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by

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THERMODYNAMICS AND TRANSPORT OF GASEOUS IRIIDIUM OXIDES IN MULTI-HUNDRED-WATT THERMOELECTRIC GENERATORS

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Dean E. Peterson

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ABSTRACT

Thermodynamic properties of the iridium oxide system were determined by using a mass spectrometer and target collection apparatus with a gas inlet system. Iridium dioxide and trioxide were identified as the predominant gaseous oxides in equilibrium with iridium metal in an oxygen atmosphere of 10^{-4} to 10^{-2} atm at 1600-1800°C. The equilibrium constants for formation of these gaseous species followed the relationships

$$\log_{10} K_{\text{IrO}_2} = -10459(\pm 698)/T^\circ\text{K} + 1.69(\pm 0.35)$$

and

$$\log_{10} K_{\text{IrO}_3} = -1188(\pm 194)/T^\circ\text{K} - 2.285(\pm 0.095).$$

The heats and entropies of formation of the two oxides at an average 1720°C were $\Delta H^\circ_{\text{IrO}_2} = 47.9(\pm 3.2)$ kcal/mole; $\Delta S^\circ_{\text{IrO}_2} = 7.7(\pm 1.6)$ eu and $\Delta H^\circ_{\text{IrO}_3} = 25.44(\pm 0.89)$ kcal/mole; $\Delta S^\circ_{\text{IrO}_3} = -10.45(\pm 0.44)$ eu. The results were compared to previous thermodynamic measurements and used to predict iridium transport within a Multi-Hundred-Watt heat source. The analyses indicated that iridium transport due to iridium oxidation by the plutonia fuel is negligible at the fuel operating temperature, but that the fuel oxygen can participate in iridium transport at higher temperatures such as occur during reentry or a launch pad fire. The effect of an iridium dioxide impurity layer on the iridium transport also is discussed.

1. INTRODUCTION

Iridium metal is important for high temperature use in oxidizing environments. Its oxidation behavior must be known accurately over wide temperature and oxygen pressure ranges to permit predictions of its usefulness. Iridium in oxygen at 1-atm pressure forms the solid dioxide below 1100° (in certain conditions, the solid sesquioxide may form). These oxides disproportionate above 800°C in vacuum to give off oxygen and gaseous iridium trioxide. The oxygen pressure over the solid dioxide reaches 1 atm at approximately 1100°C. The dioxide vapor

becomes important at oxygen pressures < 1 atm and temperatures $> 1500^\circ\text{C}$.

Iridium is used as a cladding for plutonia fuel in Multi-Hundred-Watt (MHW) radioisotopic thermoelectric generators. The basic MHW fuel sphere assembly (FSA) is shown in Fig. 1. The plutonia fuel ball is encapsulated in a 0.61-mm-thick iridium post-impact containment shell (PICS) surrounded by a graphite impact shell (GIS). Each PICS has two 0.13-mm-diam vents and associated fritted particulate filters to release the helium that the fuel generates, while containing the plutonia. Iridium transport was

Fig. 1. Multi-Hundred-Watt fuel sphere assembly.

observed¹ in test FSA's heated at approximately 1300°C for several thousand hours. The transport caused dendritic growth of iridium metal under the weld band and vent shields which plugged the vents and generally degraded the iridium parts. The most probable explanation for this transport seemed to be formation of gaseous iridium trioxide and subsequent disproportionation of the oxide molecules to deposit iridium in the cool parts of the PICS.

Review of previous sublimation studies²⁻⁹ on the iridium oxide system showed discrepancies in partial pressures of the iridium oxide vapor species. Therefore, a detailed study was undertaken to determine accurate thermodynamic properties. A Knudsen effusion technique was used to determine the equilibrium vapor pressures of gaseous iridium oxides. A quadrupole mass spectrometer was used to identify the molecular species in the effusate and to determine the temperature and oxygen dependences of the observed iridium oxide vapor species. Target collection of the molecular beam was used in total pressure measurement of the iridium oxide effusate as a function of temperature. Target collection problems necessitated use of calcium oxide to calibrate the quadrupole ion intensities in order to obtain partial pressures of the iridium dioxide and

trioxide vapors. A gas inlet tube allowed the oxygen partial pressures within the cell to be varied along with the temperature in order to measure equilibrium constants for formation of the gaseous oxide molecules. Mass spectrometric measurements on the gaseous dioxide and trioxide included determination of ionization efficiencies, appearance potentials, and temperature coefficients.

Results were used to predict amounts of iridium transported within a MHF FSA as a function of temperature and oxygen pressure. The results were also used to analyze the iridium's oxidation resistance during re-entry into Earth's atmosphere and a launch pad fire. Participation of oxygen from the fuel and from an iridium dioxide impurity layer in iridium transport within a MHF FSA also was examined theoretically.

Iridium transport within a MHF FSA at operating temperature has apparently been stopped by two combined approaches. The iridium parts are degassed for 1 h at 1500°C to remove any iridium dioxide impurities. Also, the vent diameter was increased by an order of magnitude, to 0.15 mm, which permits faster release of any oxygen gas within an FSA, thereby allowing less time for gaseous iridium oxide formation. Travis, Peterson, and Mulford¹⁰ give a more complete discussion of the importance of vent size in retaining gas within an FSA.

II. PREVIOUS WORK

Several transpiration measurements on the sublimation thermodynamics of iridium oxide have been conducted. These studies have generally involved flowing oxygen gas over heated iridium metal and analyzing the collected sublimate and/or measuring the sample weight loss. Most have been conducted at relatively low (1300°C) temperatures and high (1-atm) oxygen pressure. Alcock and Hooper's, Schafer and Heitland's, Cordfunke and Meyer's, Olevei's, and Bell and Tagami's results²⁻⁶ correlate reasonably well. All agree about the predominance of the gaseous iridium trioxide, its vapor pressure, and

the thermodynamic properties, given the conditions of their studies. The trioxide vapor molecule was identified by oxygen dependence measurements of the iridium transport rate. There is an unexplained discontinuity in Ramakrishnan and Chandrasekhariarh's⁷ second-law plot of the logarithm of the trioxide vapor pressure determined by transpiration vs the reciprocal temperature. The IrO_3 vapor pressures that Wimber and Kraus⁸ measured over a higher temperature range are significantly higher than corresponding pressures obtained by extrapolation of the other transpiration results excepting those in Ref. 7.

Norman, Staley, and Bell⁹ confirmed the presence of iridium trioxide mass spectrometrically as well as identifying the dioxide and monoxide species. The gaseous trioxide and dioxide were the important species in their study. The vapor pressure they found for $\text{IrO}_3(\text{g})$ is considerably lower than those obtained by extrapolating any of the transpiration results to higher temperatures. Their trioxide and dioxide pressures are also much lower than those that Wimber and Kraus measured over the same temperature range. These conflicting results emphasized the need for further vapor pressure measurements, especially at higher temperatures and lower oxygen pressures than those used in most transpiration studies.

III. EXPERIMENT

A. Mass Spectrometric Measurements

Equilibrium partial pressures of iridium oxide vapor species were determined using the Knudsen effusion technique. The composition of the gas effusing from a crucible was analyzed mass spectrometrically. An attempt to measure the total iridium oxide vapor pressure by a target collection method was also made. The mass spectrometer and target collection apparatus is shown in Fig. 2.

A quadrupole mass spectrometer from Extranuclear Laboratories was used to identify various vapor species effusing from the

Fig. 2. Target collection and mass spectrometer apparatus.

crucible. The 9.52-mm-diam rods and an Extranuclear Laboratories E model High Q Head allowed for analysis of up to 1000 amu while maintaining reasonably high resolution. The ion source with which ionization efficiency curves and appearance potentials were measured had an Electronic Associates Inc. configuration. The ion detector was a Bendix Channeltron that combined high gain and stability with oxidation resistance. The quadrupole was oriented perpendicular to the molecular beam to minimize condensation of material on the poles. The quadrupole could be aligned accurately with respect to the molecular beam by manipulating two threaded spacers on either side of the bellows.

A water-cooled copper cylinder was rotatable about the quadrupole head to allow for target collection of the effusate. A port through the target block enabled mass spectrometric analysis of the molecular beam. A tantalum target strip was positioned around the target block. Six targets or the port leading to the quadrupole were selected externally by correlation with a vernier reading on a rotary motion feedthrough. After the exposures, the target strip was removed through the top flange without disturbing the crucible, target block, or mass spectrometer.

The vacuum system was a Sargent-Welch Scientific Co. Model 1397 mechanical fore-pump connected to a National Research Corporation oil diffusion pump and associated liquid nitrogen trap. A gate valve could be closed to permit access to the crucible, spectrometer, or collection regions without turning off the pumps. This system can provide vacuums approaching 10^{-8} torr in the sample area.

The furnace was a tantalum heater strip surrounded by three tantalum radiation shields. The sample crucible was iridium metal supported by a tungsten outer crucible with a blackbody hole and three support rods. The crucible had a 0.80-mm-diam top orifice. An iridium gas inlet tube was welded into the side of the iridium crucible. The furnace was contained in a water-cooled copper condenser through which the heater strip and gas inlet tube passed. The temperatures were measured by sighting on the blackbody hole in the crucible base with a Pyrometer Instrument Co. pyrometer. The pyrometer was calibrated with a National Bureau of Standards standard lamp, and the optical window's adsorption was measured. Corrections for the pyrometer and window were applied to the measured temperatures.

The sample was a mixture of calcium oxide and iridium powders each weighing 0.1 g. The iridium powder* was 99.8% pure; the calcium oxide powder** was reagent grade material. Spectrochemical analyses of both powders are summarized in Table I.

B. Target Collection Measurements

The target collection measurements were performed by holding a constant temperature in the Knudsen cell while examining the vapor composition mass spectrometrically. The shutter was closed, and the target block was rotated until the selected target was in place opposite the molecular beam. Then the shutter was opened, and the target was

TABLE I

IMPURITY LEVELS IN IRIIDIUM AND CALCIUM OXIDE SAMPLES (Results preceded by < are at detection limit.)

Element	Ir ($\mu\text{g/g}$)	CaO ($\mu\text{g/g}$)	Element	Ir ($\mu\text{g/g}$)	CaO ($\mu\text{g/g}$)
Li	< 30	< 20	Zn	< 100	< 200
Be	< 3	< 2	Ga	< 30	8
B	< 10	< 2	Ge	< 30	< 6
Na	< 100	20	Sr	< 3	400
Mg	< 5	4000	Zr	< 300	200
Al	< 30	400	Nb	< 1000	< 60
Si	10	4000	Mo	< 300	< 20
P	---	< 200	Ag	< 30	< 2
K	< 300	< 200	Cd	< 100	< 6
Ca	5	Major	In	< 30	< 20
Ti	< 10	60	Sn	< 30	< 20
V	< 10	6	Sb	< 100	< 60
Cr	< 10	10	Ba	50	6
Mn	< 10	30	Ta	< 1000	< 600
Fe	< 30	400	W	< 3000	< 600
Co	< 10	< 6	Tl	< 30	< 200
Ni	< 10	< 10	Pb	< 30	< 20
Cu	< 10	< 2	Bi	< 30	< 20
Ru	< 30	---	Rh	2000	---
Pd	15	---	Hf	< 1000	---
Ir	Major	---	Pt	40	---
Au	< 10	---			

exposed to the effusate for a fixed period. The temperature and time were monitored throughout each exposure.

The iridium deposited on each of the six targets was neutron activated by being placed in a reactor for 1 h. The activated iridium contained the radioisotopes ^{192}Ir and ^{194}Ir . The targets were not analyzed for 1 week, to allow the ^{194}Ir to disappear by nuclear decay. The remaining ^{192}Ir was then gamma counted to try to determine the amount of iridium deposited on each target.

Gamma counting the tantalum targets after neutron activation gave too high a counting rate to be a sensitive method for iridium analysis. The high counting rate was thought to be due to highly radioactive daughter products from the tantalum strip, rather than excessive iridium. Other materials such as copper might have made better targets. Another approach considered involved target collection measurements using radioactive ^{192}Ir directly, followed by gamma counting of the deposit. That approach would avoid activating the target metal, but would necessitate use of a crucible material other than iridium.

*Varlacoid Chemical Co., 666 South Front St., Elizabeth, N. J. 07202.

**Matheson, Coleman, and Bell, Norwood, Ohio 45212.

IV. RESULTS

A. Mass Spectrometric Results

Mass spectral scans were conducted up to 1000 amu. The shutterability of each peak in the mass range of interest was tested, along with its intensity dependence on temperature and crucible oxygen pressure. A number of high mass peaks above 250 amu were found to be shutterable and to vary in intensity with oxygen pressure and temperature, but they were believed to be due to tungsten oxide vapor molecules and their ionization fragments from the tungsten crucible used as an outer container in these experiments. No iridium monoxide was observed.

Ionization efficiencies of the IrO_2^+ and IrO_3^+ ions were measured and plotted in Fig. 3. The dioxide and trioxide appearance potentials determined by linear extrapolation were 10.8 and 12.1 eV, respectively, based on the ionization potentials of silver (7.54 eV) and water (12.56 eV).

The shutterable ion intensity of $\text{Ca}^+(40)$ resulting from ionization of the calcium effusate in equilibrium with the CaO(s) was measured as 2.6×10^{-9} A at 1975°C . This value was obtained with no inlet oxygen, 70-eV ionizing energy, and 1.5-mA emission current. The calcium vapor pressure calculated from Classen and Veenemans' results¹¹

was 5.0×10^{-6} A in analogous conditions. Using Mann's¹² 7.0×10^{-16} cm² ionization cross section σ_i for calcium, a machine constant, C, of 6.0×10^{-16} atm cm²/K A was calculated from

$$P_i = C I_i T / \sigma_i Y_i f_i \quad (1)$$

The isotopic fraction f_i and multiplier gain Y_i for calcium were assigned a value of unity for the calculations. Calcium has only one isotope, ^{40}Ca , and the gain was not accurately measured during the experiment.

The machine constant determined for calcium from the measured $\text{Ca}^+(40)$ ion intensity was used in calculating calcium pressures over a wide range of oxygen pressures. These calcium pressures were then used to calculate oxygen partial pressures from thermodynamic properties obtained from Schick¹³ for the reaction

The partial pressures of the IrO_2 and IrO_3 vapors were also determined from Eq. 1 and the previously calculated machine constant. Mann's Ir and O ionization cross sections¹² were assumed to be additive in order to obtain molecular cross sections of 9.7×10^{-16} cm² and 1.1×10^{-15} cm², respectively, for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$. The 0.627 isotopic fraction for ^{193}Ir was used

Fig. 3. Ionization efficiencies of IrO_2^+ and IrO_3^+ .

TABLE II
PARTIAL PRESSURES AND EQUILIBRIUM CONSTANTS
FOR FORMATION OF IRIDIUM DIOXIDE AND
TRIOXIDE VAPORS

Iridium Dioxide (IrO_2)					
T (°C)	Intensity (A)	P_{O_2} (Atm)	P_{IrO_2} (Atm)	$10^4/T^\circ\text{K}$	$-\log_{10} K_{eq}$
1700	1.5×10^{-10}	1.1×10^{-3}	2.9×10^{-7}	5.07	3.585
1798	4.0×10^{-10}	2.0×10^{-3}	8.2×10^{-7}	4.85	3.386
1800	6.0×10^{-10}	2.7×10^{-3}	1.2×10^{-6}	4.82	3.339
1735	3.6×10^{-10}	2.4×10^{-3}	7.2×10^{-7}	4.98	3.534
1775	2.0×10^{-10}	1.1×10^{-3}	4.1×10^{-7}	4.88	3.438
1765	3.9×10^{-10}	2.2×10^{-3}	7.8×10^{-7}	4.91	3.449
1640	1.0×10^{-10}	2.0×10^{-3}	3.2×10^{-7}	5.23	3.800
1690	2.7×10^{-10}	2.2×10^{-3}	5.3×10^{-7}	5.09	3.620
1730	4.0×10^{-10}	2.4×10^{-3}	8.9×10^{-7}	4.99	3.500
Iridium Trioxide (IrO_3)					
1675	9.1×10^{-11}	2.4×10^{-3}	1.6×10^{-7}	5.13	2.893
1775	7.8×10^{-11}	2.2×10^{-3}	1.4×10^{-7}	4.88	2.870
1850	4.6×10^{-11}	1.5×10^{-3}	8.4×10^{-8}	4.71	2.843

in Eq. (1) to calculate the IrO_2 and IrO_3 vapor pressures given in Table II. The first and second columns give the measured temperatures and ion intensities of IrO_2^+ and IrO_3^+ , respectively. The third column shows the oxygen pressures determined from the $\text{Ca(g)}/\text{CaO(s)}$ equilibrium previously discussed. The fourth column tabulates the partial pressures calculated for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$. The fifth and sixth columns give the reciprocal temperatures and the logarithms of the equilibrium constants for the formation reaction

and

The data are plotted in Fig. 4 with least squares lines drawn through the two sets of points. Least squares treatments yielded the following relationships in Eqs. (3) and (4), respectively

$$\log_{10} K_{\text{IrO}_2} = -10459(+698)/T^\circ\text{K} + 1.69(+0.35),$$

$$\log_{10} K_{\text{IrO}_3} = -1188(+194)/T^\circ\text{K} - 2.285(+0.095).$$

The standard heats of formation for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ are $47.9(+3.2)$ and $5.44(+0.89)$ kcal/mole, respectively, at an average 1720°C . Standard entropies of formation determined at 1720°C for the gaseous dioxide and trioxide are $7.7(+1.6)$ and $-10.45(+0.44)$ eu, respectively, relative to Ir(s) and 1-atm $\text{O}_2(\text{g})$ as standard states.

In the sample residue from experiments run above 1800°C , Roof¹⁴ identified the new phase $\text{Ca}_3\text{IrO}_6(\text{s})$ which has a cryolite crystal structure. The appearance of this material is believed not to have affected the present study because Ir(s) was also present in the vaporizing solid.

B. Analysis of Iridium Transport in MHW FSA

The thermodynamic functions of gaseous iridium oxides reported here were used to calculate iridium transport within a MHW fuel sphere as a function of oxygen pressure, temperature, and fuel stoichiometry. Akermann, Faircloth, and Rand's¹⁵ thermodynamic functions of plutonia were used in these calculations. The results are presented in Fig. 5, where the logarithm of the

Fig. 4. Temperature dependences of the equilibrium constants for formation of gaseous IrO_3 and IrO_2 measured mass spectrometrically.

Fig. 5. Iridium transport rates due to oxidation by fuel oxygen in MHW FSA.

calculated iridium transport rate in a MHW FSA is plotted vs the temperature in degrees centigrade. The effect of the fuel stoichiometry on the transport rate is also shown. At an operating temperature of 1365°C, the rate of iridium transport resulting from reaction of the PICS with stoichiometric $\text{PuO}_{2.00}$ is $1.6 \times 10^{-18} \text{ g cm}^{-2} \text{ s}^{-1}$. Because each of the two PICS vents has an area about $1.3 \times 10^{-4} \text{ cm}^2$, approximately 1 μg of iridium metal could move to each vent in approximately 6 days at this temperature. Because the vent assemblies are porous, relatively large quantities of transported iridium would be required to plug a vent completely. Reduction of an initially stoichiometric fuel ball to $\text{PuO}_{1.99}$ would require transport of 0.66 g of iridium. The transported iridium should deposit in the cooler regions of the PICS, behind the weld band and vent shields. Assuming that the entire 45.6- cm^2 inner PICS surface area reacts with the fuel oxygen, the time required to reduce an initially stoichiometric fuel sphere to $\text{PuO}_{1.99}$ would be 11 days at 1365°C. Once the fuel sphere became slightly substoichiometric, the iridium transport due to oxidation by the fuel oxygen would be insignificant at MHW operating temperatures owing to the low oxygen potentials at substoichiometric compositions. Because the fuel sphere is probably slightly substoichiometric initially, very little iridium metal should be transported by PICS fuel oxidation during operation.

Cordfunke and Meyer's¹⁶ results indicate that solid iridium oxide disproportionates above 800°C to give off oxygen gas. Because of the possible high oxygen pressures obtainable from a thin iridium oxide impurity layer on the PICS, this oxygen source is another mechanism for iridium transport within a MHW FSA. Approximately 1 atm of oxygen would be produced within a closed PICS at a fuel operating temperature of 1330°C from a 10^{-4} mm thick IrO_2 layer on the inner PICS surface. An iridium oxide impurity layer as thin as 10^{-4} mm would not

be visible, but it could be detected by surface analysis. The disproportionation of iridium dioxide solid to release oxygen indicates that an iridium oxide solid impurity can be removed easily by vacuum degassing at >1100°C.

Reentry conditions equivalent to a fuel temperature of about 1760°C for 5 min initially cause rapid iridium transport by fuel oxygen until a $\text{PuO}_{1.99}$ composition is attained. Then iridium transport becomes negligible again over the relatively short period. Much of the oxygen the fuel generates should escape through the vents without contributing to vapor transport of iridium.

A launch pad fire could also cause high fuel temperatures and iridium vapor transport due to fuel interaction with the PICS. PICS oxidation by the atmosphere is probably negligible as long as the converter and/or GIS remains intact around the PICS. Iridium transport rates within a PICS depend on the fuel temperature and stoichiometry. The fuel sphere's proximity to the propellant

Fig. 6. Logarithms of equilibrium constants for formation of iridium oxide vapor species vs temperature.

and the thermal protection the converter housing offers during the exposure would be important in determining iridium transport levels.

V. DISCUSSION

Thermodynamic results from this iridium oxide sublimation study are compared with results of previous studies in Fig. 6. The logarithms of the equilibrium constants for formation of gaseous iridium dioxide and trioxide are plotted vs the reciprocal temperature. The temperature dependence of the trioxide equilibrium constant measured in this study agrees very well with the extrapolation of most transpiration measurements. Comparison of Wimber and Kraus's results⁸ with the present ones shows that the former include higher pressures for both $\text{IrO}_3(\text{g})$ and $\text{IrO}_2(\text{g})$ at equivalent temperatures, although the temperature dependencies are similar. The equilibrium constants that Norman, Staley, and Bell⁹ determined mass spectrometrically are considerably lower than those of this study, given analogous conditions. Owing to its better agreement with the transpiration study, the present work is believed to be more nearly correct. The temperature dependencies of the trioxide and dioxide equilibrium constants in the two mass spectrometric studies agree well. The IrO_2^+ and IrO_3^+ appearance potentials measured here agree very well with values previously determined by Norman and his co-workers.⁹

The vapor pressures and equilibrium constants determined mass spectrometrically in this study depend on the assumed values of ionization cross sections and multiplier gains and are influenced by the accuracy of previous thermodynamic measurements on the calcium oxide system. These equilibrium constants for $\text{IrO}_3(\text{g})$ formation and those obtained by extrapolation of the transpiration measurements agree well.

The $\text{Ir}_2\text{O}_3(\text{g})$ could become important at oxygen pressures higher than 10^{-3} atm. The isotopic distributions or mass positions of

shutterable peaks observed above 300 amu could not be characterized. Since tungsten was present and WO_2^+ and WO_3^+ had been observed at high oxygen pressures, probably the shutterable species above 300 amu were due to $\text{W}_3\text{O}_9(\text{g})$ and $\text{W}_2\text{O}_6(\text{g})$. Measurement of the temperature dependence of the peak intensities appeared to confirm this hypothesis. This conclusion does not disprove the existence of an $\text{Ir}_2\text{O}_3(\text{g})$ vapor species that could be important in different conditions from those of this study. At 900°C and 1 atm O_2 , Kuriakose, Kent, and Margrave¹⁷ observed mass spectrometrically an Ir_2O_2^+ species that is probably an ionization fragment of $\text{Ir}_2\text{O}_3(\text{g})$.

Kubaschewski, Evans, and Alcock¹⁸ give the following empirical relationship between the standard entropy, S_{298} , and the molecular weight, M , of polyatomic species

$$S_{298} = 39.0 + 0.34 M - 6.2 \times 10^{-4} M^2.$$

Use of this relationship to calculate entropies for the iridium dioxide and trioxide vapor molecules yields values of 84 and 85 eu, respectively. Using the 7.7- and -10.5-eu entropies of formation for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ measured in this study at 2000°K and assuming that the ΔC_p 's for formation of $\text{WO}_2(\text{g})$ and $\text{WO}_3(\text{g})$ are equivalent to those for the analogous iridium species, gives experimental S_{298} values of 71 and 75 eu for the dioxide and trioxide species, respectively. Considering the approximations involved in this treatment, the agreement seems reasonable.

VI. CONCLUSIONS

A. The importance of iridium dioxide and trioxide vapors in equilibrium with iridium metal in an oxidizing atmosphere at high temperature was verified mass spectrometrically.

B. The appearance potentials for the ion species IrO_2^+ and IrO_3^+ were 10.8 and 12.1 eV, respectively.

C. The temperature dependencies of the equilibrium constants for formation of

calculated iridium transport rate in a MHW FSA is plotted vs the temperature in degrees centigrade. The effect of the fuel stoichiometry on the transport rate is also shown. At an operating temperature of 1365°C, the rate of iridium transport resulting from reaction of the PICS with stoichiometric $\text{PuO}_{2.00}$ is $1.6 \times 10^{-18} \text{ g cm}^{-2} \text{ s}^{-1}$. Because each of the two PICS vents has an area about $1.3 \times 10^{-4} \text{ cm}^2$, approximately 1 μg of iridium metal could move to each vent in approximately 6 days at this temperature. Because the vent assemblies are porous, relatively large quantities of transported iridium would be required to plug a vent completely. Reduction of an initially stoichiometric fuel ball to $\text{PuO}_{1.99}$ would require transport of 0.66 g of iridium. The transported iridium should deposit in the cooler regions of the PICS, behind the weld band and vent shields. Assuming that the entire 45.6- cm^2 inner PICS surface area reacts with the fuel oxygen, the time required to reduce an initially stoichiometric fuel sphere to $\text{PuO}_{1.99}$ would be 11 days at 1365°C. Once the fuel sphere became slightly substoichiometric, the iridium transport due to oxidation by the fuel oxygen would be insignificant at MHW operating temperatures owing to the low oxygen potentials at substoichiometric compositions. Because the fuel sphere is probably slightly substoichiometric initially, very little iridium metal should be transported by PICS fuel oxidation during operation.

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Thermodynamic results from this iridium oxide sublimation study are compared with results of previous studies in Fig. 6. The logarithms of the equilibrium constants for formation of gaseous iridium dioxide and trioxide are plotted vs the reciprocal temperature. The temperature dependence of the trioxide equilibrium constant measured in this study agrees very well with the extrapolation of most transpiration measurements. Comparison of Wimber and Kraus's results⁸ with the present ones shows that the former include higher pressures for both $\text{IrO}_3(\text{g})$ and $\text{IrO}_2(\text{g})$ at equivalent temperatures, although the temperature dependencies are similar. The equilibrium constants that Norman, Staley, and Bell⁹ determined mass spectrometrically are considerably lower than those of this study, given analogous conditions. Owing to its better agreement with the transpiration study, the present work is believed to be more nearly correct. The temperature dependencies of the trioxide and dioxide equilibrium constants in the two mass spectrometric studies agree well. The IrO_2^+ and IrO_3^+ appearance potentials measured here agree very well with values previously determined by Norman and his co-workers.⁹

The vapor pressures and equilibrium constants determined mass spectrometrically in this study depend on the assumed values of ionization cross sections and multiplier gains and are influenced by the accuracy of previous thermodynamic measurements on the calcium oxide system. These equilibrium constants for $\text{IrO}_3(\text{g})$ formation and those obtained by extrapolation of the transpiration measurements agree well.

The $\text{Ir}_2\text{O}_3(\text{g})$ could become important at oxygen pressures higher than 10^{-3} atm. The isotopic distributions or mass positions of

shutterable peaks observed above 300 amu could not be characterized. Since tungsten was present and WO_2^+ and WO_3^+ had been observed at high oxygen pressures, probably the shutterable species above 300 amu were due to $\text{W}_3\text{O}_9(\text{g})$ and $\text{W}_2\text{O}_6(\text{g})$. Measurement of the temperature dependence of the peak intensities appeared to confirm this hypothesis. This conclusion does not disprove the existence of an $\text{Ir}_2\text{O}_3(\text{g})$ vapor species that could be important in different conditions from those of this study. At 900°C and 1 atm O_2 , Kuriakose, Kent, and Margrave¹⁷ observed mass spectrometrically an Ir_2O_2^+ species that is probably an ionization fragment of $\text{Ir}_2\text{O}_3(\text{g})$.

Kubaschewski, Evans, and Alcock¹⁸ give the following empirical relationship between the standard entropy, S_{298} , and the molecular weight, M , of polyatomic species

$$S_{298} = 39.0 + 0.34 M - 6.2 \times 10^{-4} M^2.$$

Use of this relationship to calculate entropies for the iridium dioxide and trioxide vapor molecules yields values of 84 and 85 eu, respectively. Using the 7.7- and -10.5-eu entropies of formation for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ measured in this study at 2000°K and assuming that the ΔC_p 's for formation of $\text{WO}_2(\text{g})$ and $\text{WO}_3(\text{g})$ are equivalent to those for the analogous iridium species, gives experimental S_{298} values of 71 and 75 eu for the dioxide and trioxide species, respectively. Considering the approximations involved in this treatment, the agreement seems reasonable.

VI. CONCLUSIONS

A. The importance of iridium dioxide and trioxide vapors in equilibrium with iridium metal in an oxidizing atmosphere at high temperature was verified mass spectrometrically.

B. The appearance potentials for the ion species IrO_2^+ and IrO_3^+ were 10.8 and 12.1 eV, respectively.

C. The temperature dependencies of the equilibrium constants for formation of

$\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$, respectively, at 1640-1850°C followed

$$\log_{10} K_{\text{IrO}_2} = -10459(+698)/T^\circ\text{K} + 1.69(\pm 0.35),$$

and

$$\log_{10} K_{\text{IrO}_3} = -1188(\pm 194)/T^\circ\text{K} - 2.285(\pm 0.095).$$

D. The heats and entropies of formation of the gaseous dioxide and trioxide at an average 1720°C were

$$\Delta H^\circ_{\text{IrO}_2} = 47.9(\pm 3.2) \text{ kcal/mole};$$

$$\Delta S^\circ_{\text{IrO}_2} = 7.7(\pm 1.6) \text{ eu},$$

and

$$\Delta H^\circ_{\text{IrO}_3} = 5.44(\pm 0.69) \text{ kcal/mole};$$

$$\Delta S^\circ_{\text{IrO}_3} = -10.45(\pm 0.44) \text{ eu}.$$

E. Iridium transport in a MHW FSA because of iridium oxidation by the fuel would not be significant at operating temperature, but could become important during reentry or launch pad fires.

F. An iridium oxide impurity layer on the PICS was also important in determining iridium transport at operating temperature.

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