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KATHAROMETRIC AND RESISTIVITY STUDIES OF PuO_{2-x} EQUILIBRIA

by

Leon M. Atlas and
Gilbert J. Schlehman

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OF PuO_{2-x} EQUILIBRIA

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Metallurgy Division

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ABSTRACT

The variation of electrical resistivity (ρ) and x with oxygen pressure has been measured for PuO_{2-x} at 1100 and 1400°C. The procedures, which are described in detail, include (a) equilibrating a ceramic in a once-through stream of $\text{H}_2\text{-H}_2\text{O-He}$ mixture, (b) reoxidizing the specimen to $\text{PuO}_{2.00}$ in a fixed volume of helium-oxygen mixture, and (c) analyzing the oxygen content with a thermal-conductivity gas detector. Some data for TiO_{2-x} at 1200 and 1300°C have also been obtained to check the gas-analysis method.

Experimental results for PuO_{2-x} are presented as plots of $\log x$ vs $\log p(\text{O}_2)$, $\log \rho$ vs $\log p(\text{O}_2)$ and $\Delta G_{\text{O}}^{\circ}$ (the relative partial molar free energy of oxygen in the solid) vs $\log x$. The log-log plots of x and ρ against $p(\text{O}_2)$ are linear over a wide range of x , and at both 1100 and 1400°C, the composition lines have steeper slopes than the resistivity lines. A mass-action analysis is presented that relates the slope difference to a variation of the activity coefficient of Pu^{+3} ions with the concentration of defects. At 1100°C, these defects are thought to be primarily quadruply dissociated interstitial plutonium atoms.

I. INTRODUCTION

Until the recent report by Markin, Bones, and Gardner,⁽¹⁾ and the earlier work of Markin, Walter, and Bones,⁽²⁾ virtually no experimental thermodynamic data were available for nonstoichiometric plutonium dioxide. However, Markin and his co-workers were limited by their experimental method to temperatures below 1140°C, leaving the higher temperature region still almost unknown, except for estimates (cf. Chikala⁽³⁾). To help fill this data vacuum, the present program is primarily focused on the

region from 1100°C up to perhaps 1600°C. This report describes in detail the experimental procedures being used and the results obtained so far at 1100 and 1400°C. An attempt is also made to interpret these results in terms of a somewhat revised version of the mass-action equilibria described by Kröger and Vink.⁽⁴⁾

Because of the relatively high temperatures involved, the solid-state electrolyte cell so effectively used by Markin and his associates was not considered practicable for the present work. Above 1100°C, there is an increasing likelihood of reactions between the electrolyte and the electrodes, and between the electrodes and any atmosphere except one having equilibrium partial pressure of oxygen. Thermogravimetry was also discarded, despite its usefulness in the study of rutile,^(5,6) because it is not readily amenable to the concomitant measurement of electrical resistance and x of PuO_{2-x} . Later in this report, it will be shown that the ratio of these two properties, and its variation with temperature, can provide information about the tendency of electrons to become self-trapped at regular cation lattice sites.

A gas equilibration method, in which the composition of the solid is deduced from gas analyses, appeared to be well-adapted for making combined resistance-composition measurements. Moreover, a thermal-conductivity detector (katharometer) gave promise of being a convenient and adequately sensitive means for carrying out the gas analyses. Evans⁽⁷⁾ found such a system satisfactory for studying the equilibria between metals and mixtures of CO and CO_2 , i.e., of the type $\text{MeO} + \text{CO} = \text{Me} + \text{CO}_2$. Berkowitz⁽⁸⁾ later used a similar method for measuring the oxidation kinetics of several refractory metals and their silicides. However, both of these investigations involved the formation of new solid phases and, consequently, rather large changes of gas composition. For defect equilibria, much smaller quantities of oxygen may be interchanged between the solid and gas phases, especially when Δx for PuO_{2-x} is small. For this reason, and also because glovebox procedures are required, it was necessary to elaborate on the systems described by Evans and by Berkowitz. Details of design and procedure are presented in the following sections.

II. DESCRIPTION OF GAS EQUILIBRATION AND ANALYSIS SYSTEM

In general terms, the apparatus consists of the following subsystems:

- (a) A katharometer gas-analysis detector.
- (b) A complex flow system for introducing various mixtures of purified gases and taking samples for analysis.

- (c) A furnace and associated controls for equilibrating the specimen at selected temperatures.
- (d) Apparatus for measuring the electrical resistance of the specimen.

A. The Detectors

The main gas-analysis sensing element is a RSCOkatharometer* mounted in an oven to provide a constant-temperature environment. This detector consists of a stainless-steel block, bored through to form two straight chambers, each containing two helical tungsten filaments. The filaments are heated by a constant-voltage source and comprise the arms of a dc bridge circuit. If the thermal conductivity of a gas mixture flowing through one chamber differs slightly from that of a standard mixture flowing through the other, the filaments reach different temperatures and the bridge is unbalanced. Since this is a differential measuring system, a suitable choice of reference gas permits the detection of very small composition changes of a gas mixture even though its components may be present in high concentrations. At present, the katharometer is being used to determine oxygen in helium-oxygen mixtures, and H_2O (above about 0.05%) in H_2 - H_2O -He atmospheres.

B. Gas Flow System

The general flow scheme of the gas-handling system is shown in the block diagrams of Fig. 1; each of the two configurations shown may be

Fig. 1

Defect Equilibria
Apparatus

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*Items for which trade names are given are described more fully in the appendix.

chosen by means of a LOENCO switching valve. In position 1, the gas is divided into two streams: one flows through the reference chamber of the katharometer, while the other passes over the specimen in the equilibrium furnace and then out through the detector sample chamber. In this configuration, the specimen is bathed in a once-through stream of gas having a known partial pressure of oxygen (e.g., $\text{H}_2\text{-H}_2\text{O}$ or CO-CO_2 mixture, or helium, passed over heated $\text{CuO/Cu}_2\text{O}$).

Position 2 isolates the sample within a closed recirculating loop, while the standard gas continues to pass through both chambers of the katharometer. Small volumes of the isolated gas may be withdrawn from the loop with a LOENCO sampling valve and inserted into the carrier stream flowing through the katharometer sample chamber. If the gas in the loop changes its composition relative to the standard carrier, the recorder trace will deflect momentarily from the base line as the gas sample passes through the detector.

A detailed schematic diagram of the apparatus as it is now used is presented in Fig. 2. This drawing shows the construction of the switching and sampling valves (38 and 39); both consist of cylinders divided into isolated chambers by O rings spaced along a loose-fitting plunger. The dark and light lines drawn within the switching valve show the locations of the chamber walls corresponding to positions 1 and 2 of Fig. 1. With a few exceptions, the gas lines are 6.35-mm (1/4-in.)-OD stainless tubing. The lines connected to the katharometer and the switching and sampling valves are 1.59-mm (1/16-in.) OD and 3.18-mm (1/8-in.) OD, respectively; the copper oxide oxidizer (20) and the titanium sponge purifier (19) are both 25.4-mm (1-in.) OD.

Cylinder gases are purified by passing them through 2-meter lengths of 6.35-mm-OD tubing, packed with Linde molecular sieve. These tubes are coiled into helices (18), which may be immersed in Dewar flasks filled with liquid nitrogen. This system is supplemented, for mixtures containing hydrogen, by a Deoxo catalytic purifier (10), and for inert gases, by a tube of heated titanium sponge (19).

The humidifiers are 50.8-mm (2-in.)-OD stainless-steel vessels. Pure dry gas enters (36A) through a fritted-glass dispersing disc and bubbles through distilled water; it then passes through (36B), which is packed with moistened glass beads. Both vessels are immersed in a bath that is normally maintained at 0°C with an ice-water mixture (27).

A short chromatographic column (a 150-mm length of 6.35-mm-OD polyethylene tubing, containing 7% of Carbowax 4000 on Haloport-F) is incorporated just before the katharometer sample chamber. This column delays the passage of water vapor to the detector without significantly affecting the movement of oxygen or hydrogen; as a result, mixtures can be independently analyzed for oxygen and water.

1. Glovebox	22. Metering valve
2. Furnace	23. 1/4-in. polyethylene tubing, containing 7% Carbowax 4000 on Haloport-F
3. Water cooler	24. Shut-off valve
4. Vacuum roughing pump	25. Check valve
5. Tapped transformer	26. Pressure-vacuum gauge
6. Differential pressure regulator	27. Constant-temperature bath
7. MSA filter (0.3 microns)	28. Water-cooling control
8. Pirani gauge	29. SCR furnace control system with current limiter
9. Digital set point controller, 0-1000°C	30. Electrical conductivity measuring system
10. Deoxo purifier	31. Water flow switch
11. Split furnace	32. Dial thermometer
12. Helium	33. Water flow regulator
13. Hydrogen-helium mixtures	34. Pressure switch
14. AEC filter	35. Katharometer power supply and bridge circuit (RSCO 605-1)
15. Millipore filter (0.22 microns)	36. Stainless humidifier
16. Pyrometer, 0-1000°C	37. Oxygen-helium mixture
17. Katharometer in oven (RSCO 600-1 in RSCO 600)	38. Gas switching valve (LOENCO L-206-4)
18. 6 ft of 1/4-in. STN tube, filled with 5A molecular sieve	39. Gas sampling valve (LOENCO L-208-6)
19. 1-in. STN tube, packed with titanium sponge	40. Gas recirculating pump
20. 1-in. STN tube, packed with CuO	41. Double-end shut-off quick coupler
21. Flowmeter	42. Controller, 0-300°C

Fig. 2. Detailed Schematic of Katharometer Gas Analysis System

Gas lines outside the glovebox are isolated from possible radioactive contamination by 0.22-micron Millipore filter elements (15). These were chosen because their low mass prevents excessive absorption of water from the humidified gas mixtures, and permits the lines to reach equilibrium with water vapor fairly rapidly.

C. Furnace System

The design of the equilibrium furnace is illustrated in Fig. 3, along with details of two cap assemblies - one (shown in place on the furnace) for measuring electrical resistance by the four-probe method, and the other for use as a solid electrolyte cell. The furnace proper incorporates two concentric sealed chambers. The interior of the closed-end alumina tube comprises the inner chamber, which contains the solid sample and the equilibrating atmospheres. The space between the alumina tube and the steel shell is the outer chamber, which encloses the furnace winding bathed in its own protective atmosphere (at present, Pt-10% Rh surrounded by helium or nitrogen).

Fig. 3. Equilibrium Furnace Assemblies

Although not shown in Fig. 3, both the specimen support and the thermocouple shield are inclined at a slight angle to the furnace axis so that they nearly meet in the hot zone. Moreover, the upper parts of both the conductivity and cell assemblies are thermally insulated by plugs of porous alumina.

D. Electrical Measurement System

Provision has been made to measure both the ac and dc electrical resistance of the solid specimen by the four-probe technique. For dc measurements, the current source is a Dressen-Barnes regulated power supply. The potential drop across the specimen, or across one of several ESI standard resistors, is measured with a Keithley differential voltmeter. In practice, polarization effects are relatively small for the dc measurements, which have been used exclusively.

III. EXPERIMENTAL PROCEDURES

The gas-analysis system described above may be applied to the study of the defect equilibria by using two different procedures.

1. The oxide sample may be equilibrated at various temperatures in a fixed volume of gas mixture (e.g., hydrogen-water diluted with argon). Samples of gas are withdrawn and analyzed for hydrogen and water at each temperature. The change of gas composition with temperature (after a blank correction) gives the corresponding change of x in PuO_{2-x} . For an absolute value of x , the oxide must either start from a known composition or be analyzed at the end of the experiment.

2. The solid may be equilibrated in a once-through stream of gas mixture having a known and constant oxygen pressure, and quenched. The sample is then reoxidized by heating in a fixed, recirculating volume of helium-oxygen gas. The composition change of this gas, corrected for blank effects, gives the oxygen exchange necessary for the specimen to reach a standard composition.

Although the second procedure is slower than the first, it has the high reliability embodied in a return to a standard state after every experiment. As a result, long-term composition errors such as might be produced by volatilization of molecules containing plutonium, do not become cumulative (except insofar as they affect the weight of the specimen).

All the data in this report have been gathered by procedure No. 2. Specific details of how this method was applied to measurements on TiO_2 and PuO_2 are presented below.

1. Both oxides were used in the form of ceramics. TiO_2 specimens were pressed from Baker Analyzed Reagent powder, fired at 1350°C in a mixture of He-50 v/o O_2 , and annealed in the same atmosphere. The final porosity was about 10 to 12 v/o.

PuO_2 ceramics were formed from a powder whose composition is described in Table I. Pressed pellets were fired at 1500°C in a dried mixture of He-50 v/o H_2 , and the final porosity was 27 v/o.

Table I
ANALYSIS* OF PuO_2 POWDER AFTER CALCINATION AT 500°C

Element	Concentration (ppm by weight)	Element	Concentration (ppm by weight)
Al	14	Mn	2
Ba	<2	Mo	<0.5
Be	<0.002	Na	<2
Ca	16	Ni	5
Co	<2	Pb	<1
Cr	12	Rb	<5
Cu	10	Sb	<20
Fe	50	Sn	<2
K	<2	Sr	<0.005
Li	<0.005	Ti	<2
Ga	<0.1	V	<5
W	<2	Zn	<2
La	<2	Zr	<2
Mg	34		

*Elements not reported were not investigated.

2. The ceramic specimens were equilibrated at either 1100 or 1400°C in preanalyzed hydrogen-helium mixtures; these were moistened to the desired level in the humidifier and analyzed with the katharometer. The detector itself was standardized against gas bubbled through water at 0°C , and by means of gravimetric analyses using an absorption bulb.

3. After a sample had been equilibrated at high temperature, the furnace was quickly cooled to 600°C (for TiO_2), or to room temperature (for PuO_2). The H_2 - H_2O -He mixture was then replaced with an oxidizing gas. TiO_{2-x} samples were reoxidized to $\text{TiO}_{2.000}$ by heating them in a mixture of He-0.4 v/o O_2 at 1200°C . PuO_{2-x} specimens were converted to $\text{PuO}_{2.00}$ by annealing in a He-4 v/o O_2 atmosphere at 800 - 900°C . In both cases, changes in the oxygen content of the 800 ml of oxidizing gas were monitored with the katharometer.

4. Before x was calculated from the change of oxygen content, the recirculating gas was normalized to a standard pressure and temperature, and blank corrections were applied. The pressure in the isolated loop was measured directly with a gauge, but the gas temperature presented

a more complicated problem since it varied from point to point within the recirculating system. An average temperature was established as being the sum of the ambient room temperature and an increment created by passage of the gas through the hot furnace. Values were set for this increment by varying the furnace temperature and measuring the corresponding pressure change in the fixed volume of gas.

Blank corrections were established by equilibrating the empty apparatus at each temperature in all of the hydrogen-helium mixtures used for the actual experiments. The magnitude of this correction was found to be essentially independent of the water content of the gas and the furnace temperature between 1100 and 1400°C, but it was sensitive to the concentration of hydrogen.

5. To minimize compositional changes during cooling, specimens were maintained in the atmospheres in which they had been equilibrated. However, this introduces the possibility that the solid might absorb hydrogen, perhaps in sufficient quantity to create a large positive error in x . To evaluate this potential error, a few experiments were carried out in atmospheres having a high concentration of hydrogen. After the PuO_{2-x} specimen had been equilibrated, it was annealed in helium at 1000°C for about an hour before being cooled to room temperature. The values of x obtained from these experiments were consistent with data obtained without a helium annealing treatment.

6. As a further check of the gas-analysis system, a PuO_{2-x} specimen that had been equilibrated at 1400°C was reoxidized and analyzed gravimetrically. The value of x so obtained (plotted as an x in Fig. 5) lies within the experimental scatter of the gas-analysis points.

7. Electrical resistance values were corrected for long-term drift (i.e., from continued densification of the ceramic) by periodically remeasuring the specimen in a He-4 v/o O_2 atmosphere at 1400°C.

IV. EXPERIMENTAL RESULTS

A. Rutile

The few results reported here for TiO_2 were obtained for comparison with recently reported data. Values of x and $p(\text{O}_2)$ at 1200 and 1300°C, derived from katharometer gas-analysis measurements, are presented in Table II. Although the points are scanty, plots of $\log x$ vs $\log p(\text{O}_2)$ fall close to straight lines of slope $-1/4.2$ at 1200°C, and $-1/4.9$ at 1300°C. This agrees rather well with slopes determined by Tannhauser⁽⁹⁾ from electrical conductivity measurements. Interpolated values of oxygen pressures at $x = 0.0025, 0.005, \text{ and } 0.0075$ have been used to calculate the relative partial

molar free energies of oxygen (F_O^M) in TiO_{2-x} at compositions that may be compared to the thermogravimetric results of Moser, Blumenthal, and Whitmore. (6) As shown in Table II, there is close agreement between the two sets of data.

Table II
MEASURED COMPOSITIONS AND EQUILIBRIUM OXYGEN
PRESSURES FOR TiO_{2-x}

T (°C)	x in TiO_{2-x}	Measured Oxygen Pressure (atm)	F_O^M (kcal/mole)	F_O^M (Moser et al.) (kcal/mole)
1200	0.0023	1.9×10^{-11}	-73	
	0.0025	-	-74*	-73
	0.0042	1.4×10^{-12}	-80	
	0.0050	-	-82*	-83
	0.0072	1.5×10^{-13}	-87	
	0.0075	-	-87*	-88
1300	0.0025	-	-62*	-63
	0.0038	5.2×10^{-10}	-67	
	0.0050	-	-72*	-71
	0.0051	6.7×10^{-11}	-74	
	0.0075	-	-78*	-76
	0.0080	6.6×10^{-12}	-81	
	0.0090	7.6×10^{-12}	-81	

*Interpolated values.

B. Plutonium Dioxide

Experimental values of x and resistivity (ρ) normalized to 0 v/o porosity are presented in the log-log plots of Figs. 4 and 5. Least-squares lines through the points have the following equations:

$$\log x (\pm 0.072) = \frac{-1}{4.20 (\pm 0.20)} \log p(O_2) - 6.18 (\pm 0.02) \quad (1100^\circ C); \quad (1)$$

$$\log 10\rho (\pm 0.076) = \frac{-1}{4.90 (\pm 0.34)} \log p(O_2) + 4.61 (\pm 0.02) \quad (1100^\circ C); \quad (2)$$

$$\log x (\pm 0.076) = \frac{-1}{3.17 (\pm 0.14)} \log p(O_2) - 5.69 (\pm 0.03) \quad (1400^\circ C); \quad (3)$$

$$\log 100\rho (\pm < 0.02) = \frac{1}{4.31 (\pm < 0.1)} \log p(O_2) + 4.19 (\pm < 0.01) \quad (1400^\circ C); \quad (4)$$

Fig. 4. Variation of x in PuO_{2-x} and Resistivity with Oxygen Pressure at 1100°C

Fig. 5. Variation of x in PuO_{2-x} and Resistivity with Oxygen Pressure at 1400°C

Normalization of ρ from a porosity of 27 v/o to zero was accomplished with the following relation:

$$1/\rho_c = [1 + V/(1 - V^{2/3})] (1/\rho_m), \quad (5)$$

where ρ_c and ρ_m are the resistivities of the nonporous and porous materials, respectively, and V is the volume fraction of pores.

Equation (5) was originally developed by Russell⁽¹⁰⁾ to describe the thermal conductivity of insulating refractories and was later adapted to correct the electrical resistivity of UO_2 ceramics by Belle and Lustman.⁽¹¹⁾ Applying this correction over a porosity range of 27 v/o creates considerable uncertainty in the absolute values of ρ ; however, it should not affect the slope of $\log \rho$ vs $\log p(\text{O}_2)$, and it probably does effectively compensate for small variations of porosity from specimen to specimen.

Figure 6 presents F_{O}^M for PuO_{2-x} as a function of $\log x$, at 1100 and 1400°C; for comparison, Markin, Bones, and Gardner's values⁽¹⁾ for 1100°C are also included. The considerable disagreement between the two sets of data may be caused by differences of oxide purity. A similar phenomenon has been observed for TiO_2 ; oxygen pressures reported by Buessem *et al.*⁽¹²⁾ are several orders of magnitude higher than those measured for purer oxides by Kofstad⁽⁵⁾ and by Moser and his associates.⁽⁶⁾ Comparison of Table I with the Harwell analysis shows that the overall purity of the PuO_2 used at Argonne is higher, which is consistent with the lower oxygen pressures reported in this paper.

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Fig. 6. Relative Partial Molar Free Energy of Oxygen in PuO_{2-x}

V. MASS-ACTION RELATIONS FOR PuO_{2-x}

The interaction between PuO_{2-x} and oxygen gas may be described in terms of the reversible formation of interstitial plutonium ions:

where Pu^{+4} and O^{-2} denote properly-charged ions at regular lattice sites; Pu^{+3} signifies a reduced cation at a regular lattice site; and Pu_i^{n+} represents an interstitial plutonium atom that has lost n electrons. Alternatively, the interaction may result in the formation of oxygen vacancies:

where V_O^{n+} represents a vacancy that has dissociated n electrons. In both of these cases, the Pu^{+3} on the right may be considered to take part simultaneously in a reaction of the form

where e (treated as a chemical component) represents mobile electrons.

The analysis that follows parallels that of Kröger and Vink⁽⁴⁾ except that reaction (6c) and the variation of certain activity coefficients will also be taken into account. The following assumptions will be made: (a) substantially all of the defects are interstitial plutonium atoms that have lost four electrons (Pu_i^{4+}); (b) these interstitials have been created entirely through the loss of oxygen from the solid; (c) changes in the concentrations of Pu^{+4} and O^{-2} are small enough to be neglected. Under these conditions, the mass-action equation for (6a) may be expressed in the form

$$[\text{Pu}_i^{4+}] \gamma_i [\text{Pu}^{+3}]^4 \gamma_r = K_4 p(\text{O}_2)^{-1}, \quad (7)$$

where γ_i and γ_r are the activity coefficients of the interstitials and trivalent cations; brackets $[ ]$ denote concentration in numbers/cm³ of solid; K_4 is the equilibrium constant; and $p(\text{O}_2)$ is the oxygen pressure.

Combining the mass-action equation for reaction (6c), $[e]\gamma_e / [\text{Pu}^{+3}]\gamma_r = K_e$, with the neutrality condition, $4[\text{Pu}_i^{4+}] = [\text{Pu}^{+3}] + [e]$, one obtains the following:

$$[\text{Pu}^{+3}] = \frac{4[\text{Pu}_i^{4+}]}{1 + \frac{K_e \gamma_r}{\gamma_e}}, \quad (8)$$

where K_e is the equilibrium constant for (6c), and γ_e is the activity coefficient of the mobile electrons. According to Rosenberg,⁽¹³⁾ γ_e may be expressed as $[e]^y$, where y is itself a function of $[e]$.

Substituting the expression for $[Pu^{+3}]$ from equation (8) into equation (7) gives the following result:

$$[Pu_1^{4\cdot}] = Nx = \left[\frac{K_4}{256\gamma_i\gamma_r^4} \left(1 + \frac{K_e\gamma_r}{\gamma_e} \right)^4 \right]^{1/5} p(O_2)^{-1/5}, \quad (9a)$$

where N is a units conversion factor.

Alternatively, the neutrality condition and the mass-action relation for (6c) may be used to replace $[Pu_1^{4\cdot}]$ and $[Pu^{+3}]$ in equation (7) by an expression containing $[e]$. This gives the equilibrium relation between conductivity (σ) and oxygen pressure:

$$[e] = \frac{\sigma}{C} = \left[\frac{4K_4K_e^4}{\gamma_e^4\gamma_i} \cdot \frac{1}{(\gamma_e/K_e\gamma_r) + 1} \right]^{1/5} p(O_2)^{-1/5}, \quad (9b)$$

where C is a constant at constant temperature.

In the general case (i.e., if the activity coefficients are variable), equations (9a) and (9b) would not result in linear log-log plots of x or σ against $p(O_2)$. However, these relations reduce to a simpler form for either of two special cases.

A. $K_e \gg 1$

This condition corresponds to a model in which the interstitials lose electrons to a conduction band. The bracketed expressions in (9a) and (9b) reduce to a single term, and after replacing γ_e by $[e]^y$, the following is obtained:

$$[Pu_1^{4\cdot}] = Nx \approx \left[\frac{K_4K_e^4}{256 \cdot 4^{4y} \cdot \gamma_i} \right]^{1/(5+4y)} p(O_2)^{-1/(5+4y)}, \quad (10a)$$

and

$$[e] = \frac{\sigma}{A\mu} \approx \left[\frac{4K_4K_e^4}{\gamma_i} \right]^{1/(5+4y)} p(O_2)^{-1/(5+4y)}, \quad (10b)$$

where μ is the Hall mobility, and A is a units conversion constant.

For this model, the variable y has an important influence on the exponent of $p(\text{O}_2)$ over the entire range of x illustrated in Figs. 4 and 5 (see Kröger⁽¹⁴⁾). As a result, equations (6a) and (6b) do not have linear relations between $\log x$ or $\log \sigma$ and $\log p(\text{O}_2)$, except for the unlikely case that the variation of γ_i just offsets the effect of y . Note also that the exponent of $p(\text{O}_2)$ in (10a) is the same as that in (10b); consequently, the observed slope differences between the composition and conductivity lines of Figs. 4 and 5 cannot be accounted for. Therefore, this model can be discarded as a description of the defect structure of PuO_{2-x} at 1100 and 1400°C.

B. $K_e \ll 1$

This condition corresponds to a mixed-valence model in which y becomes small enough to be neglected. It will now be assumed that in the experimental region, γ_i and γ_r may be described by a function of the form $(1 - bU^a)$, where a is a constant (<1), U is similar to the ionic strength in aqueous solution, and b is a constant that includes the charge (relative to a normal lattice point) of the reduced cation or interstitial. In the present case, since $[\text{Pu}^{+3}]$ and $[\text{Pu}_i^{4\cdot}]$ are interdependent, the ionic strength may be expressed in terms of $[\text{Pu}_i^{4\cdot}]$:

$$\gamma \approx 1 - b' [\text{Pu}_i^{4\cdot}]^a. \quad (11)$$

Over a limited range of $[\text{Pu}_i^{4\cdot}]$, the right side of (11) can be made to coincide approximately with expressions of the form

$$(k_r [\text{Pu}_i^{4\cdot}])^{-m} \text{ (for } \gamma_r), \quad (12a)$$

and

$$(k_i [\text{Pu}_i^{4\cdot}])^{-n} \text{ (for } \gamma_i), \quad (12b)$$

where k_r , k_i , m , and n are constants (m and n being <1), and the products $k_r[\text{Pu}_i^{4\cdot}]$ and $k_i[\text{Pu}_i^{4\cdot}]$ must be ≥ 1 .

Substituting (12a) and (12b) into the reduced form of (9a) gives the following relation between x and $p(\text{O}_2)$:

$$[\text{Pu}_i^{4\cdot}] = Nx \approx \left[\frac{K_4 k_i^n k_r^{4m}}{256} \right]^{1/(5-4m-n)} p(\text{O}_2)^{-1/(5-4m-n)}. \quad (13)$$

Electrical conduction in a mixed-valence oxide semiconductor has been described as a diffusion process in which thermally-activated electrons or holes hop from cation to cation (Heikes and Johnston⁽¹⁵⁾). Therefore, the steady-state conductivity is proportional to the number/cm³ of charge carriers that are activated at any instant, averaged over a long time. In the

present case, this corresponds to the average number/cm³ of excited Pu⁺₃, designated here as [e]. Simplifying (9b), σ may be expressed as follows:

$$[e] = \frac{\sigma}{C} = K_e \left[\frac{4K_4\gamma_r}{\gamma_i} \right]^{1/5} p(O_2)^{-1/5}. \quad (14)$$

With the aid of the relations $[Pu_i] \approx [Pu^{+3}]/4$ and $[Pu^{+3}] \approx [e]/K_e\gamma_r$, equations (12a) and (12b) can be expressed in terms of [e], rather than $[Pu_i^{4+}]$. These substitutions give

$$\gamma_r = \left(\frac{k_r[e]}{4K_e} \right)^{-m/(1-m)}, \quad (15)$$

and an analogous relation for γ_i . If m is small compared to one, the exponential term of (15) can be simplified to $-m$. Replacing γ_r and γ_i in (14) results in the following relation between σ and $p(O_2)$:

$$[e] = \frac{\sigma}{C} \approx K_e \left[\frac{K_4 k_i^n 4^{1+m-n}}{k_r^m} \right]^{1/(5+m-n)} p(O_2)^{-1/(5+m-n)}. \quad (16)$$

Equations (13) for x , and (16) for σ , both have linear log-log relations between the dependent variable and $p(O_2)$. If the exponential constants m and n equal 0 (corresponding to γ_r and γ_i being unity), the slopes of these log-log relations are identical. However, if $m > 0$, the slope of $\log x$ versus $\log p(O_2)$ should be steeper than that of $\log \sigma$ (or $\log \rho$) vs $\log p(O_2)$. Inspection of Figs. 4 and 5 shows that this is actually the case at both of the experimental temperatures. The value of m may be determined from the slope difference: dividing (16) by (13) gives a relation that (with decreasing m) approaches

$$\frac{\sigma}{x} \approx \frac{CNK_e p(O_2)^{m/5}}{k_r^m} = K_P(O_2)^{m/5}. \quad (17)$$

At 1100°C, $m \approx 0.15$.

If the arguments presented above are applied to triply-dissociated interstitial atoms (Pu_i^{3+}) or to singly-dissociated oxygen vacancies ($V_O^\bullet$), the relations listed in Table III are obtained. Note that in these relations, $p(O_2)$ has a somewhat different exponent than occurs for Pu_i^{4+} ; in principle, therefore, the slopes of the lines in Figs. 4 or 5 might be used to help determine the predominant defect type. A comparison of equations (13) and (16) shows that the resistivity lines are the more useful indicators

because the constants m and n tend to cancel each other. Assuming the quantity $(m - n)$ may be neglected, the slope of the 1100°C resistivity line suggests that the defects at that temperature are predominantly $\text{Pu}_i^{4\cdot}$. The steeper slope of the 1400°C line might equally be caused by an increased concentration of either V_O or $\text{Pu}_i^{3\cdot}$.

Table III
MASS ACTION RELATIONS FOR $\text{Pu}_i^{3\cdot}$ AND V_O

Defect Type	Equation	
	$K_e \gg 1$	$K_e \ll 1$
$\text{Pu}_i^{3\cdot}$	$N_x \approx \left[\frac{K_3 K_e^3}{27 \cdot 3^3 \gamma_i} \right]^{1/(4+3y)} p(\text{O}_2)^{-1/(4+3y)}$ $\frac{\sigma}{A\mu} \approx \left[\frac{3 K_3 K_e^3}{\gamma_i} \right]^{1/(4+3y)} p(\text{O}_2)^{-1/(4+3y)}$	$N_x \approx \left[\frac{K_3 k_i^n k_r^{3m}}{27} \right]^{1/(4-3m-n)} p(\text{O}_2)^{-1/(4-3m-n)}$ $\frac{\sigma}{C} \approx K_e \left[\frac{3^{1+m-n} K_3 k_i^n}{k_r^m} \right]^{1/(4+m-n)} p(\text{O}_2)^{-1/(4+m-n)}$
V_O	$N_x \approx \left[\frac{K_1 K_e}{\gamma_v} \right]^{1/(2+y)} p(\text{O}_2)^{-1/(4+2y)}$ $= \frac{\sigma}{A\mu}$	$N_x \approx \left[\frac{K_1 k_v^n k_r^m}{k_i^n} \right]^{1/(2-m-n)} p(\text{O}_2)^{-1/(4-2m-2n)}$ $\frac{\sigma}{C} \approx K_e \left[\frac{K_1 k_v^n}{k_r^m} \right]^{1/(2+m-n)} p(\text{O}_2)^{-1/(4+2m-2n)}$

K_3 and K_1 are the equilibrium constants for the reactions that form $\text{Pu}_i^{3\cdot}$ and V_O ; γ_v and γ_i are the activity coefficients of V_O and $\text{Pu}_i^{3\cdot}$; k_v and k_i are constants in the relations $\gamma_v = (k_v [\text{V}_\text{O}])^{-n}$, and $\gamma_i = (k_i [\text{Pu}_i^{3\cdot}])^{-n}$. All other symbols are defined in the text.

If plutonium interstitials of one charge or another do predominate at both of the experimental temperatures, an unusual reversal of the reaction $\text{Pu}_i^{3\cdot} + \text{Pu}^{+4} \rightarrow \text{Pu}_i^{4\cdot} + \text{Pu}^{+3}$ appears to occur as the temperature rises from 1100 to 1400°C. This phenomenon might be explained in terms of the additional configurational entropy (ΔS) gained by the solid if the electrons are distributed on cations at both interstitial and regular sites, rather than on just the latter. Since the product $T\Delta S$ has an increasing effect on the free energy of the reaction as the temperature rises, a critical temperature may be reached above which the controlling influence of the enthalpy term is overbalanced.

APPENDIX

Description and Source of Trade-named Apparatus

1. RSCo Katharometer

Model 600-1 tungsten-filament thermal-conductivity detector in model 600 oven, used with a model 605-1 power supply, Research Specialties Co., Richmond, Calif.

2. LOENCO Valves

Model L-206-4 switching valve and model L-208-6 sampling valve, LOENCO Inc., Altadena, Calif.

3. Linde Molecular Sieve

Molecular Sieve Type 5A, Union Carbide Corp., Linde Div., New York, N. Y.

4. Deoxo Purifier

Model D-10-50 hydrogen purifier, Englehard Industries, Inc., Newark, N. J.

5. Carbowax Adsorbent

Carbowax 4000, Union Carbide Corp., Chemicals Div., New York, N. Y.

6. Haloport Adsorbent Support

Haloport-F, F and M Scientific Corporation, New Castle, Delaware.

7. Millipore Filter Elements

Type GS filter elements, pore size 0.22μ , catalog No. GSWP14200, Millipore Filter Corp., Bedford, Mass.

8. Dressen-Barnes Power Supply

Model 20-12 12-volt regulated dc power supply, Dressen-Barnes Electronics Corp., Pasadena, Calif.

9. ESI Standard Resistors

Type SRI standard resistors, Electro Scientific Industries, Portland, Oregon.

10. Keithley Differential Voltmeter

Model 660 guarded dc differential voltmeter, Keithly Instruments Inc., Cleveland, Ohio.

11. MSA Filters

Type DZ-78001 filters, 0.3 μ pore size, Mine Safety Appliances Co., Pittsburgh, Pa.

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