Alternative Solvents for Cleaning Plutonium:
Thermodynamic and Kinetic Considerations

Prepared by Lydia Gonzales, Group NMT-5

An Affirmative Action/Equal Opportunity Employer

Alternative Solvents for Cleaning Plutonium: Thermodynamic and Kinetic Considerations

John M. Haschke

Stephanie J. Hale*

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

MASTER

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 ΔH 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

turnings. Carbon tetrachloride and 111-trichloroethane (TCA) are currently employed as cleaning solvents during manufacturing operations at Rocky Flats, but continued chlorccarbon 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[1] 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 ΔH° values presented by Walter are reproduced in Table I.

The implications of these enthalpy data are very significant. As indicated by the magnitude of ΔH°, 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 CO_2 is increased at supercritical conditions. Walter presents data showing that the heat of reaction is increased by 40 kcal/mol ($\Delta H° = -198$ kcal/mol of Pu) when the CO_2 pressure is increased from the one atmosphere reference state to the critical pressure (72.9 atm). At high pressure, the enthalpy for reaction of CO_2 is a substantial fraction of that reported for reaction of carbon tetrachloride, a solvent that is known to react violently with plutonium.[2]

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 CO_2 and CCl_4 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.[3-6] 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 CO_2. In addition to standard enthalpy changes, values of the free energies of reaction are derived to define spontaneity. The resulting $\Delta H°$ and $\Delta G°$ 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 $\Delta H°$ 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,
$\Delta G°$, and by the equilibrium constant, K, as follows: $\Delta G = \Delta G°$
$+RTlnK$. Since $K = 1/P(CO_2)$ and $\Delta G°$ is constant at -144.2
kcal/mol over a limited temperature range, the ΔG derived for
Equation 1 at the critical point ($T_c = 31.2°C$, $P_c = 72.9$ atm) is
-146.8 kcal/mol.

$\Delta H°$ 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, $\Delta H°$ is more
negative than $\Delta G°$ by 14.1 kcal/mol. This difference arises
because $\Delta S°$ 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. ΔS 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^o values are applicable.[3,5] 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.[7] Consequently, the $T\Delta S$ term is -10.4 kcal/mol and ΔH 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,[8] consideration should be given to the thermodynamic behavior of Equation 1 at substantially higher pressures. At these conditions, ΔG is -147.6 kcal/mol and S for CO_2 34.8 cal/K mol. The resulting ΔH value for Equation 1 is -157.2 kcal/mol.

We are unable to duplicate the heat of reaction derived by Walter[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 ΔG 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_2C_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_2C_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,[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.[4] The ΔH^o 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 $S°$ of 45.7 cal/K mol derived for $PuCl_4(s)$ using Latimer's method,[9] a $\Delta G°$ 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 $\Delta H°$ and $\Delta G°$ 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 $\Delta H°$ 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, $\Delta H°$ and $\Delta G°$ 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 ΔH° 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 ΔG and ΔH 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 ΔG is required for reaction, the rate is not determined by ΔG or ΔH. 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 ΔG° 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^2hr. 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^2hr. 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 μmol CO_2/cm^2hr) 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 ($\ll$ 1 pmol/cm^2hr). 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[2] involving reaction of 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 CCl_4. Violent reaction occurred because the rate of the $Pu+CCl_4$ 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 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,[4] an alternative nonflammable solvent being evaluated for plutonium cleaning, is catalyzed by acids and by dissolved inorganic salts.[13] The corrosion reaction is enhanced by cations that hydrolyze to form 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 CCl_4 to form $PuCl_3$ is sharply accelerated by the presence of alcohols and other protonic species in the solvent.[14] 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 ΔH 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 and 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.[15] Since kinetic studies show that self-sustained oxidation occurs at temperatures below 500°C,[10] 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,[1] 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

1.   S. W. Walter, "Centrifuge for Plutonium Chip Cleaning," in
      Waste Minimization Program Review, EG&G Rocky Flats, June
      12-13, 1991, pp. 229-238.

2.   S. A. Putzier, USAEC Report RFP-621, Dow Chemical Company,
      Rocky Flats Division, Golden, CO,   1965, p. 9.

3.   L. R. Morss, in The Chemistry of the Actinide Elements, Vol.
      2, Ch. 17, J. J. Katz, G. T. Seaborg, and L. R. Morss, eds.,
      Chapman and Hall, New York, 1986.

4.   J. Fuger, V. B. Parker, W. N. Hubbard, and F. L. Oetting, in
      The Chemical Thermodynamics of Actinide Elements and
      Compounds: Part 8, F. L. Oetting, ed., International Atomic
      Energy Agency, Vienna, 1983.

5.   JANAF Thermochemical Tables, NSRDS-NBS 37, National Bureau
      of Standards, Washington, 1971.

6.   D. F. Rossi, K. F. Pitzer, R. L. Arnett, h. M. Braun and G.
      C. Pimentel, Selected Values of Physical and Thermodynamic
      Properties of Hydrocarbons and Related Compounds, Carnegie
      Press, Pittsburgh, 1953.

7.   Thermodynamic Functions of Gases, Vol. 1, Butterworth,
      London, 1956.

8.   K. M. Motyl, USDOE Report RFP-4150, Rockwell International,
      Rocky Flats Plant, Golden, CO, 1988.

9.   W. M. Latimer, Oxidation Potentials, 2nd ed., Prentice Hall,
      Englewood Cliffs, NJ, 1952.

10.   J. Stakebake and L. L. Lewis, J. Less-Common Met., 136, 349
      (1988).

11.   J. Ogden, C. Alexander, C. Colmenares and R. Stone, USDOE
      Report UCRL 84307, Lawrence Livermore Laboratory, Livermore,
      CA, 1980.

12.   J. T. Waber, "Corrosion and Oxidation" in Plutonium
      Handbook, O. J. Wick, ed., Vol. 1, Chapter 6, American
      Nuclear Society, LaGrange Park, IL, 1980.

13. J. M. Haschke, A. E. Hodges, III, G. E. Bixby and R. L. Lucas, USDOE Report RFP-3416, Rockwell International, Rocky Flats Plant, Golden, CO, 1983.

14. L. R. Crisler, USDOE Report RFP-2181, Dow Chemical Company, Rocky Flats Division, Golden, CO, 1974.

15. J. Mishima, USAEC Report BNWL:-357, Battelle Northwest, Pacific Northwest Laboratory, Richland, WA, 1966.

Table I. Enthalpy Values Presented for Potentially Hazardous
Reactions Between Plutonium Metal and Selected Cleaning
Solvents in Reference 1.[a]

Reaction			ΔH°(kcal/mol)
CO_2 + Pu	=	PuO_2 + C	-158
CCl_4 + Pu	=	$PuCl_4$ + C	-298
2ROR + Pu	=	PuO_2 + 2R-R	-30
R + Pu	=	No Reaction	--

a. 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.

Compound	$-\Delta H^{\circ}_f(298)$ (kcal/mol)	$-\Delta G^{\circ}_f(298)$ (kcal/mol)	Ref.
$PuO_2(s)$	252.4	238.5	3
$PuCl_3(s)$	229.4	213.4	4
$PuH_2(s)$	39.2	31.1	3
$Pu_2C_3(s)$	35.7	37.2	3
$CO_2(g)$	94.1	94.3	5
$CCl_4(l)$	22.9	12.8	5
$(CH_3)_2O(g)$	44.3	27.3	6
$(CH_3CH_2)_2O(l)$	65.2	27.7	6
$CH_4(g$	17.9	12.1	6
$C_2H_6(g)$	20.2	7.9	6
$n-C_4H_6(g)$	29.8	3.8	6
$n-C_{10}H_{22}(l)$	59.7	-8.2	6

Table III. Calculated Enthalpy and Free Energy Changes for Thermodynamically Favorable Reactions of Plutonium with Selected Cleaning Solvents.

Eqn.	Reaction	$\Delta H^\circ (298)$ (kcal/mol of Pu)	$\Delta G^\circ (298)$ (kcal/mol of Pu)
1.	$Pu(s) + CO_2(g) \rightarrow PuO_2(s) + C(s)$	-158.3	-144.2
2.	$Pu(s) + 3/5\ CO_2(g) = 3/5\ PuO_2(s) + 1/5 Pu_2C_3(s)$	-112.1	-94.5
3.	$Pu(s) + 3/4\ CCl_4(l) = PuCl_3(s) + 3/4\ C\ (s)$	-213.2	-203.8
4.	$Pu(s) + 2(CH_3)_2O(g) \rightarrow PuO_2(s) + 2\ C_2H_6(g)$	-204.2	99.7
5.	$Pu(s) + 2(CH_3CH_2)_2O(l) = PuO_2(s) + 2\ n\text{-}C_4H_{10}(g)$	-181.6	-140.5
6.	$Pu(s) + 1/2\ CH_4(g) = PuH_2(s) + 1/2\ C(s)$	-30.3	25.1
7.	$Pu(s) + 1/11\ n\text{-}C_{10}H_{22}(l) = PuH_2(s) + 10/11\ C(s)$	-4.8	-31.8
8.	$Pu(s) + H_2(g) = PuH_2(s)$	-39.2	31.1
9.	$Pu(s) + O_2(g) = PuO_2(s)$	-252.4	-238.5