Alternative Solvents for Cleaning Plutonium:
Thermodynamic and Kinetic Considerations
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John M. Haschke
Stephanie J. Hale

*EG&G Rocky Flats, P.O. Box 464, Golden, CO 80402

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ALTERNATIVE SOLVENTS FOR CLEANING PLUTONIUM: THERMODYNAMIC AND KINETIC CONSIDERATIONS

by

John M. Haschke and Stephanie J. Hale

ABSTRACT

Thermodynamic and kinetic data for selected reactions of plutonium metal are reevaluated as a basis for assessing the risk of a violent exothermic reaction during solvent-based cleaning operations. The enthalpy data are in disagreement with values reported in a recent overview of the topic. Our results show that all credible solvents, including ethers and light hydrocarbons, react spontaneously and exothermically with plutonium. The need for considering kinetic behavior of a reaction in assessing its thermal risk is demonstrated. The independence of thermodynamic and kinetic properties is discussed and the unpredictable effects of catalytic substances are described. Criteria for objectively evaluating cleaning technologies are presented.

INTRODUCTION

Certain safety issues concerning the use of supercritical fluid (SCF) carbon dioxide as a cleaning solvent for removing organic residues from plutonium metal were presented at the Waste Minimization Program Review held at the Rocky Flats Plant in June, 1991.1 The potential for violent exothermic reaction was cited as a primary reason for questioning the advisability of proceeding with efforts to evaluate and develop a CO$_2$-based process as a replacement for the chlorocarbon-based cleaning methods presently used for degreasing components and machine
Carbon tetrachloride and 111-trichloroethane (TCA) are currently employed as cleaning solvents during manufacturing operations at Rocky Flats, but continued chlorocarbon use will be prevented by impending regulation and unavailability. Since an acceptable cleaning method must be developed and since the most viable alternatives are solvent-based, the hazards associated with the incompatibilities of candidate cleaning agents must be correctly understood.

The thermodynamic and kinetic data presented in this report were compiled and evaluated in an effort to identify possible reactivity hazards associated with solvent cleaning and to place the concerns in proper perspective. Although the concepts and calculations are rudimentary, the correct interpretation and application of the results are essential for accurately assessing the risks posed by violent reactions between potential solvents and plutonium during cleaning.

PRIOR RISK ASSESSMENT FOR SOLVENT-BASED CLEANING

In an evaluation of centrifugal cleaning as a method for removing oil from plutonium chips, Walter correctly cites two concerns associated with solvent cleaning. These concerns originate because of differences in the properties of solvents. In one case, solvent-based "cleaning methods may be unsafe" because of the explosive potential of flammable solvent vapors in air. In the second case, concern is associated with the incompatibility between a solvent and an active metal like plutonium. Walter notes that "exothermic reaction with carbon dioxide may be a hazard." In conjunction with this point, enthalpy (heat of reaction) data are presented for the reaction of Pu with potential solvents. The chemical reactions and corresponding $\Delta H^\circ$ values presented by Walter are reproduced in Table I.

The implications of these enthalpy data are very significant. As indicated by the magnitude of $\Delta H^\circ$, the violence of the thermal hazard posed by CO$_2$ is five-fold greater than for
an ether and is infinitely more dangerous than that encountered with an unreactive solvent such as a paraffinic hydrocarbon, R. The risk associated with CO₂ is increased at supercritical conditions. Walter presents data showing that the heat of reaction is increased by 40 kcal/mol ($\Delta H^o = -198$ kcal/mol of Pu) when the CO₂ pressure is increased from the one atmosphere reference state to the critical pressure (72.9 atm). At high pressure, the enthalpy for reaction of CO₂ is a substantial fraction of that reported for reaction of carbon tetrachloride, a solvent that is known to react violently with plutonium.

The data in Table I suggest that solvents fall into two general hazard categories: (1) Certain solvents such as ethers and hydrocarbons do not react violently with plutonium, but have flammable vapors. (2) Others such as CO₂ and CC₄ are non-flammable, but react exothermically with plutonium. Carbon dioxide and carbon tetrachloride are stable and non-flammable because of the strong interactions of oxygen and chlorine with carbon. However, these oxidants have a stronger affinity for plutonium than for carbon and reactions of solvents containing oxygen and chlorine are highly exothermic.

EVALUATION OF THERMODYNAMIC PROPERTIES

Thermodynamic Data

Recalculation and reevaluation of thermodynamic properties for the reactions in Table I are merited. Pertinent reference data are given in Table II. For each set of reactions the most stable product configuration is determined for the case in which excess solvent is present relative to the quantity of available plutonium. An example of the impact that reactant quantities have on the equilibrium configuration of products is presented in the next section on the reaction of CO₂. In addition to standard enthalpy changes, values of the free energies of reaction are derived to define spontaneity. The resulting $\Delta H^o$ and $\Delta G^o$ values at 298 K are given in Table III. Results relevant to the four solvent-metal reactions in Table I are discussed in the following section.
Enthalpies and Free Energies of Reaction

The Reaction of CO$_2$. As seen by comparing $\Delta H^\circ$ values in Tables I and III, the results presented by Walter$^1$ accurately define the thermal effect for the reaction of plutonium with carbon dioxide at one atmosphere pressure. Although CO$_2$ is an extremely stable molecule, reaction is driven by the greater stability of plutonium dioxide. The reaction is clearly spontaneous and the potential hazard posed by the heat product cannot be ignored.

As implied in the preceding discussion of risk, increasing the CO$_2$ pressure above one atmosphere should shift the equilibrium point of Equation 1 toward products and increase the heat of reaction. However, the 40 kcal/mol enthalpy change reported by Walter$^1$ for CO$_2$ at the critical pressure is inordinately large and is not reproduced by our calculation of pressure effects on thermodynamic properties of Equation 1. At constant temperature, the free energy for a reaction at non-standard conditions is defined by the standard state free energy, $\Delta G^\circ$, and by the equilibrium constant, $K$, as follows: $\Delta G = \Delta G^\circ + RT \ln K$. Since $K = 1/P(CO_2)$ and $\Delta G^\circ$ is constant at $-144.2$ kcal/mol over a limited temperature range, the $\Delta G$ derived for Equation 1 at the critical point ($T_C = 31.2^\circ$C, $P_C = 72.9$ atm) is $-146.8$ kcal/mol.

$\Delta H^\circ$ for Equation 1 at the critical point is derived using the Gibbs equation: $\Delta H = \Delta G + T \Delta S$. The difference between the enthalpy and free energy changes is defined by the temperature and the entropy change. As seen in Table III, $\Delta H^\circ$ is more negative than $\Delta G^\circ$ by 14.1 kcal/mol. This difference arises because $\Delta S^e$ is a negative quantity determined primarily by the decrease in entropy accompanying the conversion of gaseous CO$_2$ to solid products.

Calculation of the enthalpy change at a non-standard pressure depends on the availability of entropy data at the condition of interest. $\Delta S$ is the difference between the absolute entropies of products and reactants, and for Equation 1 is strongly dependent on $S$ for CO$_2$. Since the entropies of solids
are insensitive to pressure over the range of interest, $S^0$ values 
are applicable. However, the entropy of CO$_2$ is decreased by 
increasing the pressure and changes from 51.1 cal/K mol at one 
atmosphere to 34.7 cal/K mol at 72.9 atm. Consequently, the TAS  
term is -10.4 kcal/mol and $\Delta H$ is -156.9 kcal/mol at the critical 
pressure.

Since the operating conditions for SCF CO$_2$ are expected to 
lie in a region near 40°C and 200 atm, consideration should be  
given to the thermodynamic behavior of Equation 1 at 
substantially higher pressures. At these conditions, $\Delta G$ is 
-147.6 kcal/mol and $S$ for CO$_2$ 34.8 cal/K mol. The resulting $\Delta H$ 
value for Equation 1 is -157.2 kcal/mol.

We are unable to duplicate the heat of reaction derived by 
Walter\textsuperscript{1} for the reaction of plutonium with carbon dioxide at high 
pressure. Instead of increasing by 40 kcal/mol, the heat produced by the reaction at the critical point is slightly less 
than at 25°C and 1 atm pressure. The pressure-induced change in  
$\Delta G$ is offset by a decrease in $S$ for CO$_2$.

The impact of reactant quantities on the equilibrium point 
is demonstrated by Equations 1 and 2. As shown by data in Table 
II, Pu$_2$C$_3$ is a stable phase in the Pu-C system. However, the 
carbide appears as an equilibrium product (Equation 2) only if 
the molar ratio of CO$_2$:Pu is less than one. In this case, 
unreacted Pu combines with carbon after all oxygen is bound as 
oxide. If Pu$_2$C$_3$ forms in the presence of excess CO$_2$, its 
existence is transient and the phase oxidizes to an equilibrium 
mixture of plutonium oxide and carbon.

The Reaction of CCl$_4$. Different equations are presented for 
the reactions of Pu with CCl$_4$ in Tables I and III. According to 
Walter,\textsuperscript{1} PuCl$_4$ forms by a reaction that is almost twice as 
exothermic as that for CO$_2$. Although the source of these data 
are unknown, they are inconsistent with the thermodynamic 
properties described for the Pu-Cl system in a recent review by 
Fuger et al.\textsuperscript{4} The $\Delta H^0$ value of -230.3 kcal/mol reported by these 
authors for PuCl$_4$(s) is consistent with unsuccessful attempts to 
prepare condensed tetrachloride. By combining their enthalpy
value for PuCl$_4$ with enthalpy and entropy data for PuCl$_3$(s), CCl$_4$(l) and Cl$_2$(g)$^{4,5}$ and with an estimated $S^\circ$ of 45.7 cal/K mol derived for PuCl$_4$(s) using Latimer's method,$^9$ a $\Delta G^\circ$ value of -4.9 kcal/mol is obtained for disproportionation of tetrachloride into trichloride and chlorine at 25°C. The formation of PuCl$_3$ is expected as described by Equation 3.

Although the heat of reaction for Pu+CCl$_4$ is substantially less than stated in Table I, the molar heat product is large. Similar thermal excursions are possible in all plutonium operations employing halocarbons such as trichloroethane and freons.

The Reaction of Ethers. The $\Delta H^\circ$ and $\Delta G^\circ$ values for reactions of plutonium with dimethyl ether and diethyl ether are presented in Table III, Equations 4 and 5, respectively. The heats of reaction are near -200 kcal/mol and stand in sharp disagreement with the $\Delta H^\circ$ value of -30 kcal/mol presented by Walter$^1$ for reaction of a generic ether, ROR. The enthalpy is determined by the stability of PuO$_2$ and is comparable to that for reaction of CCl$_4$.

All oxygen-containing organic compounds, including ethers, have the potential for violent exothermic reaction with plutonium. The heats of reaction exceed that for SCF CO$_2$. For example, $\Delta H^\circ$ and $\Delta G^\circ$ for the reaction of n-amyl alcohol to form PuO$_2$ and n-pentane are -163.0 and -164.7 kcal/mol, respectively. Such results suggest that oxygenated organic solvents present a two-fold hazard, the potential for forming flammable or explosive mixtures in air and the potential for violent exothermic reaction when placed in contact with plutonium.

The Reaction of Paraffinic Hydrocarbons. According to the data presented in Table I, hydrocarbons do not react with plutonium.$^1$ This implies that their use as cleaning solvents poses no thermal hazard. The basis for this information is not known, because it stands in obvious conflict with the need for a cleaning process to remove oils and other organic residues from plutonium. Removal of such materials from metal surfaces is
necessary prior to storage in order to prevent spontaneous corrosion reactions of the type described by Equations 6 and 7. In addition to consuming metal, these reactions create an additional hazard by forming pyrophoric plutonium hydride.

As shown by the $\Delta H^0$ values for Equations 6 and 7, the heats of reaction for hydrocarbons are modest and more than a factor of five less than those for oxygenated or chlorinated solvents. The apparent thermal hazard appears to be much less than for other solvents, but kinetic factors must be considered.

EVALUATION OF KINETIC PROPERTIES

Consideration of $\Delta G$ and $\Delta H$ is essential for determining if a reaction is spontaneous and for defining the heat it generates, but thermodynamic properties are insufficient for determining if a thermal hazard exists. A hazardous situation occurs only when the rate of reaction (rate of heat production) is such that unacceptable temperature excursions are encountered. Unfortunately, the kinetic behavior of many plutonium reactions is undefined and the rates of so-called "known" reactions are often poorly characterized. A consideration of kinetic factors follows.

Kinetic Observations

Rate-Spontaneity Independence. As implied by the preceding discussion, kinetic and thermodynamic properties of a reaction are not correlated. Although a negative $\Delta G$ is required for reaction, the rate is not determined by $\Delta G$ or $\Delta H$. For example the heat of oxidation of aluminum is -200.3 kcal/mol of Al, but this metal is routinely handled in air and used in numerous applications at elevated temperatures.

The independence of kinetic and thermodynamic properties is shown by the rates for hydriding and oxidizing plutonium according to Equations 8 and 9. The -238.5 kcal/mol free energy for forming PuO$_2$ is almost eight times more negative than the
-31.1 kcal/mol \( \Delta G^0 \) for hydriding, but kinetic properties do not reflect a similar relationship. The oxidation rate of delta-phase Pu by \( O_2 \) at 0.67 atm and room temperature is obtained by extrapolating Arrhenius data\(^{10}\) below the 150°C limit of the experimental range. The estimated rate at 25°C is 30 nmol \( O_2/cm^2/hr \). Kinetic results for the hydriding reaction of delta-phase metal at 25°C and 1 atm \( H_2 \) pressure\(^{11}\) show a rate of 60 mmol \( H_2/cm^2/hr \). Although hydriding is thermodynamically less favorable than oxidation, the reaction rate of \( H_2 \) exceeds that of \( O_2 \) by a factor of 10\(^6\). As with Al, the rate of Pu oxidation is controlled by diffusion of oxygen through an adherent oxide layer formed on the metal surface. In practice, the highly exothermic oxidation reaction presents a minor thermal hazard compared to hydriding.

Although rate data are not available for oxidation of plutonium by carbon dioxide, kinetic experiments reported for the reaction of Pu-Zr alloys with \( CO_2 \) at elevated temperatures\(^{12}\) provide essential data for estimating the behavior at conditions of interest. Combination of Arrhenius results for the 40%Pu-60%Zr alloy with the trend established by lower-composition alloys at 600°C leads to an estimate of kinetic behavior for Equation 1. At 500°C, the rate (90 \( \mu \)mol \( CO_2/cm^2/hr \)) is less than that for \( O_2 \)\(^{10}\) by a factor of 300. Extrapolation to room temperature suggests that the rate of \( CO_2 \) reaction with Pu is immeasurably small (<< 1 pmol/cm\(^2\)hr). Since the ignition of plutonium in \( O_2 \) is only observed at temperatures above 400°C\(^{10}\) self-sustained reaction of \( CO_2 \) is not anticipated unless very high temperatures are reached.

The predicted kinetic behavior for Equation 1 is consistent with results of recent compatibility tests conducted by the authors. Oxide was burnished from the surfaces of gram-sized samples of delta-phase plutonium foil (3 cm\(^2\) area) and the metal was exposed to flowing SCF \( CO_2 \) at pressures up to 300 atm and temperatures up to 100°C. After one-hour exposures, sample masses were unchanged and the surfaces were visually indistinguishable from the freshly burnished condition.
An incident involving reaction of \( \text{CCl}_4 \) according to Equation 3 is cited as an example of the extreme hazard associated with the use of chlorocarbon solvents for cleaning plutonium. The situation must be understood from a kinetic perspective. A violent reaction caused physical injury to a glovebox worker after a sample of burning plutonium chips was accidentally dropped into a bath of \( \text{CCl}_4 \). Violent reaction occurred because the rate of the Pu-\( \text{CCl}_4 \) reaction is temperature dependent and was accelerated to a self-sustaining condition by the burning metal. As evidenced by many years of use as a solvent for plutonium cleaning, the reaction of \( \text{CCl}_4 \) is kinetically controlled and unobserved at room temperature.

**Catalysis.** The rates of many reactions are enhanced by catalytic substances. According to the classical definition, a catalyst increases the reaction rate without being consumed during the over-all process. Catalytic substances provide an alternate pathway to the equilibrium state, but extensive knowledge of the reaction mechanism is usually required before insight can be gained into how the catalyst works. The empirical kinetic data available for most reactions do not permit catalysts to be identified or predicted.

Catalysts are known for only a limited number of reactions of interest. The reaction of water, an alternative nonflammable solvent being evaluated for plutonium cleaning, is catalyzed by acids and by dissolved inorganic salts. The corrosion reaction is enhanced by cations that hydrolyze to form \( \text{H}^+ \) and by anions that apparently promote the electron transfer step of the redox process. This knowledge is useful in selecting conditions and detergents that are noncorrosive.

The reaction of \( \text{CCl}_4 \) to form \( \text{PuCl}_3 \) is sharply accelerated by the presence of alcohols and other protonic species in the solvent. Since the alcohol is consumed by a reaction that produces plutonium alkoxide in addition to the trichloride, it does not conform to the classical definition of catalysis. However, the altered reaction presents a thermal hazard equal to Equation 3 and poses a greater hazard because of the rate. A
small amount of methanol in the solvent might seem insignificant, but the heat produced by the altered reaction could initiate the direct chlorination process. Inadvertent contamination of a process by a catalytic substance can only be precluded by extensive compatibility testing and stringent control of solvent quality and process operation.

A final example of catalysis is provided by effects induced by radioactive decay of plutonium. The reactions of hydrocarbons to form plutonium hydride are enhanced by interaction of alpha particles with surface residues of these compounds. Hydrogen gas produced by radiolysis reacts with plutonium via the facile hydriding reaction described in the preceding section. Radiolytic formation of dissociation products is an inherent property of solvent-based processes for cleaning plutonium, but the decay rate of the 239 isotope is too slow to create a credible hazard during the time period of cleaning.

Other Kinetic Considerations

As mentioned in the preceding discussion, an exothermic reaction presents a thermal hazard only when the accompanying temperature increase is unacceptable. An assessment of the risk cannot be made on the basis of a single parameter such as the $AH$ for reaction or the rate of reaction. These parameters are essential, but other factors must be considered as part of a credible risk assessment. Since the possibility always exists for an unanticipated occurrence of a spontaneous reaction, consideration should be given to factors that can mitigate a thermal excursion.

In addition to the rate of heat production, the thermal change depends on the total quantity of heat produced and the rate at which heat is lost to the surroundings. Minimization of the amount of metal and/or solvent available for reaction is an important consideration of equipment design and process operation. The rate of heat production is countered by the rate of loss. Equipment design should attempt to maximize heat capacity and heat dissipation.
The importance of considering other factors is demonstrated by efforts to ignite samples of plutonium metal in air. Since kinetic studies show that self-sustained oxidation occurs at temperatures below 500°C, one would expect plutonium metal to readily ignite when heated by an arc welding unit. However, difficulties were encountered in igniting a 1.8 kg test sample even when it was placed on a block of asbestos insulation. Although the authors attribute this behavior to the large mass of metal, other factors are undoubtedly involved.

The impetus for considering design features and process operation is not to accommodate a cleaning procedure with marginal safety, but to reduce the severity of an unanticipated incident. Any solvent that reacts at a rate sufficient to produce an observable temperature excursion is far too corrosive for cleaning applications.

CONCLUSIONS

As stated in the introduction, the objective of this report is to place thermodynamic and kinetic information in the perspective necessary for properly assessing the thermal risks associated with solvent-based cleaning processes for plutonium. Our reevaluation of thermodynamic properties shows that all solvents with credible potential for replacing chlorocarbons react spontaneously and exothermically with plutonium. The potential for reaction is unavoidable. The risk of a violent thermal excursion can only be determined from experimental kinetic information for the reaction.

The multiplicity of needs associated with risk assessments for cleaning technologies are placed in better perspective. Decisions based on single properties are clearly inadequate and imprudent. Collection of pertinent experimental data is imperative. The compatibility of materials must be established over a range bracketing the conditions of operation, and if possible, kinetic data should be collected. The advisability of pursuing solventless cleaning technologies is evident. In
addition to the centrifugal method proposed by ter, other technologies such as the use of oxygen-rich plasmas should be investigated. Complete definition of alternative methods is essential. Each technology must be assessed with regard to cleaning efficiency, environmental health and safety, waste minimization, effect on the reactivity and properties of the metal surface, and suitability for use in a production operation. The most important need is to evaluate the alternatives with objectivity on the basis of sound technical data.
REFERENCES


Table I. Enthalpy Values Presented for Potentially Hazardous Reactions Between Plutonium Metal and Selected Cleaning Solvents in Reference 1.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^\circ ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 + \text{Pu} ) = ( \text{PuO}_2 + \text{C} )</td>
<td>-158</td>
</tr>
<tr>
<td>( \text{CCl}_4 + \text{Pu} ) = ( \text{PuCl}_4 + \text{C} )</td>
<td>-298</td>
</tr>
<tr>
<td>( 2\text{ROR} + \text{Pu} ) = ( \text{PuO}_2 + 2\text{R}-\text{R} )</td>
<td>-33</td>
</tr>
<tr>
<td>( \text{R} + \text{Pu} ) = No Reaction</td>
<td>--</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \( \text{R} \) = paraffinic hydrocarbon molecule or moiety.
Table II. Standard-State Enthalpies and Free Energies of Formation for Selected Solvents and Compounds of Plutonium at 25°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^0_f(298)$ (kcal/mol)</th>
<th>$\Delta G^0_f(298)$ (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO$_2$(s)</td>
<td>252.4</td>
<td>238.5</td>
<td>3</td>
</tr>
<tr>
<td>PuCl$_3$(s)</td>
<td>229.4</td>
<td>213.4</td>
<td>4</td>
</tr>
<tr>
<td>PuH$_2$(s)</td>
<td>39.2</td>
<td>31.1</td>
<td>3</td>
</tr>
<tr>
<td>Pu$_2$C$_3$(s)</td>
<td>35.7</td>
<td>37.2</td>
<td>3</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>94.1</td>
<td>94.3</td>
<td>5</td>
</tr>
<tr>
<td>CCl$_4$(l)</td>
<td>22.9</td>
<td>12.8</td>
<td>5</td>
</tr>
<tr>
<td>(CH$_3$)$_2$O(g)</td>
<td>44.3</td>
<td>27.3</td>
<td>6</td>
</tr>
<tr>
<td>(CH$_3$CH$_2$)$_2$O(l)</td>
<td>65.2</td>
<td>27.7</td>
<td>6</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>17.9</td>
<td>12.1</td>
<td>6</td>
</tr>
<tr>
<td>C$_2$H$_6$(g)</td>
<td>20.2</td>
<td>7.9</td>
<td>6</td>
</tr>
<tr>
<td>n-C$_4$H$_6$(g)</td>
<td>29.8</td>
<td>3.8</td>
<td>6</td>
</tr>
<tr>
<td>n-C$<em>{10}$H$</em>{22}$(l)</td>
<td>59.7</td>
<td>-8.2</td>
<td>6</td>
</tr>
</tbody>
</table>
Table III. Calculated Enthalpy and Free Energy Changes for Thermodynamically Favorable Reactions of Plutonium with Selected Cleaning Solvents.

<table>
<thead>
<tr>
<th>Eqn.</th>
<th>Reaction</th>
<th>$\Delta H^\circ(298)$ (kcal/mol of Pu)</th>
<th>$\Delta G^\circ(298)$ (kcal/mol of Pu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pu(s) + CO$_2$(g) $\rightarrow$ PuO$_2$(s) + C(s)</td>
<td>-168.1</td>
<td>-144.2</td>
</tr>
<tr>
<td>2.</td>
<td>Pu(s) + 3/5 CO$_2$(g) $\rightarrow$ 3/5 PuO$_2$(s) + 1/5 Pu$_2$C$_3$(s)</td>
<td>-112.1</td>
<td>-94.5</td>
</tr>
<tr>
<td>3.</td>
<td>Pu(s) + 3/4 CCl$_4$(l) $\rightarrow$ PuCl$_3$(s) + 3/4 C (s)</td>
<td>-214.2</td>
<td>-204.8</td>
</tr>
<tr>
<td>4.</td>
<td>Pu(s) + 2(CH$_3$)$_2$O(g) $\rightarrow$ PuO$_2$(s) + 2 C$_2$H$_6$(g)</td>
<td>-204.2</td>
<td>99.7</td>
</tr>
<tr>
<td>5.</td>
<td>Pu(s) + 2(CH$_3$CH$_2$)$_2$O(l) $\rightarrow$ PuO$_2$(s) + 2 n-C$<em>4$H$</em>{10}$(g)</td>
<td>-181.6</td>
<td>-191.5</td>
</tr>
<tr>
<td>6.</td>
<td>Pu(s) + 1/2 CH$_4$(g) $\rightarrow$ PuH$_2$(s) + 1/2 C(s)</td>
<td>-10.3</td>
<td>25.1</td>
</tr>
<tr>
<td>7.</td>
<td>Pu(s) + 1/11 n-C$<em>{10}$H$</em>{22}$(l) $\rightarrow$ PuH$_2$(s) + 10/11 C(s)</td>
<td>-4.8</td>
<td>-31.3</td>
</tr>
<tr>
<td>8.</td>
<td>Pu(s) + H$_2$(g) $\rightarrow$ PuH$_2$(s)</td>
<td>-39.7</td>
<td>-41.1</td>
</tr>
<tr>
<td>9.</td>
<td>Pu(s) + O$_2$(g) $\rightarrow$ PuO$_2$(s)</td>
<td>-212.4</td>
<td>-198.5</td>
</tr>
</tbody>
</table>