Thermodynamics of the Conversion of Plutonium Dioxide to Plutonium Monocarbide

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PLUTONIUM MONOCARBIDE

Theodore M. Besmann and Terrence B. Lindemer

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THERMODYNAMICS OF THE CONVERSION OF PLUTONIUM DIOXIDE TO
PLUTONIUM MONOCARBIDE*

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ABSTRACT

The present study contains an equilibrium thermodynamic analysis of the Pu-C-O system and a discussion from an equilibrium thermodynamic point of view of the direct carbothermic reduction and two-step carbothermic-hydrogen reduction of PuO_2 to PuC_{1-x} . Included are considerations of the partial pressures of the various species in the Pu-C-O and Pu-C-H systems, the process parameters required for conversion of the oxide to the carbide, and the loss of plutonium due to vapor species.

1. Introduction

The recently renewed interest in advanced nuclear fuels has resulted in the consideration of the monocarbide of plutonium as a fuel component. The primary means of production investigated to date has been the carbothermic reduction of PuO_2 either in vacuum or flowing inert gas. Disagreement exists, however, as to whether carbothermic reduction can actually yield sufficiently oxygen-free monocarbide.

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Several researchers have reported experimental efforts to prepare plutonium monocarbide [1-4]. Only Potter [5], however, has attempted a relatively complete thermodynamic analysis of the carbothermic reduction process. As an alternative, Sowden et al. [6] have reported a preliminary investigation of a two-step process involving carbothermic reduction of the oxide to the sesquicarbide followed by hydrogen stripping of carbon to produce the monocarbide. This process may avoid the difficulties of direct carbothermic reduction.

It is the object of the present study to perform a thermodynamic analysis similar to that of Potter's [5] using the most recent thermodynamic data. Additionally, the effect of temperature on the Pu-C-O system will be investigated and the two-step reduction process analyzed.

2. Phase Relations in the Pu-C-O System

Potter [5] has reviewed the phase relations in the Pu-C-O system and has developed a phase diagram for ~ 1570 K (fig. 1).^{*} An independent evaluation of the phase relations performed for the present study using the equilibrium calculations described below indicates agreement with his diagram.

An interesting feature of the Pu-C-O system is that the plutonium monocarbide phase requires carbon-site vacancies for stability such that the maximum homogeneity range of PuC_{1-x} is $0.64 \leq x \leq 0.94$ at 907 K [7]. Potter [5] notes that a PuC_xO_y solid solution (plutonium monoxycarbide) exists as a result of oxygen substituting for carbon in the monocarbide.

^{*}The following notation is used throughout: < > pure element or compound in the solid state; [] solid solution (subscript denotes solvent); { } liquid state; () gaseous state.

Fig. 1. Ternary phase diagram for the Pu-C-O system at ~ 1570 K after Potter [5].

A similar phase is found in the U-C-O system, although the maximum oxygen substitution in the Pu-C-O system is 67 at. % as opposed to 34 at. % for uranium monoxycarbide [8].

Reaction paths for the carbothermic reduction of PuO_2 to the monocarbide have been postulated by Skavdahl [2] and Yahata and Ouchi [4]. Skavdahl [2] notes that the dioxide can react with carbon to form $\text{PuC}_{1.5}$, $\text{PuO}_{1.5}$, and PuC_xO_y , thus liberating CO gas during the reduction. Yahata and Ouchi [4] also observed these phases, but they suggest that PuO_{2-x} may be present as a nonequilibrium intermediate phase. The regions of the phase diagram in fig. 1 which must be considered in an equilibrium thermodynamic analysis are:

3. Equilibrium Thermodynamic Analysis

The feasibility of the carbothermic reduction of PuO_2 to PuC_{1-x} is ultimately governed by the thermodynamic equilibrium composition of the system, i.e., the composition in the absence of any limiting effects (chemical kinetic or mass transport). The equilibrium composition is found by computing the equilibrium partial pressures for the gaseous species over the appropriate regions of the Pu-C-O phase diagram. It is the partial pressure of CO which is of greatest importance since the evolution of CO gas is the primary reduction mechanism. The partial

pressures of other possibly important species must be known, however, since a high partial pressure of another species, such as plutonium, may result in a change in the composition of the condensed phases.

The equilibrium composition in each of the condensed phase regions listed above was computed using the method of direct minimization of the system free energy outlined by Eriksson [9]. A general computer program, SOLGAS, developed by him and modified for more convenient use with the type of systems considered here was used to perform the calculations. Several manual calculations were also performed to insure the validity of the machine calculations. Table 1 includes the thermodynamic values for all the species considered. The data have been obtained from the most recent and reliable reported values of the thermodynamic properties of the various species. These values are used throughout the equilibrium calculations. The inclusion of the relatively large number of gaseous species was for the purpose of insuring that no possibly important species would be omitted.

3.1 Phase Field $\text{PuO}_{2-x} + \text{C}$

In the $\text{PuO}_{2-x} + \text{C}$ phase region where $0.0 \leq x \leq 0.39$, the equilibrium CO partial pressure is both a function of temperature and x [17]. At $T \geq 1600$ K, p_{CO} is greater than 0.02 atm (0.002 MPa), and the partial pressures of any plutonium-bearing species are several orders of magnitude below p_{CO} . Under these conditions, the CO evolution rate at equilibrium will be much higher than in the other regions of the phase diagram listed above, and the rate of plutonium evaporation will be much lower. As a result, the carbothermic reduction of PuO_{2-x} to $\text{PuO}_{1.61}$ is not believed to be limiting the reduction process to produce PuC_{1-x} and will not be considered in detail here.

Table 1
Thermodynamic Values

Species	Temperature (K)	ΔH_f°		ΔS_f°		Reference
		kcal/mol	(kJ/mol)	eu	(J/mol - K)	
Carbothermic reduction of PuO_2 to $\text{PuC}_{0.88}$						
(CO)	1800	-28.032	(-117.29)	20.17	(84.39)	[10]
(CO_2)	1800	91.696	(386.22)	0.030	(0.13)	[10]
(O)	1800	59.55	(249.2)	15.93	(66.65)	[11]
(Pu)	1800	78.11	(326.8)	21.23	(88.83)	[12]
(PuO)	1600-2150	-28.5	(-119)	9.7	(41)	[13]
(PuO_2)	1600-2150	-112.6	(-471.1)	-6.6	(-28)	[13]
(PuC_2)	1800	136	(569)	50	(210)	*
< $\text{PuO}_{1.5}$ >	1600-2150	-199.8	(-836.0)	-31.90	(133.5)	[13]
< $\text{PuO}_{1.61}$ >	1600-2150	-210.	(-879)	-33.0	(-138)	[13]
< $\text{PuC}_{0.88}$ >	1800	-7.77	(-32.5)	2.94**	(12.3)	[16]
< $\text{PuC}_{1.5}$ >	1800	-19.63	(-82.13)	-0.936**	(-3.92)	[16]
Hydrogen reduction of $\text{PuC}_{1.5}$ to $\text{PuC}_{0.88}$						
(H)	1300	53.5	(224)	13.89	(58.12)	[11]
(CH_4)	1300	-21.971	(-91.929)	-26.54	(-111.0)	[10]
(C_2H_2)	1300	53.128	(222.29)	12.63	(52.85)	[10]
(Pu)	1300	78.01	(32.64)	21.18	(88.62)	[12]
(PuC_2)	1600	136	(569)	54.3	(190)	*
< $\text{PuC}_{0.88}$ >	1300	-12.93	(-54.10)	-0.328**	(-1.37)	[16]
< $\text{PuC}_{1.5}$ >	1300	-21.37	(-89.41)	-2.06**	(-8.62)	[16]

* Calculated from the fef° of Faircloth et al. [14] and the ΔH_f° and S_{298}° of Schumm et al. [15] for the analogous species CeC_2 .

** Calculated from respective S_T° for $\text{PuC}_{0.88}$ and $\text{PuC}_{1.5}$ [16], and S_T° for plutonium [12] and carbon [11].

3.2 Phase Field $\text{PuO}_{1.61} + \text{PuO}_{1.5} + \text{C}$

Eight gaseous species (CO , CO_2 , O , O_2 , Pu , PuO , PuO_2 , and PuC_2) were included in the equilibrium calculations. Only the species CO , Pu , and PuO were found to have significant partial pressures. These are plotted versus temperature in fig. 2 for three phase fields, including the $\text{PuO}_{1.61} + \text{PuO}_{1.5} + \text{C}$ field. Potter [5] has made similar calculations of the equilibrium CO partial pressure in this phase field, and his results agree closely with those reported here. Such agreement should be expected, however, since the thermodynamic data used in the respective analyses differ only slightly.

Pickles [8] has reported CO vapor pressure measurements over $\text{PuO}_{1.61} + \text{PuO}_{1.5} + \text{C}$, although in his reaction (10), he incorrectly indicates that PuO_2 reacts with C to form $\text{PuO}_{1.5}$ and CO . In spite of the fact that his condensed phase compositions were not well defined, the results seen in fig. 2 are in reasonable agreement with the equilibrium values.

3.3 Phase Field $\text{PuO}_{1.5} + \text{PuC}_{1.5} + \text{C}$

The computed partial pressures for the species over the $\text{PuO}_{1.5} + \text{PuC}_{1.5} + \text{C}$ phase field are also shown in fig. 2. Again Potter's [5] calculated equilibrium p_{CO} values correspond closely to those given here. Partial pressures of CO , measured by Pascard and Rouillet and reported by Potter [5], are a factor of 4 greater than those calculated in the present study. Pickles [18] gives CO partial pressures for this region at $T > 1770 \text{ K}$ found during the carbothermic reduction of the oxide. His results are as much as a factor of 7 higher than the calculated equilibrium pressures. It is possible that a small amount of the nonequilibrium phase

Fig. 2. Calculated equilibrium partial pressures of CO, Pu, and PuO and Pascard and Roulett's [5] and Pickles [18] measured CO partial pressures over regions of the Pu-C-O phase diagram versus reciprocal temperature.

PuO_{2-x} , where $x \leq 0.39$, was present in his samples, prevented the system from equilibrating, and yielded the higher pressure.

3.4 Phase Field $\text{PuO}_{1.5} + \text{PuC}_{1-x}\text{O}_x + \text{PuC}_{1.5}$

The computation of reliable equilibrium partial pressures above the three-phase region bounded by sesquicarbide, monoxycarbide, and sesquioxide is hindered by a lack of thermodynamic data for the monoxycarbide. Potter [5], in order to perform equilibrium calculations, assumed that plutonium monoxycarbide was a solid solution of PuO and PuC and used both the ideal and regular solution models. In light of the recently assessed thermodynamic values for the plutonium carbides [16], the ideal solution model described below appears most appropriate and is used in the present study.

The monoxide of plutonium is not a stable phase, and thus in order to utilize the ideal solution model, an expression for the molar free energy of PuO must be derived. Potter [5] notes that the partial molar free energy can be determined from the three-phase region containing liquid plutonium, $\text{PuO}_{1.5}$, and $\text{PuC}_{0.27}\text{O}_{0.67}$ shown in fig. 1. The chemical reaction

would thus exhibit a $\Delta G_{\text{rxn}}^{\circ} = 0$ at equilibrium and, therefore,

$$\Delta \bar{G}_f[\text{PuO}] = 2/3 \Delta G_f^{\circ} \langle \text{PuO} \rangle + RT \ln x \quad (1)$$

where x is the mol fraction of PuO present in the solution. Thus at $x = 0.67$

$$\Delta G_f^{\circ} \langle \text{PuO} \rangle = 2/3 \Delta G_f^{\circ} \langle \text{PuO}_{1.5} \rangle - RT \ln x. \quad (2)$$

The monocarbide of plutonium only exists at C/Pu ratios less than 1.0 and detailed thermodynamic data is reported for $\text{PuC}_{0.88}$ [16]. It is this phase which is assumed to dissolve PuO to form the solid solution. For simplicity, however, the solid solution is written $\text{PuC}_{1-x}\text{O}_x$. The partial molar free energy for the dissolved monocarbide is expressed as

$$\Delta \bar{G}_f[\text{PuC}] = \Delta G_f^{\circ} < \text{PuC}_{0.88} > + RT \ln (1-x). \quad (3)$$

The equilibrium between $\text{PuC}_{1.5}$, $\text{PuC}_{1-x}\text{O}_x$, and $\text{PuO}_{1.5}$ permits the reaction

to have a $\Delta G_{\text{rxn}}^{\circ} = 0$. This reaction can be used with expressions of the free energies given above to derive, as a function of temperature, the mol fraction of [PuO] in the solid solution. The results are plotted in fig. 3 as x versus temperature.

The validity of the ideal solution model described above is strengthened by the experimental results of Brett et al. [19] and Potter [3]. Brett et al. at 1773 K determined that $x = 0.34$, and, at 1573 K, Potter found that $x = 0.38$. These are almost identical to the predicted values plotted in fig. 3.

The ideal solution model in the form of eqs. (1), (2), and (3) was used to find $\Delta \bar{G}_f$ for $[\text{PuO}]_{\text{PuC}}$ and $[\text{PuC}]_{\text{PuO}}$ as a function of x. These values were used to compute the equilibrium partial pressures above the condensed phase region $\text{PuC}_{1.5} + \text{PuC}_{1-x}\text{O}_x + \text{PuC}_{1.5}$ which are plotted in fig. 2. Potter [5] reports calculated equilibrium CO pressures derived both from ideal and regular solution models. The results of his ideal solution calculations agree reasonably with the p_{CO} values reported in the present study.

Fig. 3. Mol fraction of PuO in the solid solution $\text{PuC}_{1-x}\text{O}_x$ in equilibrium with $\text{PuC}_{1.5} + \text{PuO}_{1.5}$ versus temperature.

3.5 Phase Fields $\text{PuO}_{1.5} + \text{PuC}_{1-x}\text{O}_x$ and $\text{PuC}_{1.5} + \text{PuC}_{1-x}\text{O}_x$

Equations (1), (2), and (3) were also used to calculate the equilibrium partial pressures of the various species over $\text{PuO}_{1.5} + \text{PuC}_{1-x}\text{O}_x$ and $\text{PuC}_{1.5} + \text{PuC}_{1-x}\text{O}_x$. The partial pressures of CO, Pu, and PuO versus x are plotted in fig. 4 for 1600 and 1900 K. It is important to note that p_{CO} becomes less than p_{Pu} as $x \rightarrow 0$ and as $x \rightarrow 0.67$. It is also observed that lower temperatures favor a larger compositional region over which $p_{\text{CO}} < p_{\text{Pu}}$.

Using a regular solution model, Potter [5] has calculated a set of curves for 1600 K (incorrectly reported as being for 1500 K in his fig. 11) similar to those in fig. 4 for the partial pressures of CO, Pu, PuO, and PuO_2 . Reasonable agreement is found for the equilibrium partial pressures above the phase fields.

Some vacuum vaporization experiments with the monoxycarbide have been performed by Potter [3]. He reported that in the range 1598-1723 K the $\text{PuC}_{0.5}\text{O}_{0.5}$ phase appears to vaporize congruently. This agrees with the results of the equilibrium calculations shown in fig. 4, i.e., $p_{\text{CO}} = p_{\text{Pu}}$ at $x \cong 0.5$. Using the Langmuir free evaporation relation with the assumptions of minimum surface area for vaporization (surface of a sphere) and no kinetic limitations on evaporation, Potter found plutonium partial pressures at several temperatures. The results of his calculations are, however, one order of magnitude too great due to an arithmetic error in the third equation in his Section 6.2. The correct values between 1598 and 1723 K are between 2.18×10^{-7} and 2.13×10^{-6} atm (0.0221 and 0.216 Pa), respectively. These are in good agreement with the equilibrium values shown in fig. 4.

Fig. 4. Calculated equilibrium partial pressures of CO, Pu, and PuO at 1600 K and 1900 K above the ideal solid solution $\text{PuC}_{1-x}\text{O}_x$, present with $\text{PuO}_{1.5}$ or $\text{PuC}_{1.5}$, versus x .

Yahata and Ouchi [4] report preparing mixtures of PuC_{1-x} and $\text{PuC}_{1.5}$ by the direct carbothermic reduction of the oxide in vacuum over the temperature range 1273-1623 K. Unfortunately, they do not appear to have considered the possible retention of oxygen by the monocarbide and did not analyze for oxygen. They report a lattice parameter for the monocarbide of 0.4978 nm which, according to Potter [5], indicates a phase composition of $\text{PuC}_{0.87}\text{O}_{0.13}$. Additionally, the thermodynamic equilibrium calculations presented here indicate that at a composition of approximately $\text{PuC}_{0.8}\text{O}_{0.2}$, $p_{\text{CO}} = p_{\text{Pu}}$ and continued reduction of the monoxycarbide becomes impossible. Thus it is likely that Yahata and Ouchi [4] prepared a monocarbide containing a significant quantity of oxygen which they did not detect.

4. Assessment of Direct Carbothermic Reduction

The results of both the thermodynamic equilibrium calculations performed by Potter [5] and those of the present study indicates that it is not possible to prepare relatively oxygen-free plutonium monocarbide, under equilibrium conditions, by the direct carbothermic reduction of the oxide. In the reduction process, a monoxycarbide solid solution phase forms which cannot be completely reduced to the monocarbide. Assuming that $\text{PuC}_{1-x}\text{O}_x$ initially forms in the presence of $\text{PuC}_{1.5}$ and $\text{PuO}_{1.5}$, it can be seen from fig. 4 that as x decreases, p_{CO} will decrease and p_{Pu} will increase. Eventually, p_{CO} approaches p_{Pu} , effectively preventing the continued reduction of the phase.

From fig. 4, it can be seen that in the presence of $\text{PuC}_{1.5}$, as temperature increases, the value of x at which $p_{\text{CO}} = p_{\text{Pu}}$ decreases. Thus it might

be expected that at high enough temperatures p_{CO} remains significantly greater than p_{Pu} to very low values of x (< 0.001), permitting the efficient carbothermic reduction to PuC_{1-x} . Unfortunately, plutonium monocarbide decomposes peritectically at 1918 K [20]. A reduction process carried out much above 1900 K would, therefore, result in the formation of a liquid plutonium phase which would be undesirable due to the high volatility and chemical reactivity of the liquid.

The results of attempts to carbothermically reduce the oxide to the monocarbide appear to confirm the implications of the thermodynamic equilibrium calculations. Skavdahl's [2] efforts to prepare oxygen-free PuC_{1-x} by the carbothermic reduction of PuO_2 both in 1 atm (0.1 MPa) of inert gas and in vacuum were unsuccessful. Mulford et al. [21] and Potter [3] report a congruently vaporizing $\text{PuC}_{1-x}\text{O}_x$ composition that prevents the formation of the monocarbide. Yahata and Ouchi [4], as noted earlier, probably only formed the monoxycarbide in attempts to prepare PuC_{1-x} . Ainsley et al. [1] heated pellets of PuO_2 -C mixtures in vacuum for 50 min at 1943 K, which is above the peritectic decomposition temperature for PuC_{1-x} . They report the product as plutonium monocarbide containing a minor amount of sesquicarbide. A plutonium loss of 1.54% was also observed.

At present the only chemical kinetic study of the carbothermic reduction of PuO_2 has been that of Yahata and Ouchi [4]. They observed that pellets which originally had a C/O ratio of 1.45, when heated in vacuum reacted initially at a low rate and produced a so-called transient stable phase. Increasing the reaction temperature, however, reduced the length of time at this low rate such that the step essentially disappears at $T \geq 1600$ K. They noted that the conversion rates follow those expected

for the decreasing reacting surface area of spherical particles. This indicates that the process is rate-controlled by solid-state mechanisms over the temperature range studied, 1273-1623 K. An apparent activation energy of 102 kcal/mol (427 kJ/mol) was derived for the process.

5. Assessment of Two-Step Reduction

A possibly attractive alternative to the direct carbothermic reduction of PuO_2 to PuC_{1-x} is a two-step reduction process that has been successfully used by Sowden et al. [6]. The primary overall reaction for each step is:

Weber and Greenhalgh [22] have devised a similar multistep process for preparing nitride nuclear fuels in which free carbon is removed by reaction with hydrogen.

The first step in the two-step process is the carbothermic reduction of the oxide to $\text{PuC}_{1.5}$ in vacuum or flowing inert gas. It is expected that the use of excess carbon will prevent the formation of the ternary solid solution $\text{PuC}_{1-x}\text{O}_x$, and thus avoid the problem of significant plutonium vaporization. Ainsley et al. [1], Potter [3], and Yahata and Ouchi [4] report successfully preparing $\text{PuC}_{1.5}$ in vacuum, and Ainsley et al. [1] indicate a plutonium loss of only 0.036%.

The regions of the Pu-C-O phase diagram, fig. 1, which must be considered in converting the oxide to the sesquicarbide are $\text{PuO}_{2-x} + \text{C}$ ($0.0 \leq x \leq 0.39$), $\text{PuO}_{1.61} + \text{PuO}_{1.5} + \text{C}$, and $\text{PuO}_{1.5} + \text{PuC}_{1.5} + \text{C}$. The reactions are:

and

Again, at temperatures greater than 1600 K, the equilibrium CO partial pressure above $\text{PuO}_{2-x} + \text{C}$ is greater than 0.02 atm (0.002 MPa), and, therefore, is not considered as limiting the reduction process. The equilibrium partial pressures above the remaining phase fields are shown in fig. 2.

A likely conversion process would use a stream of flowing inert gas at 1 atm (0.1 MPa) in which the oxide is converted to the sesquicarbide. The volume of inert gas required to complete reactions (4), (5), and (6), assuming the condensed phases are in equilibrium with the gas, can be found from

$$V = 22.4 \frac{Z}{p_{\text{CO}}} \quad (7)$$

where V is the volume in liters (STP), Z is the mols of CO liberated per mol of oxide reduced, and p_{CO} is the equilibrium CO partial pressure, in atmospheres, in the appropriate phase field. As might be expected, reaction (6) is the limiting reaction since it requires 1.5 mols of CO to be formed per mol of oxide reacted and p_{CO} above $\text{PuC}_{1.5} + \text{PuO}_{1.5} + \text{C}$ is small compared to that above the other phase fields. Using the p_{CO} values shown in fig. 2, the volume of gas required to convert one mol of PuO_2 to $\text{PuC}_{1.5}$ is plotted as a function of temperature in fig. 5.

Figure 5 can be seen to also contain a plot of temperature versus the percent plutonium vaporized from a charge of oxide and carbon reacting to form the sesquicarbide. Interestingly, although the volume of

Fig. 5. Liters of inert gas (STP) required to convert PuO_2 to $\text{PuC}_{1.5}$ and the percentage of plutonium vaporized versus temperature. Thermodynamic equilibrium conditions are assumed.

inert gas required for conversion of PuO_2 to $\text{PuC}_{1.5}$ decreases with increasing temperature, the percentage of plutonium vaporized remains relatively constant at $\sim 0.0015\%$. The percentage remains constant because the partial pressures of CO and plutonium increase with temperature to maintain an approximately constant ratio, i.e., the reactions forming the two gaseous species have similar $\Delta H_{\text{rxn}}^{\circ}$.

In order to perform an analysis of the hydrogen reduction of $\text{PuC}_{1.5}$ to PuC_{1-x} analogous to that described above, the computation of equilibrium partial pressures of the gaseous species in the Pu-C-H system is required. In particular, the partial pressures in hydrogen above the condensed phases $\text{PuC}_{1.5} + \text{PuC}_{0.88}$ must be established. The data in Table 1 were used with the computer program SOLGAS to calculate the equilibrium partial pressures of the species H , H_2 , CH_4 , C_2H_2 , Pu , and PuC_2 . The calculations indicated that over the temperature range 1000-1700 K the only species having significant partial pressures were H_2 , CH_4 , and Pu .

In the hydrogen reduction of $\text{PuC}_{1.5}$ to $\text{PuC}_{0.88}$, caution must be exercised so that the monocarbide is not further reduced to the liquid metal via

This can be ensured by adding CH_4 to the hydrogen stream so that p_{CH_4} is maintained greater than the equilibrium value in reaction (8).

Using a relation analogous to eq. (7) the volume of hydrogen required to reduce one mol of $\text{PuC}_{1.5}$ to $\text{PuC}_{0.88}$ was computed and plotted versus temperature in fig. 6. It was assumed that sufficient CH_4 is added to the hydrogen before it contacts the carbide so that p_{CH_4} in the reactant stream is greater than the equilibrium value for reaction (8). Also plotted as

Fig. 6. Liters of hydrogen (STP) required to reduce PuC_{1.5} to PuC_{0.88} and the percentage of plutonium vaporized versus temperature. Thermodynamic equilibrium conditions are assumed.

a function of temperature in fig. 6 is the percentage of plutonium vaporized during the reduction.

A typical, complete, two-step reduction process might use a 10-g charge of oxide-graphite mixture reacting to $\text{PuC}_{1.5}$ at 1900 K in a 6 ℓ/min (STP) inert gas stream. Figure 5 indicates that, at equilibrium, 8 min is required to reduce the oxide with 0.0015% of the plutonium volatilizing. The subsequent hydrogen reduction at 1300 K in a 6 ℓ/min (STP) stream of hydrogen would require 18.6 hrs and volatilize about 0.0003% of the plutonium.

Sowden et al. [6] have successfully prepared PuC_{1-x} by the hydrogen reduction of $\text{PuC}_{1.5}$. The most efficient conversion they report was performed at 1273 K in a 1 ℓ/min (STP), 1 atm (0.1 MPa) H_2 stream. The powdered 0.25-g $\text{PuC}_{1.5}$ sample had a $1.8\text{-m}^2/\text{g}$ surface area and required 6 hrs for complete conversion. The results are in contrast to the 2.6 hrs conversion time predicted for these conditions from equilibrium calculations (fig. 6). The discrepancy in conversion time is most likely due to rate-limiting effects preventing the attainment of equilibrium between the gas and the condensed phases. It should be noted that even if one assumed that the system were at equilibrium for 6 hrs, the predicted plutonium loss would only be approximately 0.0002%.

6. Conclusions

1. The thermal properties of plutonium monoxycarbide can be successfully modeled by assuming the phase is an ideal solid solution of $\text{PuC}_{0.88}$ and PuO .

2. Both the results of our equilibrium thermodynamic calculations and the experiments of others indicate that PuC_{1-x} cannot practically be prepared by the carbothermic reduction of PuO_2 . During the reduction process, the ternary solid solution $\text{PuC}_{1-x}\text{O}_x$ forms and under equilibrium conditions, as x decreases, $p_{\text{CO}} \rightarrow p_{\text{Pu}}$ and prevents the phase composition from approaching that of the monocarbide.
3. Carbothermic reduction of PuO_2 at temperatures greater than the peritectic decomposition temperature of PuC_{1-x} may remove essentially all the oxygen from the system. However, the resulting formation of liquid plutonium would be undesirable.
4. Calculations indicate that the two-step reduction of PuO_2 to PuC_{1-x} appears feasible and will minimize plutonium loss. Carbothermic reduction with an excess of carbon can produce $\text{PuC}_{1.5}$ from the oxide and avoid the ternary solid solution phase ($\text{PuC}_{1-x}\text{O}_x$). The sesquicarbide could then be reduced by hydrogen to PuC_{1-x} .

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Appendix

Calculated Equilibrium Partial Pressures (atm)*

1. Phase Region: $< \text{PuO}_{1.61} > + < \text{PuO}_{1.5} > + < \text{C} >$

$$\ln p_{\text{CO}} = - \frac{32600}{T} + 15.2$$

$$\ln p_{\text{Pu}} = - \frac{69900}{T} + 19.2$$

$$\ln p_{\text{PuO}} = - \frac{62900}{T} + 18.4$$

2. Phase Region: $< \text{PuC}_{1.5} > + < \text{PuO}_{1.5} > + < \text{C} >$

$$\ln p_{\text{CO}} = - \frac{46300}{T} + 20.5$$

$$\ln p_{\text{Pu}} = - \frac{48200}{T} + 10.5$$

$$\ln p_{\text{PuO}} = - \frac{56000}{T} + 15.7$$

3. Phase Region: $< \text{PuC}_{1.5} > + < \text{PuC}_{1-x}^{\text{O}} > + < \text{PuO}_{1.5} >$

$$\ln p_{\text{CO}} = - \frac{72900}{T} + 30.2 + \ln x - 5 \ln (1 - x)$$

$$\ln p_{\text{Pu}} = - \frac{31300}{T} + 5.32 + 3 \ln (1 - x)$$

$$\ln p_{\text{PuO}} = - \frac{52800}{T} + 16.0 + \ln x$$

4. Phase Region: $< \text{PuO}_{1.5} > + < \text{PuC}_{1-x}^{\text{O}} >$

$$\ln p_{\text{CO}} = - \frac{56900}{T} + 17.4 + \ln (1 - x) - 5 \ln x$$

$$\ln p_{\text{Pu}} = - \frac{39300}{T} + 11.9 + 3 \ln x$$

$$\ln p_{\text{PuO}} = - \frac{52800}{T} + 16.0 + \ln x$$

* To find the partial pressures in MPa subtract 2.29 from each equation.

5. Phase Region: $\langle \text{PuC}_{1.5} \rangle + \langle \text{PuC}_{1-x}\text{O}_x \rangle$

$$\ln p_{\text{CO}} = - \frac{72900}{T} + 30.5 + \ln x - 5 \ln (1 - x)$$

$$\ln p_{\text{Pu}} = - \frac{31300}{T} + 5.31 + 3 \ln (1 - x)$$

$$\ln p_{\text{PuO}} = - \frac{52800}{T} + 16.0 + \ln x$$

6. Phase Region: $\langle \text{PuC}_{1.5} \rangle + \langle \text{PuC}_{0.88} \rangle$ in hydrogen

$$\ln p_{\text{CH}_4} = \frac{4230}{T} - 12.0 + 2 \ln p_{\text{H}_2}$$

$$\ln p_{\text{Pu}} = - \frac{39800}{T} + 8.69$$

7. Phase Region: $\langle \text{PuC}_{0.88} \rangle + \{\text{Pu}\}$ in hydrogen

$$\ln p_{\text{CH}_4} = \frac{3630}{T} - 13.2 + 2 \ln p_{\text{H}_2}$$

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