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Vaporization chemistry of hypo-stoichiometric $(U, Pu)O_2$

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Abstract

Calculations were performed on hypo-stoichiometric uranium plutonium di-oxide to examine its vaporization behavior as a function of O/M ($M = U + Pu$) ratio and plutonium content. The phase $U_{(1-y)}Pu_yO_z$ was treated as an ideal solid solution of $(1-y)UO_2 + yPuO_{(2-x)}$ such that $x = (2-z)/y$. Oxygen potentials for different desired values of y, z, and temperature were used as the primary input to calculate the corresponding partial pressures of various O-, U-, and Pu-bearing gaseous species. Relevant thermodynamic data for the solid phases UO_2 and $PuO_{(2-x)}$, and the gaseous species were taken from the literature. Total vapor pressure varies with O/M and goes through a minimum. This minimum does not indicate a congruently vaporizing composition. Vaporization behavior of this system can at best be quasi-congruent. Two quasi-congruently vaporizing compositions (QCVCs) exist, representing the equalities $(O/M)_{vapor} = (O/M)_{mixed-oxide}$ and $(U/Pu)_{vapor} = (U/Pu)_{mixed-oxide}$, respectively. The (O/M) corresponding to QCVC1 is lower than that corresponding to QCVC2, but very close to the value where vapor pressure minimum occurs. The O/M values of both QCVCs increase with decrease in plutonium content. The vaporization chemistry of this system, on continuous vaporization under dynamic condition, is discussed.

1. Introduction

The urania–plutonia mixed-oxide is used as fuel in fast reactors. Here, in the mixed-oxide fuel MO_2 ($U_{(1-y)}Pu_yO_z$), y denotes the Pu-fraction $[Pu/(U + Pu)]$ and z denotes the overall O-by-M ratio $[O/(U + Pu)]$. The choice of values of y and z for a fresh fuel is made by considering various factors such as thermal conductivity, clad-corrosion, fabrication ease, and vaporization behavior. The vaporization chemistry of this ternary system is quite interesting due to its trivariant nature (dictated by y, z, and the temperature T) and due to the presence of different oxide species in the equilibrium vapor, the major ones of significant abundance at $T = 2000$ K, for instance, being $UO_2(g)$, $UO_3(g)$, $PuO(g)$, and $PuO_2(g)$. Mass spectrometric studies of vaporization of this system were conducted by Ohse and Olson [1] (for $y = 0.15$; $z = 1.94$ to 2.00; $T = 1800$ to 2350 K) and by Battles et al. [2] (for $y = 0.20$; $z = 1.92$ to 2.00; $T = 1905$ to 2411 K). Calculations were performed by Rand and Markin [3] (for $y = 0.15$; $z = 1.95$ to 2.10; $T = 2000$ K), by Tetenbaum [4] (for $y = 0.20$; $z = 1.92$ to 1.96; $T = 2150$ to 2550 K), and by Green et al. [5] (for $y = 0.0$ to 0.3; $z = 1.90$ to 2.00; $T = 2500$ to 6000 K). Vapor pressure measurements were carried out by Dean et al. [6] with a Knudsen effusion cell using ^{239}Pu and ^{233}U, and the results presented for $y = 0.50$, $z = 1.90$ to 2.10 at $T = 1814$ K.

At a given y and T, the vapor pressure varies with z and goes through a minimum. There exist two different z values, one corresponding to the equality $z^{vapor} = z^{mox}$, and the other corresponding to the equality $y^{vapor} = y^{mox}$, where 'mox' refers to the mixed-oxide condensed phase. Without the superscript 'vapor', y and z also denote y^{mox} and z^{mox}, respectively. One might, in analogy with binary systems, attribute the existence of the vapor pressure minimum and the two equalities to congruent vaporization. Refs. [1–4] contain a brief discussion of these three apparently stationary features, pertinent to $y = 0.15$ and 0.20. To better understand how these features and the vaporization chemistry of $(U, Pu)O_2$ vary with y, we performed vapor pressure calculations for $y = 0.10, 0.15, 0.20, 0.25, 0.30, 0.35$, and 0.40 and for the z values amenable for oxygen potential calculations using the simple computation model developed previously

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in our laboratory [7]. To compare with the results of Dean et al. [6], we have extended our calculations to $y = 0.50$.

2. Vapor pressure calculations

The oxygen potentials $\Delta\bar{G}(O_2)$ for $U_{(1-y)}Pu_yO_z$ at desired T, y, and z, using the model developed by Krishnaiah and Sriramamurti [7], were used as input for a program with which vapor pressures and vapor compositions were calculated.

Our vapor pressure calculations were restricted to hypo-stoichiometric $(U,Pu)O_2$ because the interesting vaporization chemistry associated with this system can be realized in this composition range. The $U_{(1-y)}Pu_yO_z$ fuel was assumed to be an ideal solid solution of $(1-y)UO_2$ and $yPuO_{(2-x)}$ such that $x = (2-z)/y$, and activities of UO_2 and $PuO_{(2-x)}$ are $(1-y)$ and y, respectively. $\Delta\bar{G}(O_2)$ gives the partial pressure of $O_2(g)$. Then from the known Gibbs free energies of formation for O(g), U(g), $UO_i(g)$ ($i = 1$–3), Pu(g), $PuO_i(g)$ ($i = 1, 2$), $UO_2(s)$, and $PuO_{(2-x)}(s)$, the equilibrium constants for the following reactions (1)–(8) were first calculated $(-RT\ln K_i = \Delta(\Delta_f G^\circ))$ and subsequently the partial pressures of the gaseous species, the total vapor pressure, the relative abundance of each gaseous species, the atomic fractions of the three elements in vapor, and finally the values of $z^{\text{vapor}} = [O/(U+Pu)]_{\text{vapor}}$ and $y^{\text{vapor}} = [Pu/(U+Pu)]_{\text{vapor}}$ were calculated.

$$O_2(g) = 2O(g);$$
$$K_1 = p^2(O)/p(O_2) \tag{1}$$
$$U(g) + O_2(g) = UO_2(s);$$
$$K_2 = (1-y)/[p(U)\,p(O_2)] \tag{2}$$
$$UO(g) + 0.5O_2(g) = UO_2(s);$$
$$K_3 = (1-y)/[p(UO)p^{0.5}(O_2)] \tag{3}$$
$$UO(g) + 0.5O_2(g) = UO_2(g);$$
$$K_4 = p(UO_2)/[p(UO)p^{0.5}(O_2)] \tag{4}$$
$$UO_2(g) + 0.5O_2(g) = UO_3(g);$$
$$K_5 = p(UO_3)/[p(UO_2)p^{0.5}(O_2)] \tag{5}$$
$$Pu(g) + (2-x)/2\ O_2(g) = PuO_{(2-x)}(s);$$
$$K_6 = y/[p(Pu)p^{(2-x)/2}(O_2)] \tag{6}$$
$$PuO(g) + (1-x)/2O_2(g) = PuO_{(2-x)}(s);$$
$$K_7 = y/[p(PuO)p^{(1-x)/2}(O_2)] \tag{7}$$
$$PuO_{(2-x)}(s) + x/2O_2(g) = PuO_2(g);$$
$$K_8 = p(PuO_2)/[yp^{x/2}(O_2)]. \tag{8}$$

The $\Delta_f G^\circ$ values except for $PuO_{(2-x)}(s)$ were taken from the $\Delta_f G^\circ$ versus T equations given by Green et al. [5]. The $\Delta_f G^\circ$ values for $PuO_{(2-x)}(s)$ were obtained by interpolation of the values obtained from the $\Delta_f G^\circ = A + BT$ type equations given by Tetenbaum for $x = 0.4$, 0.35, 0.30, 0.25, and 0.20, by Ackermann and Chandrasekaraiah [8] for $x = 0.00$, and by Rand and Markin [3] for $x = 0.15$, 0.10, and 0.05. The coefficients (A and B) in the equations given by Rand and Markin [3] were normalized so as to make them consistent with those recommended later by Tetenbaum [4] and Ackermann and Chandrasekaraiah [8]. The normalization involved simple addition of some constants to the coefficients of R&M, since we noted that for all common values of x ($x = 0.00$, 0.20, 0.25, 0.30, 0.35, and 0.40), $A(\text{R\&M}) = A(\text{Refs. [4,8]}) + 500$ and $B(\text{R\&M}) = B(\text{Refs. [4,8]}) - 2.3$.

3. Results and discussion

Fig. 1 shows the total vapor pressures (VP) calculated at $T = 2000$ K as a function of $z = [O/(U+Pu)]$ for different values of y. Each curve goes through a minimum. The corresponding values of VP and z^{mox} are

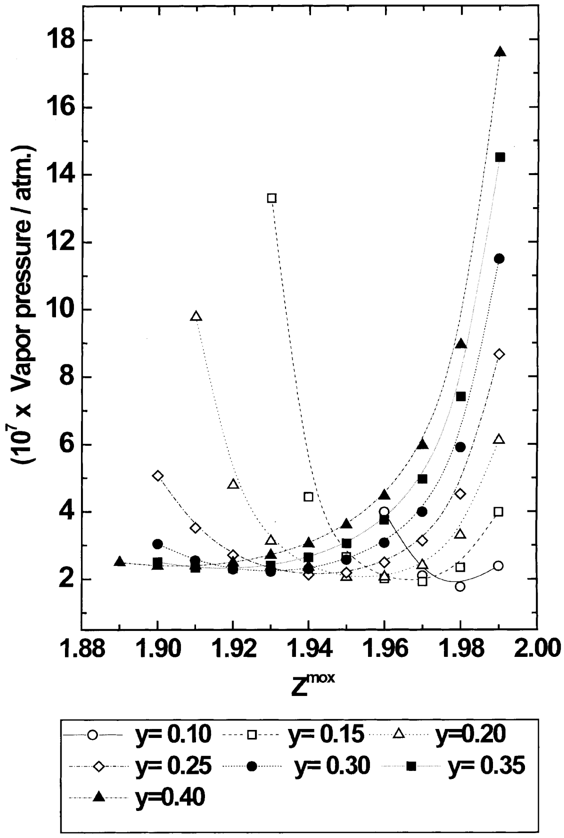

Fig. 1. Total vapor pressures (VP) of the mixed-oxide fuel $U_{(1-y)}Pu_yO_z$ as a function of z for $y = 0.10$ to 0.40; $T = 2000$ K. VP = sum of the partial pressures of the gaseous species O, O_2, U, UO, UO_2, UO_3, Pu, PuO, and PuO_2.

Table 1
$z = \mathrm{O}/(\mathrm{U}+\mathrm{Pu})$ values corresponding to vapor pressure minimum and quasi-congruently vaporizing compositions at $T = 2000$ K in mixed-oxide fuel $\mathrm{U}_{(1-y)}\mathrm{Pu}_y\mathrm{O}_z$

y^{mox}	Values at VP minimum		(QCVC1) $z^{\mathrm{mox}} = z^{\mathrm{vapor}}$	(QCVC2) z^{mox} when $y^{\mathrm{mox}} = y^{\mathrm{vapor}}$
	$10^7\times$ (VP/atm.)	z^{mox}		
0.10	1.76	1.9792	1.9792	1.9900
0.15	1.91	1.9669	1.9665	1.9798
0.20	2.03	1.9543	1.9532	1.9679
0.25	2.13	1.9415	1.9395	1.9552
0.30	2.22	1.9287	1.9255	1.9416
0.35	2.30	1.9160	1.9113	1.9227
0.40	2.37	1.9034	1.8970	1.9134

given in Table 1. The value of z (at VP minimum) decreases with the increase in the value of y. In analogy with binary systems, one might misinterpret the vapor pressure minimum to have arisen as a consequence of congruent vaporization, if it were not the fact that at these 'stationary points', the vapor compositions are not the same as the condensed phase compositions. In analogy with the binary systems, one can however expect the existence of a global minimum in vapor pressure corresponding to certain y and z values. Fig. 1 conveys that the value of VP minimum decreases with decrease in the value of y, and one infers from this trend that the global minimum might be at $y = 0$. In other words, even though both $\mathrm{UO_2}$ and $\mathrm{PuO_2}$ phases can vaporize congruently, a solid solution between them might not, and consequently, continuous vaporization of the ternary system at $T = 2000$ K might only lead to total removal of Pu and to a congruently vaporizing $\mathrm{UO_2}$ phase. Other possibilities are discussed later.

Fig. 2 shows how the ratio $z^{\mathrm{vapor}}/z^{\mathrm{mox}}$ varies with z^{mox} for different values of y^{mox} at $T = 2000$ K. A value of one represents quasi-congruently vaporizing composition with respect to O/(U + Pu) ratio. We would call this composition QCVC1. When $z^{\mathrm{mox}} > z$(QCVC1), the vapor is O-rich relative to the condensed phase and when $z^{\mathrm{mox}} < z$(QCVC1), the vapor is O-deficient relative to the condensed phase. The z(QCVC1) values are given in Table 1. The z(QCVC1) values are evidently not the same as the z (VP, minimum) values.

Fig. 3 shows how the ratio $y^{\mathrm{vapor}}/y^{\mathrm{mox}}$ varies with z^{mox} for different values of y^{mox} at $T = 2000$ K. A value of one represents quasi-congruently vaporizing composition with respect to Pu/(U + Pu) ratio. We would call this composition QCVC2. The z(QCVC2) values are given in Table 1. The values are evidently higher than the z(QCVC1) values, but the difference narrows down as y^{mox} decreases. When $z^{\mathrm{mox}} > z$(QCVC2), the vapor is U-rich relative to the condensed phase and when $z^{\mathrm{mox}} < z$(QCVC2), the vapor is Pu-rich relative to the condensed phase.

Fig. 4 shows how for $y = 0.20$ and $T = 2000$ K, the relative compositions of the major species vary with z^{mox}. In the same plot, the vapor pressure variation is also shown. The relative abundance of $\mathrm{UO_2(g)}$ in the vapor goes through a maximum at a value of z^{mox} where the VP goes through a minimum. The maximum of the $\mathrm{PuO_2(g)}$ curve is relatively broader and occurs at slightly higher value of z^{mox}. The $\mathrm{UO_3(g)}$ and $\mathrm{PuO(g)}$ curves intersect between these two 'maxima' z^{mox} values.

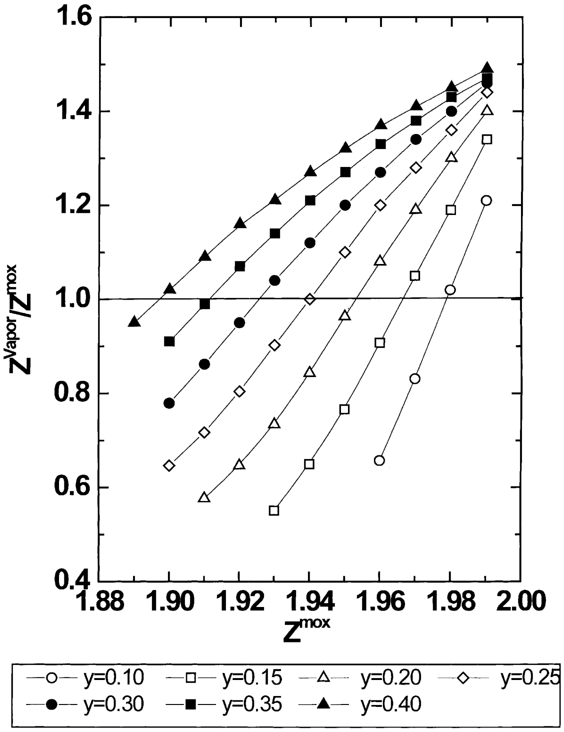

Fig. 2. $\mathrm{O}/(\mathrm{U}+\mathrm{Pu})$ ratio in vapor phase relative to that in the condensed phase $\mathrm{U}_{(1-y)}\mathrm{Pu}_y\mathrm{O}_z$ as a function of z for $y = 0.10$ to 0.40; $T = 2000$ K.

Table 2 gives the $\Delta\overline{G}(\mathrm{O_2})$, VP, vapor compositions of the major species, and the $y^{\mathrm{vapor}}/y^{\mathrm{mox}}$ and $z^{\mathrm{vapor}}/z^{\mathrm{mox}}$ ratios corresponding to QCVC1 and QCVC2 as well as at z^{mox} values differing by 0.005 units from them.

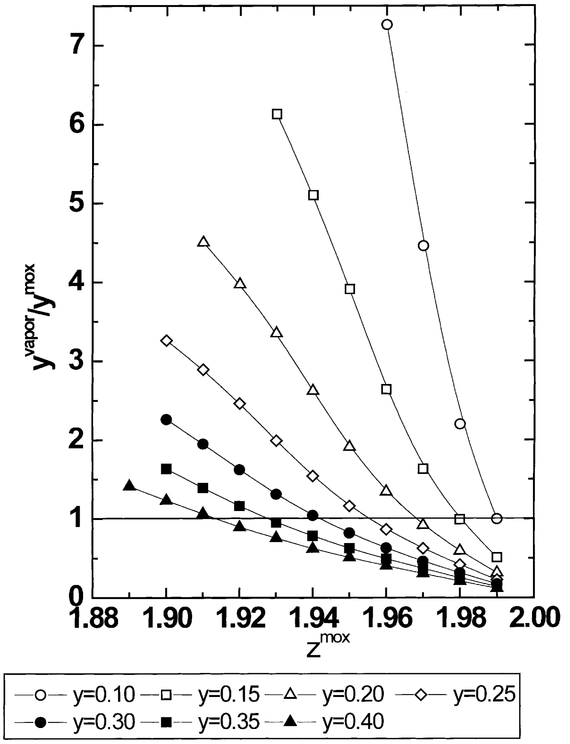

Fig. 3. Pu/(U + Pu) ratio in the vapor phase relative to that in the condensed $U_{(1-y)}Pu_yO_z$ as a function of z for $y = 0.10$ to 0.40; $T = 2000$ K.

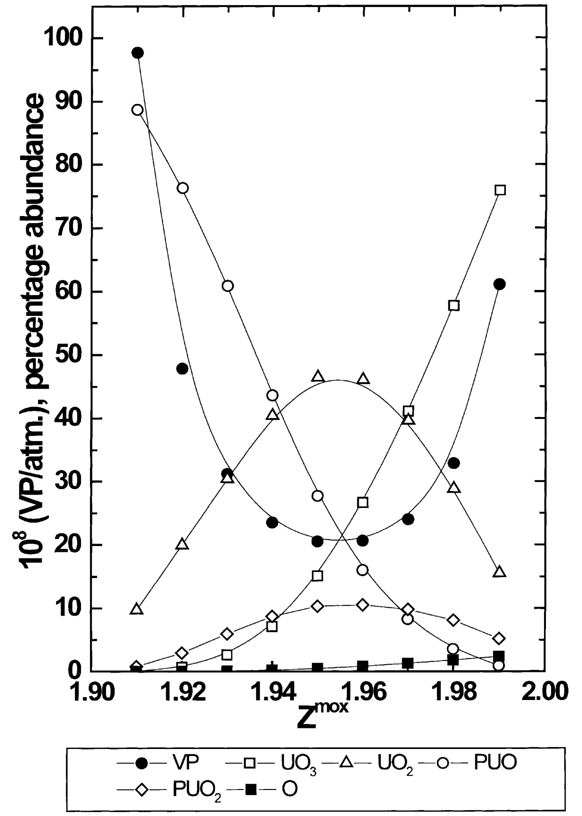

Fig. 4. VP (in atmosphere) and relative abundances of major gaseous species (in percentage) over the condensed phase $U_{0.8}\,Pu_{0.2}\,O_z$ as a function of z; $T = 2000$ K; percentage abundance = $100 \times p(i)/\mathrm{VP}$, where $p(i)$ is the partial pressure and VP is the total vapor pressure.

To examine the consequences of continuous vaporization under dynamic conditions, we denote the z^{mox} and y^{mox} at any time t as $z^{\mathrm{mox},t}$ and $y^{\mathrm{mox},t}$. Continuous vaporization for a time interval Δt will change the values to $z^{\mathrm{mox},t+\Delta t}$ and $y^{\mathrm{mox},t+\Delta t}$. Consider two situations: $z^{\mathrm{mox},t} < z(\mathrm{QCVC1})$ and $z^{\mathrm{mox},t} > z(\mathrm{QCVC2})$. In the first situation, the condensed phase will preferentially lose plutonium and z will increase. This process can go on as long as $z^{\mathrm{mox},t+\Delta t}$ continues to be less than the $z(\mathrm{QCVC2})$ for $y = y^{\mathrm{mox},t+\Delta t}$. In the second situation, the condensed phase would lose both O and U, and would continue to do so as long as the $z^{\mathrm{mox},t+\Delta t} > z(\mathrm{QCVC2})$ for $y = y^{\mathrm{mox,t+\Delta t}}$. Obviously, two different kinds of vaporization processes occur, depending on the position of the initial value of z^{mox} with respect to the narrow 'window' constituted by the two QCVC values. This aspect presents three possibilities. *Case* 1: the vaporization process that has started can continue in the same direction for ever; that is, eventually, one can arrive at either a pure PuO_2 phase if the initial z^{mox} was greater than $z(\mathrm{QCVC2})$ or a pure UO_2 phase if the initial z^{mox} was less than $z(\mathrm{QCVC1})$. *Case* 2: relative rates of loss of O, U and Pu (determined by the $y^{\mathrm{mox},t+\Delta t}, z^{\mathrm{mox},t+\Delta t}$, and the QCVC values) will vary continuously and in such a way that ultimately only one of the two vaporization processes will prevail; that is, one will always get the same pure phase irrespective of whether the initial value of z was greater than the $z(\mathrm{QCVC2})$ or less than the $z(\mathrm{QCVC1})$. *Case* 3: the molar rates of loss of O, U, and Pu will become equal at some time after which the ternary phase ($0 < y < 1$) will vaporize congruently.

A seemingly analogous situation to case 1 can occur in binary systems (in some temperature ranges) where two congruently vaporizing compositions (each CVC representing a vapor pressure minimum) can exist on either side of what is termed as an 'euatmotic point' [9,10]. If, for instance, the overall composition of the sample lies between the two CVCs, then continuous vaporization can lead the system to either of the two CVCs via two vaporization processes which are mutually divergent in nature. There is no thermodynamic reason to view that the 'window' formed by the two QCVCs in the U–Pu–O system has the same significance as the 'euatmotic point' in a binary system. Therefore, occurrence of case 1 is highly unlikely. The data in columns 10 and 11 of Table 2 indicate that the case 3

Table 2
Properties pertaining to vaporization chemistry at 2000 K of the mixed-oxide fuel $U_{(1-y)}Pu_yO_z$

y^{mox}	z^{mox}	$\Delta\overline{G}(O_2)$ (kJ/mol)	VP (atm)	Vapor composition of major species in percentage for					y^{vapor}/y^{mox}	z^{vapor}/z^{mox}
				O(g)	UO_2(g)	UO_3(g)	PuO(g)	PuO_2(g)		
At $z = z(\text{QCVC1}) - 0.005$										
0.1	1.9742	−474.3	1.85×10^{-7}	0.23	57.8	8.3	28.8	4.7	3.37	0.91
0.15	1.9615	−459.8	1.96×10^{-7}	0.34	51.4	11.4	29.4	7.5	2.46	0.93
0.20	1.9482	−450.7	2.08×10^{-7}	0.42	45.7	13.4	30.4	10.1	2.04	0.94
0.25	1.9345	−444.0	2.19×10^{-7}	0.48	40.7	14.6	31.4	12.8	1.78	0.95
0.30	1.9205	−438.7	2.23×10^{-7}	0.54	36.3	15.3	32.4	15.5	1.60	0.96
0.35	1.9063	−434.1	2.38×10^{-7}	0.60	32.4	15.6	33.2	18.2	1.48	0.96
0.40	1.8920	−430.1	2.46×10^{-7}	0.65	28.9	15.7	33.8	20.9	1.38	0.97
At QCVC1 where $z^{mox} = z^{vapor}$										
0.1	1.9792	−454.8	1.76×10^{-7}	0.43	60.5	15.6	18.0	5.3	2.34	1.00
0.15	1.9665	−446.8	1.91×10^{-7}	0.51	52.9	17.4	21.2	8.0	1.95	1.00
0.20	1.9532	−441.0	2.03×10^{-7}	0.57	46.8	18.4	23.6	10.6	1.72	1.00
0.25	1.9395	−436.2	2.13×10^{-7}	0.63	41.7	18.9	25.6	13.2	1.56	1.00
0.30	1.9255	−432.1	2.23×10^{-7}	0.68	37.3	19.1	27.1	15.8	1.44	1.00
0.35	1.9113	−428.5	2.32×10^{-7}	0.72	33.3	19.0	28.5	18.5	1.35	1.00
0.40	1.8970	−425.2	2.40×10^{-7}	0.78	29.6	18.7	29.6	21.3	1.28	1.00
At QCVC2 where $y^{mox} = y^{vapor}$										
0.1	1.9900	−410.8	2.38×10^{-7}	1.2	44.8	44.2	4.6	5.2	1.00	1.21
0.15	1.9798	−412.1	2.32×10^{-7}	1.2	43.4	40.6	7.2	7.6	1.00	1.19
0.20	1.9679	−412.8	2.30×10^{-7}	1.2	41.3	37.8	9.7	10.1	1.00	1.17
0.25	1.9552	−412.3	2.32×10^{-7}	1.2	38.4	35.7	12.0	12.7	1.00	1.15
0.30	1.9416	−411.8	2.33×10^{-7}	1.2	35.6	33.6	14.3	15.4	1.00	1.14
0.35	1.9227	−410.8	2.37×10^{-7}	1.2	32.6	31.7	16.4	18.2	1.00	1.12
0.40	1.9134	−409.6	2.41×10^{-7}	1.2	29.5	29.7	18.4	21.1	1.00	1.11
At $z^{mox} = z(\text{QCVC2}) + 0.005$										
0.1	1.9950	−381.0	3.89×10^{-7}	1.8	27.4	65.4	1.5	3.9	0.55	1.34
0.15	1.9848	−397.2	2.84×10^{-7}	1.5	35.6	52.0	4.1	6.8	0.74	1.26
0.20	1.9729	−402.6	2.58×10^{-7}	1.4	36.7	45.6	6.7	9.5	0.82	1.22
0.25	1.9602	−404.5	2.50×10^{-7}	1.4	35.7	41.8	9.0	12.1	0.86	1.20
0.30	1.9466	−405.4	2.46×10^{-7}	1.4	33.8	38.5	11.5	14.9	0.89	1.07
0.35	1.9327	−405.4	2.45×10^{-7}	1.4	31.4	35.9	13.6	17.7	0.90	1.16
0.40	1.9184	−404.5	2.46×10^{-7}	1.4	28.9	33.5	15.6	20.6	0.92	1.14

may never happen either. That is, congruency with respect to both y and z may never be achieved. It is much easier to infer that only case 2 may occur; even in this case, one needs to examine which of the two vaporization processes will ultimately prevail. The vapor pressure minimum moving towards lower y^{mox} and higher z^{mox} values supports the eventual generation of a congruently vaporizing UO_2 phase, while the data in columns 10 and 11 of Table 2 support the generation of a congruently vaporizing hypo-stoichiometric PuO_2 phase (both ratios getting closer to unity as y^{mox} increases).

A very time consuming vaporization experiment would be needed to find out which of the events discussed above can actually happen. Battles et al. [2] conducted a Knudsen effusion mass spectrometric experiment to examine how the ion intensities varied as a function of time when the sample $U_{0.8}Pu_{0.2}O_z$ was heated at 2264 K for about 800 min. The O/M ratio decreased from 1.973 to 1.945 and this decrease was reflected in their measurements: decrease in the intensity of UO_3^+, UO_2^+, and PuO_2^+, and increase in the intensity of UO^+ and PuO^+. The change in Pu content of the sample was not mentioned. They also conducted two series of experiments, each series consisting of many runs of alternate mass-loss Knudsen effusion and mass spectrometric temperature dependency measurements. The ratio of $Pu/(U + Pu)$ in the solid phase increased to 0.22 at the conclusion of these experiments. The $O/(U + Pu)$ ratio decreased to ~1.93 where there was a broad minimum in vapor pressure. These results show that in their experiments, the vaporization process was always one of loss of U and O from the condensed phase. However, since these measurements were not continued until clear evidence for congruent vaporization was obtained, one cannot predict whether the same vaporization process involving preferential loss of U and O would have continued. In preliminary mass-loss and mass spectrometric vaporization experiments on a sample with $(U_{0.80}\ Pu_{0.20})\ O_{1.68}$, Battles et al. obtained evidence for the preferential loss of Pu and for the vapor pressure being significantly higher than for O/(U + Pu) = 1.92. From these results, they predicted that there could exist a CVC at some yet unknown composition associated with a minimum in total pressure (at $z^{\mathrm{mox}} = 1.93$). In our opinion, these results and experiments are inadequate to predict that there will exist a CVC within the ternary phase.

Ohse and Olson [1] conducted isothermal heat treatments of several U–Pu–O samples ($y = 0.15$; $z = 1.94$ to 2.08) in open effusion cells for different durations. A quasi-congruently vaporizing composition of ~1.97 was approached from both sides. They measured the total pressures of U- and Pu-bearing species by the effusion-collection method, and deduced the partial pressures by combining with mass spectrometric ion intensity determinations. The following features were deduced from the partial pressure isotherms at $T = 2108$ K: (a) the quasi-equilibrium $(O/M)_g = (O/M)_s$ occurs at $O/M = 1.964$; (b) the quasi-equilibrium $(U/Pu)_g = (U/Pu)_s$ occurs at $(O/M)_s = 1.968$; and (c) the total vapor pressure minimum occurring around (O/M)s = 1.97 is rather flat.

We conducted a thermal ionization mass spectrometric study (TIMS) of the U–Pu–O system [11] using a triple filament assembly basically to identify the dominant gaseous species and confirm the influence of the O/M stoichiometry on the U^+/Pu^+ ratio. Our sample loading procedure rendered each of the two thin vaporization filaments (rhenium; 9 × 0.7 × 0.04 mm) to have at the centre a well-adhered mixed-oxide deposit in microgram levels. Thermal ionization efficiency curves for the oxide and metallic ions as a function of ionization filament current confirmed that U^+ and Pu^+, which dominate the mass spectrum at normal operating conditions, are mainly formed due to dissociative surface ionization of oxide gaseous species. The $^{233}U^+/Pu^+$ ratios bore no relation with the U/Pu ratios in the original mixed-nitrate solutions (^{233}U and ^{239}Pu), and even an unmixed Pu-sample which had only ~1% of natural U yielded a rather high $^{238}U^+/^{239}Pu^+$ ratio, which however, decreased with time. These observations were taken to confirm that the initial high U^+/Pu^+ was caused by the O/M of the sample being greater than the QCVC2, and that decrease in the ratio with time was due to the preferential loss of oxygen. Results from other filaments which contained higher U/Pu ratios were also of similar nature. To confirm the influence of the $(O/M)_s$ further, oxidation of the samples were effected by heating the vaporization filaments (inside the mass spectrometer) for ~45 min after isolating the source-chamber from vacuum-pump (i.e., under no-evacuation condition). In a few experiments, atmospheric air was let into the source-chamber to enhance the extent of oxidation. The U^+/Pu^+ values increased from the values obtained (under identical filament current conditions) before the oxidation. In the case of the most Pu-rich sample, the ratio increased from 0.4 to 0.6, 1.0, and 2.0 in three attempts before the value decreased again as a function of time. No experiment was conducted long enough to confirm that complete removal of Pu might eventually occur, a situation predicted to occur by Rand and Markin [3], and partly supported by the statement of Ohse and Olson that unlike in the binary oxide systems Pu–O and U–O, a true CVC does not exist in the U–Pu–O system.

Table 3 compares some of the results of our calculations with those by Rand and Markin [3] and Tetenbaum [4], and with the experimental results of Battles et al. [2], Ohse and Olson [1], and Dean et al. [6]. Considering the trivariant nature of the system, comparison is best made at an $(O/M)_s$ where the total vapor pressures do not vary steeply. Accordingly, we chose

Table 3
Comparison of our calculated results with previously reported results for mixed-oxide fuel $U_{(1-y)}Pu_yO_z$

Ref.	VP/atm.	$p(UO_3)$/atm.	$p(UO_2)$/atm.	$p(PuO_2)$/atm.	$p(PuO)$/atm.	K_9
$y = 0.15$; $z = 1.97$; $T = 2000$ K						
This work	1.9×10^{-7}	4.3×10^{-8}	1.0×10^{-7}	1.5×10^{-8}	3.1×10^{-8}	1.1
Rand and Markin [3]	1.9×10^{-7}	2.6×10^{-8}	1.2×10^{-7}	4.7×10^{-9}	3.2×10^{-8}	0.7
Ohse and Olson [1]	2.1×10^{-7}	3.6×10^{-8}	1.4×10^{-7}	8.8×10^{-9}	2.7×10^{-8}	1.3
$y = 0.20$; $z = 1.95$; $T = 2241$ K						
This work	9.1×10^{-6}	2.9×10^{-6}	4.2×10^{-6}	7.4×10^{-7}	1.2×10^{-6}	0.93
Tetenbaum [4]	4.2×10^{-6}	9.9×10^{-7}	2.3×10^{-6}	2.9×10^{-7}	6.5×10^{-7}	0.96
Battles et al. [2]	8.1×10^{-6}	3.6×10^{-7}	6.3×10^{-6}	2.9×10^{-7}	1.2×10^{-6}	4.2
$y = 0.50$; $z = 1.91$; $T = 1814$ K						
This work	7.1×10^{-9}	1.4×10^{-9}	1.5×10^{-9}	2.3×10^{-9}	1.5×10^{-9}	1.6
Dean et al. [6][a]	1.2×10^{-8}	–	2.3×10^{-9}	1.4×10^{-9}	4.7×10^{-9}	–
$y = 0.50$; $z = 1.95$; $T = 1814$ K						
This work	8.8×10^{-9}	3.8×10^{-9}	1.5×10^{-9}	2.5×10^{-9}	7.2×10^{-10}	1.4
Dean et al. [6][a]	8.4×10^{-9}	5.1×10^{-10}	2.3×10^{-9}	2.0×10^{-9}	1.3×10^{-9}	6.9

[a] VP = sum of experimentally measured Uranium P(U,exp) and Plutonium P(Pu,exp) total pressures by Dean et al.; the partial pressures were those calculated by Dean et al. For $z = 1.91, P(U, exp) = 5.5 \times 10^{-9}$atm.; $P(Pu, exp) = 6.2 \times 10^{-9}$atm.; and $p(UO_3) < 4.0 \times 10^{-10}$ atm; for $z = 1.95, P(U, exp) = 5.5 \times 10^{-9}$atm.; and $P(Pu, exp) = 2.9 \times 10^{-9}$ atm.

$z = 1.97$ for $y = 0.15$, $z = 1.95$ for $y = 0.20$, and $z = 1.91$ for $y = 0.50$. In the case of $y = 0.50$, comparison is additionally made at $z = 1.95$ to be complete. The results from Battles et al. [2], Rand and Markin [3], and Dean et al. [6] were read off from the figures given by the authors at $T = 2241$ K, $T = 2000$ K, and $T = 1814$ K, respectively, while the results from Tentenbaum [4] and Ohse and Olson [1] were calculated from the P–T relations given in their papers. The equilibrium constant K_9 for the following pressure independent reaction was also calculated:

$$UO_3(g) + PuO(g) = UO_2(g) + PuO_2(g); \quad K_9 = [p(UO_2)\ p(PuO_2)]/[p(UO_3)\ p(PuO)]. \tag{9}$$

In general the agreement between the total vapor pressures is much better than that between the partial pressures, and this aspect is clearly reflected in the K_9 values. The accuracy of the calculated values depends on those of the thermodynamic data input and on the validity of the models employed, while the accuracy of the mass spectrometric results depends on the conversion factors used (to compute the partial pressures from ion-intensities) and on the validity of assuming no change in the value of y. Admittedly, experiments provide information that is relatively more authentic; however, we feel that the ease of partial pressures calculations for various values of y, z, and T, and a proper presentation of such results will help to arrive at a better understanding of the trends in the vaporization chemistry of this system. The results presented and discussed in this work have contributed towards that goal. For instance, the strikingly similar $\Delta\overline{G}(O_2)$ and VPs at z = QCVC2 (see Table 2) may perhaps have never been realized, without the calculations. Furthermore, the results of the calculations suggest that one may choose a fuel composition between the two QCVCs to minimize migration effects involving U and Pu [12].

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