*c*). Single oxygen atoms, either singly or doubly charged, would be more easily accommodated, but charged species of O_2 are not precluded as one end of a molecular ion protrudes in all three kinds of position.

Tables 4 and 5 illustrate simple calculations of the maximum V_0/V_{m} values for each position in $(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$ and in UO_2, on surfaces corresponding to the (111), (110), and (100) crystallographic planes, and also their average which would correspond to a surface on which equal areas of these three planes are exposed. Because the (111) plane is electrically neutral, it might be expected that this would be the plane with the largest exposed area, although electron micrographs of ThO_2 and UO_2 show (100) as the preferred form.[22] It is clear from these figures that the occupation of positions of type (*a*) positions could not, by itself, account for the observed V_0/V_{m} values. Unless type (*a*) positions in sub-surface layers are accessible in the act of chemisorption it must be supposed that type (*c*) and possibly type (*b*) positions would be utilised as well.

TABLE 4.

Area per unit cell of planes exposed on the surfaces of UO_2 and $(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$.

Oxide	Length of unit-cell side (Å)	(100) plane (Å^2)	(110) plane (Å^2)	(111) plane (Å^2)
$(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$	11·14	124·1	175·4	53·4
UO_2	10·9 *	118·8	168·0	51·4

* The actual unit-cell side has been doubled to obtain a unit cell equivalent to that of $(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$.

TABLE 5.

Calculation of maximum V_0/V_{m} values for each type of surface position if occupied by one atom of chemisorbed oxygen. (The number of positions cited refers to a unit-cell section.)

	(100) plane		(110) plane		(111) plane		V_0/V_{m} (calc.) for equal areas
Oxide	No. of positions	V_0/V_{m} (calc.)	No. of positions	V_0/V_{m} (calc.)	No. of positions	V_0/V_{m} (calc.)	of (100), (110), and (111) planes
$(\mathrm{PrO}_{1\cdot5})_{\mathrm{C}}$: position *a*	4	0·19 *	4	0·14	2	0·23	0·18
position *b* † ...	8	0·39	8	0·28	0	0·00 ¶	0·22
position *c*	16	0·78 ‡	16	0·56	8	0·92	0·75
UO_2: position *b* †	8	0·41	8	0·29	0	0·00 ¶	0·23
position *c*	16	0·81 ‡	16	0·58	8	0·94	0·78

* Calc. by assuming that the anion vacancies in the layer immediately below the surface layer of cations are filled by chemisorbed oxygen.

† It is assumed that positions *b* above the surface layer of cations are too unstable to be occupied by chemisorbed oxygen. Since an electrically neutral surface is most favoured, the most probable exposed (111) section is a plane passing through the centre of the cations. There are no positions *b* in this plane. The possibility of positions *b* in the layer below the surface has been ignored.

‡ Calc. by assuming that an oxygen layer of the fluorite lattice is completed above the surface layer of cations.

¶ It is assumed that penetration of the (111) section through the centres of the cation layer to *b*-type positions is not possible at the temperature of chemisorption, as this layer is closely packed, with consequent absence of gaps through which entrance could be effected.

It seems unlikely, however, that vacant positions in sub-surface layers would be occupied at the very low temperatures at which chemisorption measurements were made, in spite of the possibility that the activation energy for what is, in effect, the first diffusion

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[22] Anderson, Harper, Moorbath, and Roberts, unpublished electron-micrographic observations.

step may be much lower than the activation energy for bulk lattice diffusion.[23] One reason for asserting this is that if one or more diffusion steps were possible, one would expect to observe a tailing-off in the chemisorption rate. No such effect was observed. A time-dependent uptake of oxygen has indeed been observed at temperatures lower than are necessary to effect measurable diffusion-controlled bulk oxidation, but only at temperatures that are still much higher than those at which chemisorption was measured. This process has been interpreted as the occupation of positions in the immediate sub-surface layers.

Comparison of Chemisorption of Oxygen on $(PrO_{1\cdot5})_A$ *with that on* $(PrO_{1\cdot5})_C$.—The chemisorptive capacity of $(PrO_{1\cdot5})_A$ for oxygen is much lower than that of $(PrO_{1\cdot5})_C$, as is shown by the V_0/V_m values listed in Table 3. It is unlikely that this difference was due to greater poisoning of hydrogen on $(PrO_{1\cdot5})_A$, although a higher pumping-out temperature was used (see above for the possibility that temperatures higher than 500—600° may be less favourable for completely removing hydrogen from the oxide). There are no vacant sites inherent in the type A structure, so that no favoured chemisorption sites of type (*a*) are exposed on the surface. This might account for the lower chemisorption value on $(PrO_{1\cdot5})_A$. Since neither type (*a*) nor type (*b*) positions are provided by the structure, chemisorption can only take place " on " the surface rather than " in " the surface layer, by occupation of type (*c*) positions. It is reasonable to suppose that similar factors, *e.g.*, similar energetics, might govern the extent to which chemisorption would take place by occupation of the type (*c*) sites on both structures, so that measurement of the chemisorption of oxygen on $(PrO_{1\cdot5})_A$ might, in the absence of poisoning, give a figure for the amount of chemisorption on type (*c*) positions. If this is added to the average V_0/V_m values calculated for type (*a*) and type (*b*) adsorption sites on $(PrO_{1\cdot5})_C$, we obtain a figure of 0·53, which is not very different from the maximum value measured for $(PrO_{1\cdot5})_C$.

The V_0/V_m value of 0·13 measured for $(PrO_{1\cdot5})_A$ is certainly much lower than would correspond to the number of type (*c*) positions theoretically available. One possible explanation of this is that most type (*c*) positions are occupied already. This would mean that they were not fully vacated in the reduction process. This might arise from two causes. First, to maintain a minimum ratio of oxygen anions to praseodymium cations of 3 : 2 some type (*c*) positions will have to be occupied; the number of these will represent the minimum obtainable by reduction. Secondly, since the praseodymium cation is much smaller than the oxygen anion it would be expected from simple electrostatics that a co-ordination number of less than half the maximum is energetically much less probable for surface cations than for surface anions.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MELBOURNE,
PARVILLE, N.2, VICTORIA, AUSTRALIA.

[Present addresses: J. S. A.: NATIONAL CHEMICAL LABORATORY, TEDDINGTON, MIDDLESEX.
K. J. G.: DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
SWANSEA, WALES.]

[*Received, January* 30*th* 1962.]

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[23] Harrison, Morrison, and Rose, *J. Phys. Chem.*, 1957, **61**, 1314.