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COMMENTS

Comment on "Controversy on the First Ionization Potential of PuO_2 (Nearly) Settled by New Experimental Evidence"

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Capone et al.[1] recently reported a new IE(PuO_2) derived from mass spectrometric measurements of plutonium oxide vapor species effusing from a Knudsen cell at high temperatures. The IE(PuO_2) = 6.6 eV obtained from a "new type of experiment"[1] is a revision of their earlier value of 10.1 eV obtained from traditional electron impact appearance potential measurements.[2] We are gratified that this revised value of 6.6 eV[1] is in better agreement with our published value, IE(PuO_2) = 7.03 ± 0.12 eV,[3] but consider that the methodology used to derive this new value[1] is sufficiently problematic to warrant a cautionary assessment.

In the new Knudsen effusion study,[1] the measured ion intensity ratio at 2670 K—without an ionizing electron beam—was $[PuO^+]/[PuO_2^+] = 2.1 \pm 0.03$. Evidently, it was assumed that thermodynamic equilibrium of the ions was established in the cell, which allowed the following relationship to be derived by Capone et al.:[1] IE(PuO_2) − IE(PuO) = 0.42 ± 0.005 eV. Their assigned IE(PuO) = 6.2 eV[1] (essentially the same as our value of 6.1 ± 0.2 eV from FTICR-MS experiments[4]) and IE(PuO_2) = 6.6 eV[1] (smaller than our value of 7.03 ± 0.12 eV[3]) provide their derived difference of 0.4 eV.

It is true that thermodynamic equilibrium of ions may be approached in a Knudsen cell under certain circumstances,[5] but for the experimental conditions employed by Capone et al.,[1] this assumption appears to be unwarranted. Their evaluation[1] assumes that the species PuO(g), PuO_2(g), PuO^+(g), and PuO_2^+(g) are all in equilibrium in the effusion cell.

For a Boltzmann energy distribution, the probability that a molecule will have an energy of at least IE (ionization energy) is given by: $P(E \geq IE) = \exp(-IE/kT)$.[6] For $T = 2670$ K ($kT = 0.230$ eV), the probability that a molecule will have an energy of at least IE(PuO) = 6.2 eV is 2×10^{-12}; the corresponding probability for an energy of at least IE(PuO_2) = 6.6 eV is 3×10^{-13}. The ratios $[PuO^+]/[PuO] = 1.5 \times 10^{-3}$ and $[PuO_2^+]/[PuO_2] = 1.1 \times 10^{-4}$, derived from the equilibrium pressures given in Table 2 of the Capone et al. publication,[1] appear incompatible with the thermal energy available at 2670 K. By assuming that the enthalpy differences for ionization obtained from Table 1 of ref 1 (case A) are close to the ionization free energies, we instead obtain ratios of $[PuO^+]/[PuO] = 1.3 \times 10^{-12}$ and $[PuO_2^+]/[PuO_2] = 2.0 \times 10^{-13}$, in accord with a Boltzmann energy distribution.

We believe a critical flaw in the Capone et al. report[1] is the assumption that in their Knudsen cell there was equilibrium among the ions. In particular, it has been demonstrated[7] that the materials used for Knudsen cells can substantially affect ion pressures in such effusion experiments. The full experimental details are not provided in ref 1, but it is implied that they were the same as those used for their earlier work on plutonium oxide vaporization:[2,8,9] "We repeated some of the previous experiments...".[1] It is therefore inferred here that the Knudsen cell material(s) used in the recent work were tungsten, thoria, and/or alumina.[2,8,9] The assumption that the equilibrium pressures of PuO^+ and PuO_2^+ are established inside a tungsten, thoria, or alumina cell is not justified.

The work functions of tungsten, 4.54 eV,[10] thoria, 3.1 eV,[10] and alumina, ≤3.7 eV,[11] are all substantially below IE(PuO) = 6.1 ± 0.2 eV[4] and IE(PuO_2) = 7.03 ± 0.12 eV,[3] so both PuO^+ and PuO_2^+ will abstract an electron from these cell materials. Accordingly, the proposed equilibrium among the PuO(g), PuO_2(g), PuO^+(g), and PuO_2^+(g) species would not be achieved inside a tungsten, thoria, or alumina cell. In essence, these cell materials do not fulfill the requirement that the cell used in such experiments must be "inert" toward the vapor species.

Using a tungsten cell and a $(Pu_{0.62}Cm_{0.38})_2O_3$ sample, Hiernaut and Ronchi[9] found that for $T > 2400$ K "strong deviations from the Knudsen regime" were observed, affecting the measured pressures of PuO(g) and PuO_2(g). The authors also concluded that "while the condensable species can be easily maintained in equilibrium in the cell, the gaseous ones require much more stringent conditions on the sublimation rates in order to maintain thermodynamic equilibrium".[9] If comparable conditions were employed in the recent study,[1] similar deviations would be expected at $T = 2670$ K, shedding further doubt on the validity of the interpretation.

Capone et al.[1] also appear to conclude in their recent efforts that the results represent only effusion of ions from their cell: "By switching off the MS ion-source beam, we eventually realized that signals were still detected, which were apparently due to ions produced thermally in the cell (Figure 4)".[1] There was no indication of confirmation that the plutonium oxide ions measured without the ionizing source were actually produced inside the cell. The formation of positive ions outside high-temperature Knudsen cells absent an intended ionization source is a well-established and understood phenomenon.[12]

It is very probable that some plutonium oxide condensed on the heat shields and/or other surfaces outside of the effusion cell, and when the cell temperature was increased to 2670 K, some of this material could easily revaporize from these sources. An example of this is the emission of plutonium oxide ions from heated metal surfaces in thermal ionization mass spectrometry.[13] Such thermal ionization could likely account for the observed "source-off" plutonium oxide ion signals Capone et al. observed at high cell temperatures.

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Further, a higher ionization energy for PuO_2 than PuO would explain the "source-off" oxide ion relative intensities (i.e., intensities obtained under nonequilibrium conditions). In summary, considering the reported "source-off" ion intensities as representing equilibrium values in the cell[1] does not seem to be justified.

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