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Curium vaporization from $(Cm,Pu)_2O_3$ and from irradiated oxide fuel: Mass spectrometric measurement

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Abstract

The equilibrium vapour pressure over a mixed curium oxide of type $(^{244}Cm_{0.76},^{240}Pu_{1.24})O_3$ was measured by Knudsen-effusion experiments. Plutonium was formed in the samples during 25 years decay of curium in an initial Cm_2O_3 sintered pellet. The same measurements were repeated on seven reactor-irradiated UO_2 and MOX samples to obtain the vaporization enthalpy of curium present in typical spent nuclear fuel. The samples were annealed in a tungsten Knudsen cell up to 2800 K and the effusion rates of the different vapour components were analyzed on line by a quadrupole mass spectrometer. The vapour pressures of the curium-bearing species were accurately measured and the results compared with published data obtained under different conditions. The obtained results show that CmO(g) is the only effective vapour species and the measured equilibrium pressure confirms the trend observed in the actinide oxides that the high temperature volatility is more pronounced in compounds where the cation can easily attain a higher oxidation state than that of the condensed phase.

1. Introduction

Curium is formed in nuclear fuel during reactor irradiation. In Light Water Reactor spent fuel the curium concentration is the order of 0.01–0.04%, depending on burn-up (b.u.). The half-lives of some of the formed curium isotopes are sufficiently long to strongly affect the radiation field of spent fuel. Therefore – in spite of the considerable costs entailed by processing such highly γ-active and neutron emitting nuclides – partitioning and nuclear transmutation of curium and other minor actinides in dedicated reactors is presently considered as a possible option in the context of nuclear waste disposal.

Fabrication of large amounts of nuclear transmutation targets – most probably sintered ceramic oxides – containing several percents of curium, requires a strict limitation of curium vaporization to avoid losses that might produce impermissible contamination levels in the sintering furnaces. In this paper, the vaporization rate of curium oxide from a mixed oxide of type $(^{244}Cm_{0.76},^{240}Pu_{1.24})O_3$ was studied and the deduced equilibrium vapour pressure was compared with the only existing data obtained in the Savannah River Site (SC) by Smith and Peterson [1].

2. Experiment

The method adopted was Knudsen's effusion with mass spectrometric measurement of the vapour molecular beam. Signals of the vapour species effusing from the aperture hole of a tungsten cell were measured during thermal annealing of the samples in a temperature range up to 2800 K. The effusion rate and the vapour composition were deduced from the measured

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current of the various elementary and molecular ionic species created in the mass spectrometer ionization source, by taking into account possible electron dissociation processes occurring at the chosen electron ionization energy (in our case 70 eV) [2].

The equilibrium vapour pressures of the volatile species were calculated from the ionic currents through classical Knudsen's relationships. The absolute calibration factor was obtained by inserting in the cell a spike of silver. This factor was extended to the different individual atomic or molecular species by using the corresponding appearance potentials and cross-sections [2]. A similar procedure was adopted to calculate fragmentation of vapour molecules.

The samples, typically small pieces of some tens of milligrams, were placed in a tungsten cell and annealed in an ultra high vacuum at increasing temperatures until total vaporization. The species vaporizing and effusing through the aperture hole of the cell were measured continuously by a quadrupole mass spectrometer. The temperature of the cell was given by a W–W 10% Re thermocouple up to 2300 K and, additionally, by a pyrometer from 800 to 2800 K.

3. Samples

3.1. Curium–plutonium sesquioxide

The samples consisted of small particles from 0.1 to 1 mm size obtained from a sintered small pellet of $^{244}Cm_2O_3$ after 26 years storage in inert atmosphere. Since the original main isotope ^{244}Cm decays according to the chain

$$^{244}\mathrm{Cm}(\alpha/18.11\ \mathrm{y}) \rightarrow {}^{240}\mathrm{Pu}(\alpha/6555\ \mathrm{y}) \rightarrow {}^{236}\mathrm{U}$$

at the time of the experiment the samples contained ~62 at.% ^{240}Pu and ~0.01 at.% ^{236}U. The actual formula was $(^{244}Cm_{0.76},{}^{240}Pu_{1.24},{}^{236}U_{0.002})O_3$.

In Table 1 the isotopic compositions measured by mass spectrometry are compared with the results of the decay calculations. The larger discrepancy obtained for ^{236}U is due to the low precision of the weak mass spectrometer (MS) signals for this isotope.

The stoichiometry of the sample was obtained from the concentration of plutonium and curium and the oxygen potential, ΔG_{O_2}, of the mixed oxide, determined from electromotive force measurements (e.f.m.) between 600 and 1200 K in a miniaturized galvanic cell formed by a solid electrolyte (Y-doped ZrO_2) and a reference redox electrode (Fe/FeO) [3]. The O/M ratio of the sample was initially estimated to be slightly above 1.50. A stoichiometry control of the sample during the effusion experiment resulted, however, to be hardly practicable. In fact, though the cell was provided with a gas-inlet system, the buffer gas flow calibration would have required a larger amount of material than that permitted. The experiments were therefore carried out under possibly non-constant O/M stoichiometry. In this context, the actual evolution of the oxygen pressure during the effusion experiments represents an important issue that is discussed in the following sections.

Table 1
Comparison of the measured main isotope composition with the composition calculated with Nuclide 2000 [5]

Isotope	MS measurement, at.%	Calculated, at.%
^{244}Cm	37.1	37.36
^{240}Pu	62.04	62.54
^{236}U	0.0087	0.0098

3.2. Irradiated fuels

The fuels studied were UO_2, irradiated in LWR up to burn-ups of 60–70 GWd t^{-1}, and stored during ~10 years, or MOX prepared by a powder-mixture sintering method and irradiated up to, respectively, 20 and 45 GWd t^{-1}. The minor actinide content of these fuel measured by mass spectrometry is in good agreement with the prediction of the code Origen-2. For instance, in UO_2 at 70 GWd t^{-1} and after 10 years cooling time, the ^{244}Cm content is ~0.033% of the heavy atom inventory.

4. Results

4.1. Curium–plutonium sesquioxide

The effusion rates of ^{244}Cm(g), ^{244}CmO(g), $^{244}CmO_2$(g), ^{240}Pu(g), ^{240}PuO(g) and $^{240}PuO_2$ (g) were continuously monitored and measured during the entire thermal annealing programme. The behaviour of the equilibrium partial pressures of the vapour, plotted in Figs. 1–3, can be summarized as follows:

- While the species CmO_2(g) was effectively absent in the vapour, the observed fraction of Cm(g) (Fig. 2) was to be attributed to fragmentation of CmO(g), since after this correction the residual pressure of Cm(g) possibly coming from evaporation was below the signal noise level. This indicates that Cm_2O_3 sublimation was effectively controlled by the reaction

$$Cm_2O_3(cr) = 2CmO(g) + O \tag{1}$$

The measured pressure is interpolated in the temperature range 2100–2500 K by the expression (Fig. 1)

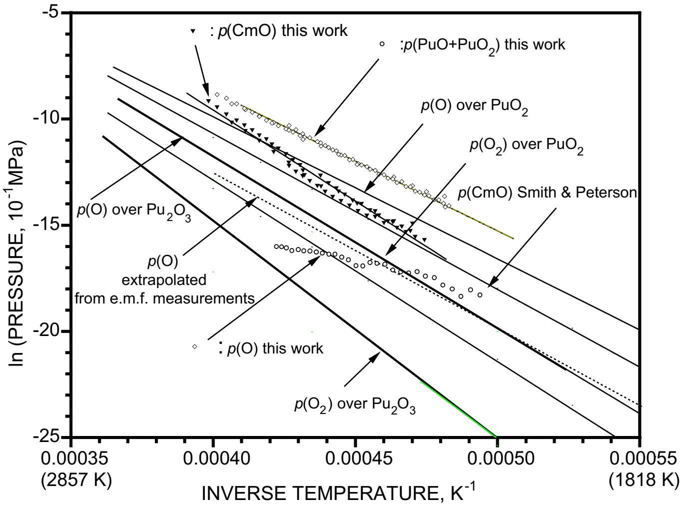

Fig. 1. Measured equilibrium vapour pressures (symbols) taken on four different samples of $(Pu_{0.62},Cm_{0.38})_2O_3$. The full lines represent data from the THERMO database and the Smith and Peterson results, originally evaluated in the temperature range 1843–2609 K. The dotted line represents the extrapolation of the oxygen potential measured on the sample in the temperature interval 1000–1300 K.

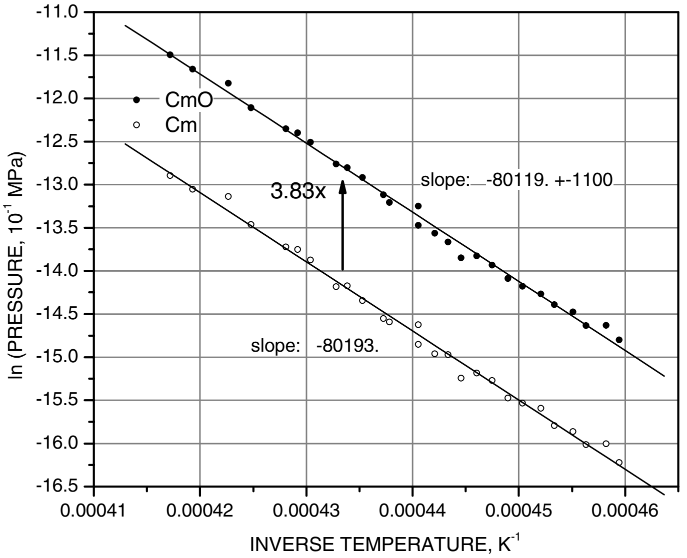

Fig. 2. Partial pressures of CmO(g) and Cm(g) calculated from the intensities of the respective mass spectrometer signals. In reality, the virtual pressure of Cm(g) is due to fragmentation of CmO(g) in the mass spectrometer ion source.

$$\ln(p(\mathrm{CmO})) = (22.42 \pm 0.68) - (85783 \pm 1681)/T\ (\mathrm{K})\quad (p \text{ in MPa}). \tag{2}$$

- As for the plutonium oxide vaporization, previous measurements were available together with a consolidated database that made it possible to analyze the results obtained from our specific experiments on the curium–plutonium mixed oxide. The evolution of the plutonium oxide vapours during the applied annealing programme is plotted in Fig. 3. At lower temperatures, $PuO_2(g)$ was the major component, and the O/M ratio of the plutonium bearing species was above the sesquioxide congruent value of 1.5. However, with increasing temperature the O/M ratio progressively decreased to 1.35. At $T > 2400$ K it decreased further to 1.2 and, at the same time, signs of depletion in the cell appeared, indicating strong deviations from the Knudsen regime. From the graph of

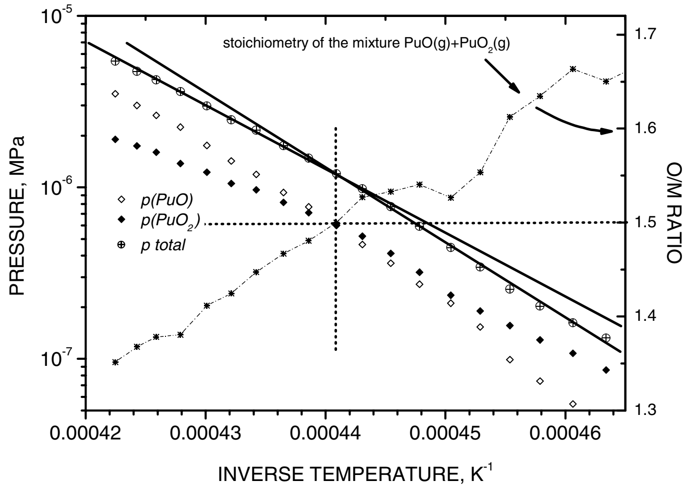

Fig. 3. Measured equilibrium partial pressures of PuO_2(g) and PuO(g) and stoichiometry of the mixture of the Pu-bearing species as functions of temperature. The pressures are normalized to Pu_2O_3 from the Pu-content of the (ideal) solid solution $(Pu_{0.62},Cm_{0.38})_2O_3$.

the plutonium oxide vapour pressure in the valid temperature range, shown in Fig. 3, it can be clearly seen that the slope of the Arrhenius plot of the total pressure slightly changes by crossing the congruent vapour composition. In fact, 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. In our case, due to the small size of the sample, in the Knudsen cell the relatively high pressure of oxygen at high temperatures was expected to be controlled by the evacuating speed rather than by equilibrium conditions.

Though under this aspect our experimental conditions were not fully under control, from the measurement of the vapour components and from the assumption that the examined mixed oxide was an ideal solution, i.e.

$$p(\mathrm{PuO}+\mathrm{PuO_2})_{\mathrm{Pu_2O_3}} = \frac{p(\mathrm{PuO}+\mathrm{PuO_2})_{\text{mixed oxide}}}{x(\mathrm{Pu_2O_3})_{\text{mixed oxide}}},$$

$$x = \text{plutonium fraction} \tag{3}$$

the problem of evaluating the effective oxygen potential during the experiment could be consequently solved.

The oxygen partial pressure was deduced from the reaction

$$\mathrm{PuO(g)} + \mathrm{O(g)} = \mathrm{PuO_2(g)} \tag{4}$$

whose thermodynamic parameters are well established [4]. Since the free energy of reaction (4) can be calculated from the measured partial pressures of the plutonium oxides, the effective oxygen partial pressure p(O) is readily deduced from the ratio $p(\mathrm{PuO})/p(\mathrm{PuO_2})$. The measurement results are plotted in Figs. 1 and 3. The trend of p(O) as a function of the effusion temperature is clear; it starts from values near to those predicted by the extrapolated e.f.m. measurements at lower temperatures that gave

$$\Delta G(\mathrm{O}) = -605.01 + 1.38230 \times 10^{-1} T\ (\mathrm{K})\ \mathrm{kJ\,mol^{-1}} \tag{5}$$

and increases until it reaches the values of the order of magnitude of 10^{-9} MPa, a value above which the effective oxygen pressure is more and more controlled by the vessel evacuation rate. Under this regime the pressure dependence on temperature is obviously much weaker than expected under equilibrium conditions.

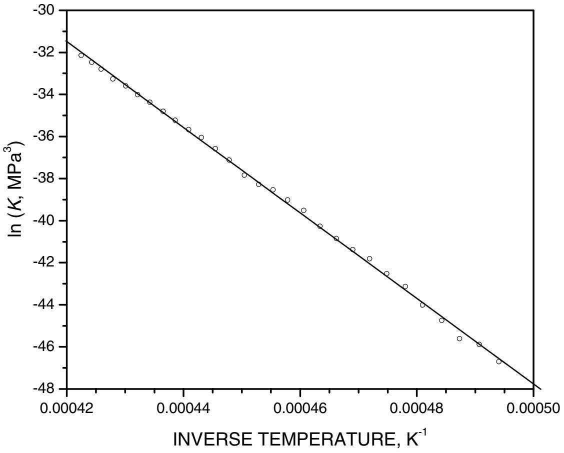

Fig. 4. Arrhenius plot of the equilibrium constant of the Cm_2O_3 sublimation reaction.

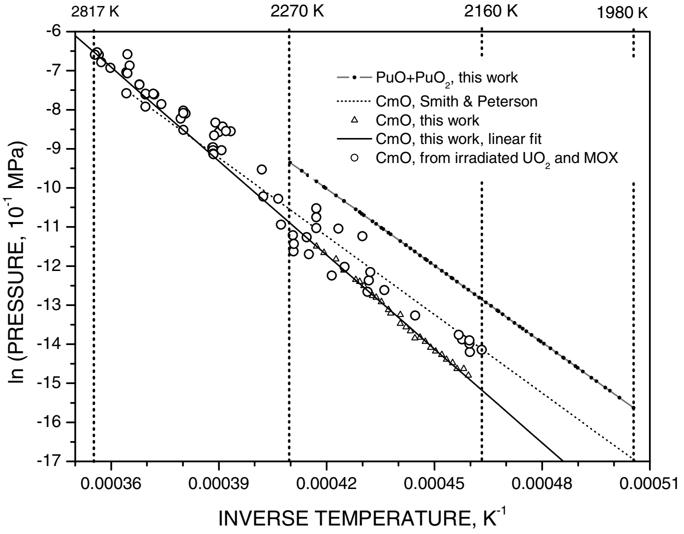

Fig. 5. Plot of p(CmO) vs. T^{-1} measured over the $(Pu_{0.62},Cm_{0.38})_2O_3$ mixed oxide and over reactor-irradiated MO_2 fuel.

The empirical values of p(O) were eventually used to calculate the equilibrium constant of reaction (1)

$$K = p(\mathrm{CmO})^2 p(\mathrm{O}),\ \ \mathrm{MPa}^3 \tag{6}$$

The experimental measurements of K exhibit an excellent alignment in the Arrhenius plot of in Fig. 4.

The following temperature dependence of K was eventually found

$$\ln(K) = (40.143 \pm 0.54) - (203442 \pm 1322)/T\ \ (\mathrm{K}). \tag{7}$$

The resulting value of the reaction enthalpy at $T = 2225$ K

$$\Delta H = 1685.3 \pm 11\ \ \mathrm{kJ\,mol^{-1}}$$

is slightly higher than that obtained by Smith and Peterson (1668.1 ± 33 kJ mol^{-1}), but the difference is within the probable error. This agreement is particularly significant since our experimental conditions were not the same and, in particular, the two sets of measurements of the p(CmO) as a function of T were affected by different oxygen potentials.

4.2. Irradiated fuels

The vaporization of curium from irradiated fuel was measured under the same conditions as described above, in the broader temperature range of 2200–2800 K, in seven different samples of UO_2 (b.u. ~70 GWd t^{-1}) and MOX (b.u. ~30 GWd t^{-1}). The ^{244}Cu content in these samples was between 0.01% and 0.04% of the heavy metal inventory. As for the Cm–Pu mixed oxide, we assumed that the vapour pressure of CmO above the solid solution (CmO_x–MO_2, M = Pu and/or U) follows Henry's law and is directly proportional to its concentration. The vapour pressure of CmO was thus normalized from the concentrations calculated by the code Origen-2, whose results were checked to be in good agreement with the concentration determined by mass spectrometry. The total curium oxide vapour pressure is plotted in Fig. 5. Again, though curium was dissolved in MO_2 only the CmO(g) species was observed. Furthermore, within a larger scatter, the points are aligned with the curve of p(CmO) measured over the mixed sesquioxide. The reason is that the effective oxygen partial pressure during the measurement was probably not very different from that of the mixed oxide experiments. This was confirmed by the observed progressive disappearance of PuO_2(g) with a corresponding increase of PuO(g) in the effusing vapour at higher temperatures, as in the case of $(Cm,Pu)_2O_3$.

5. Conclusions

- Analysis of Knudsen-effusion and mass spectrometric measurement of curium–plutonium sesquioxide shows that this behaves like an ideal solid solution.
- It could be directly proved that Cm_2O_3 vaporizes exclusively as CmO(g) and atomic oxygen. Though the experiments were conducted under a relatively low oxygen partial pressure, no Cm(g) component was found in the vapour. This behaviour, first conjectured by Smith and Peterson, is therefore experimentally confirmed.
- The slope of the p(CmO) vs. T^{-1} curve measured in our work

$$\ln(p(\mathrm{CmO}),\ \mathrm{MPa}) = (22.42 \pm 0.68) - (85\,783 \pm 1681)/T\ (\mathrm{K})$$

is significantly different from that of these authors (66 890 ± 1360). However, this is explained by the different oxygen potentials in the two experiments. In fact, between 2000 and 2500 K the equilibrium constant of the reaction $Cm_2O_3(cr) = CmO(g) + O$, interpolating our data has the expression

$$\ln(K) = (40.143 \pm 0.54) - (203\,442 \pm 1322)/T\ (\mathrm{K}),$$

which is in good agreement with that found by Smith and Peterson.

- Finally, it was found that the vaporization of curium from irradiated UO_2 and MOX fuel under reducing conditions can be described by the same vaporization enthalpy as in the case of the $(Cm,Pu)_2O_3$ samples. Cm_2O_3 appears to be significantly less volatile than Pu_2O_3 at the same oxygen chemical potential. This confirms the trend observed in the actinide oxides that the high temperature volatility is more pronounced in compounds where the cation can easier attain a higher oxidation state than that of the condensed phase.

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