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Vaporization of Actinide Oxides in Thermal Treatment Processes for Mixed Waste

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Vaporization of Actinide Oxides in Thermal Treatment Processes for Mixed Waste[*]

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Abstract

The purpose of this study is to evaluate the volatilities of U, Pu, and Am in thermal treatment processes for mixed wastes. The thermodynamics of vaporization of U and Pu oxides in the presence of oxygen and water vapor and of U oxide in the presence of oxygen and chlorine were studied. Experimental studies of U oxide volatilities by previous authors have also been reviewed. For species where data are unavailable estimation methods were used to obtain free energies of formation of the gaseous species. The data are applied to thermal treatment processes in general and then more specifically to conditions representative of the Rocky Flats Plant Fluidized Bed Unit (RFP FBU), a molten salt oxidizer, and an incinerator. U volatilities are greatest ranging from 2.67×10^{-7} gU/h in the RFP FBU to 4.00 gU/h for typical incinerator conditions. Pu volatilities are almost 5 orders of magnitude less than U and Am volatilities are about 3 orders of magnitude less than Pu.

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Introduction

Federal land disposal restrictions allow radioactive wastes to be disposed of in geologic repositories. Although no repository is currently available for high-level wastes (HLW) or transuranic (TRU) wastes, they are expected to be available in the not too distant future. Wastes which contain hazardous organics as well as radioactive materials are designated as mixed waste and cannot be disposed of directly because any sort of geologic disposal for hazardous organics is not permitted. These wastes must first be treated to destroy or remove the hazardous organics. If the organic constituents are designated as having characteristic hazards, the mixed waste can be converted to a radioactive only waste by just removing the characteristic hazards. Normally this would be achieved by incineration of the waste. If the organics in the waste are designated as listed wastes, then the procedure would be a little more complicated. After treatment by incineration, an exemption for geologic disposal would be required before the waste could be disposed of as a radioactive only waste.

Public concern that incinerators are inherently unsafe has forced the DOE laboratories to terminate operation indefinitely of almost all of their radioactive and mixed waste incinerators. In response to both real and perceived safety concerns, the DOE is currently looking for acceptable alternatives to treat organic-based mixed waste. In the meantime, the combination of federal land disposal restrictions along with a lack of treatment facilities for organic-based mixed waste has created a major problem for the DOE laboratories which must store all their mixed wastes on site indefinitely. The proposed alternative-to-incineration technologies include molten salt oxidation, supercritical water oxidation, mediated electrochemical oxidation, plasma arc processing, and ChemChar processing. Although each process offers some specific advantages, incineration remains an acceptable candidate if the various real and perceived safety concerns can be addressed. With the exception of the mediated electrochemical oxidation method, the proposed alternatives are thermal treatment technologies which generate off-gases.

The primary safety concern for any mixed waste thermal treatment process is the possibility that radionuclides and to a lesser extent heavy metals could be emitted to the atmosphere in the off-gas stream. For any thermal treatment technology, there are at least two sources of radioactive and heavy metal emissions in the off-gas, volatilization and entrainment (e.g. flyash). Radionuclides and heavy metals which vaporize in the thermal treatment process condense as aerosols or on fine particulates in the off-gas. Generally, the off-gas particles containing volatile material condensate are less than 1 μm in diameter. Much of the non-volatile flyash, however, is greater than 1 μm in diameter.

Any process which emits off-gases will have an off-gas air pollution control system to remove particulates. Typically this would include a series of air pollution control devices. The most efficient device for removing fine particulates from the off-gas is the high-efficiency particle air (HEPA) filter. HEPA filters are normally used in the final stage of off-gas treatment. Although these filters have collection efficiencies greater than 99.999% for most particulate sizes, there is a window of least efficiency for particulates less than 1 μm in diameter but greater than about 0.1 μm in diameter. In this size range, the HEPA filter may only be 99.97% efficient. Other types of off-gas filters have greater windows of inefficiency in about the same range of particle sizes. As a result, volatiles which condense as particulates in this size range are much harder to capture in an air pollution control device than entrained material. Thus, an accurate assessment of the off-gas emissions of a particular treatment technology must rely on accurate volatility data for the radioactive and hazardous materials in the treatment process. With the exception of uranium, no volatility data were available until recently for actinide vapor species that would be important in thermal oxidation treatment processes.

This paper reviews actinide volatility work performed at LLNL and by other workers, expands the data by making estimates, and applies the data to conditions representative of several thermal treatment processes. Most of the volatility work at LLNL was done in support of the Rocky Flats Plant Fluidized Bed Unit (RFP FBU). However, some of the work was supported by defense programs for other thermal treatment processes that may be used to treat organic-based mixed waste. Primarily this included molten salt oxidation and incineration.

Background

In each of the above thermal treatment processes, RFP FBU, molten salt oxidizer, and incinerator, the environment is oxidizing enough that U, Pu, and Am vapors are expected to be present primarily in their highest oxidation states. For U this is the +6 oxidation state and for Pu and Am this is also expected to be the +6 oxidation state but could be a lower oxidation state such as the +4 state depending upon relative stabilities of the vapor species and on processing conditions. For U a considerable amount of data is already available. A number of authors have reported thermodynamic data for $UO_3(g)$ [1-4] and $UO_2F_2(g)$ [5-7] and data for these species are well established. Dhardwadkar, et al. have reported data for $UO_2(OH)_2(g)$ [2] and Cordfunke and Prins have reported data for $UO_2Cl_2(g)$ [8].

Data for $UO_2(OH)_2(g)$ were obtained [2] using the transpiration method by reacting $U_3O_8(s)$ with water vapor and oxygen according to the reaction

$$1/3\ U_3O_8(s) + 1/6\ O_2(g) + H_2O(g) = UO_2(OH)_2(g). \quad (1)$$

Because the water vapor pressures used were very low, <0.1 atm, and because $UO_3(g)$ is also an important vapor species, the data obtained by Dhardwadkar, et al. are very uncertain.

Data for $UO_2Cl_2(g)$ were also obtained [8] by the transpiration method by reacting $U_3O_8(s)$ with chlorine and oxygen according to the reaction

$$1/3\ U_3O_8(s) + Cl_2(g) = UO_2Cl_2(g) + 2/3\ O_2(g). \quad (2)$$

Because the vapor pressures of chlorine and oxygen were not varied, the assumed formula for the vapor species could not be confirmed. Additional data for both $UO_2(OH)_2(g)$ and $UO_2Cl_2(g)$ have been obtained in our laboratories using the transpiration technique.

No data are available for mixed vapor species of U, i.e. $UO_2ClOH(g)$, $UO_2FOH(g)$, and $UO_2FCl(g)$, and no data are available for any of the possible +6 vapor species of Pu and Am. Data for $PuO_3(g)$ and $PuO_2(OH)_2(g)$ have been obtained in our laboratories using the transpiration technique. Very limited data for Am species have also been obtained. Data for $PuO_2Cl_2(g)$ and $PuO_2F_2(g)$ were estimated from bond energy correlations relating hydroxide, fluoride, and chloride bond energies in the U species to those in the Pu species. Data for all the mixed species were estimated form their counterpart species and their symmetries.

Approach

To measure volatilities of the oxides of U, Pu, and Am the transpiration method was used [9]. In the transpiration method, a known amount of carrier gas is slowly passed over a solid or liquid such that the vaporized material is entrained in the gas flow, carried out of the system, and deposited in a cooler region on a collection device. The carrier gas can contain reactive gasses which react with the solid or liquid to enhance its volatility. In these experiments, oxygen, water vapor, and chlorine were used as reactive gases. The amount of the collected material can be determined either by quantitative chemical analysis or by weight gain if the amount collected is sufficiently large. From the carrier gas flow rate, duration of experiment, and amount of volatilized material, a vapor pressure is then calculated.

A schematic diagram for the transpiration apparatuses used in the U and Pu oxide volatility experiments in the presence of oxygen and water vapor is shown in Figure 1. In these experiments, mixtures of argon and oxygen were passed through a water bath held at temperatures ranging from 45 to 95°C. This controlled the water vapor pressure. The gasses were flowed over the actinide oxide sample and vaporized species were deposited on a quartz collection tube downstream in the furnace. The water vapor exiting the system was collected in a Drierite ($CaSO_4$) cartridge. Heating tape was used between the water saturator and furnace and between the furnace and Drierite cartridge in order to keep the water vapor from condensing. Total moles of water passed during the experiment were determined from the weight gain of the cartridge during the experiment, and the total moles of argon and oxygen were determined from the flow rates and duration of the experiment. The apparatus for U oxide volatility experiments in the presence of oxygen and chlorine was very similar to that used for the U and Pu oxide volatility experiments in the presence of oxygen and water vapor. The primary differences were that the water bath, Drierite cartridge, and heating tapes were removed and the chlorine gas was collected in a solution of $Na_2S_2O_4$ to which a few drops of KI were added.

Discussion of Volatility Data

The molecular formulas for the volatile species in several cases were determined by applying the law of mass action. As series of experiments were conducted at constant temperature where the partial pressures of the reactive gasses were varied from experiment to experiment. For the plutonium oxide volatility experiments in the presence of oxygen and water vapor, p(Pu total) divided by $p(O_2)$ to the 1/2 power is plotted as a function of $p(H_2O)$ at 1475 K in Figure 2. The plot increases in a linear fashion with a slope about equal to 1 indicating that the oxyhydroxide vapor species is indeed $PuO_2(OH)_2(g)$. At $p(H_2O) = 0$ the plot shows some Pu still in the vapor. This is due either to an oxide of Pu or to dust carry over, but the consistency of the data and the precautions taken in the experiments suggest that the observed Pu carryover at $p(H_2O) = 0$ is not dust. Also, known thermodynamic data for $PuO_2(g)$ and $PuO(g)$ [10] indicate that the vapor species is neither $PuO(g)$ nor $PuO_2(g)$. In analogy with the U system, the species is taken to be $PuO_3(g)$, although theoretically some other unknown species may be possible.

For the uranium oxide volatility experiments in the presence of oxygen and chlorine, p(U total) times $p(O_2)^{2/3}$ is plotted as a function of $p(Cl_2)$ at 1175 K in Figure 3. The plot increases in a linear fashion with a slope about equal to 1 which confirms that $UO_2Cl_2(g)$ is the vapor species being formed. Similar plots were obtained for the uranium oxide volatility experiments in the presence of oxygen and water vapor which confirmed that $UO_2(OH)_2(g)$ and $UO_3(g)$ were the vapor species being formed. The data for $UO_3(g)$ agreed very well with previous authors [1,2]. However, the measured vapor pressures of $UO_2(OH)_2(g)$ were about two orders of magnitude lower than those measured by previous authors [2]. The experiments conducted by previous authors only used small amounts of water vapor. Therefore, the data for $UO_2(OH)_2(g)$ were very uncertain because the pressure of $UO_2(OH)_2(g)$ was small in comparison to the pressure of $UO_3(g)$. Outside of this observation, no explanation for the large discrepancy is apparent. The present authors being more confident in their work have rejected the previous work in this analysis. Further details of the PuO_2 and U_3O_8 volatility experiments and results are discussed elsewhere [11,12].

In order to treat the volatility data over a wide range of temperatures, accurate thermal functions were required for the gaseous actinide species. Entropies, free energy functions, and heat capacities were calculated by the molecular constant method using known and estimated molecular parameters. These parameters were estimated from known constants of actinide, chromium, molybdenum, and tungsten vapor species. The details of these calculations will be discussed in other publications. Free energy functions for the actinide species of interest are summarized in Table 1. Free energy functions for $U_3O_8(s)$ and $PuO_2(s)$ were taken from Cordfunke and Konings [10] and free energy functions for $O_2(g)$, $H_2O(g)$, $HCl(g)$, and $HF(g)$ were taken from Gurvich, et al. [14]. Treatment by the third law method of the volatility data from previous work [1,2,5-8] and from the present authors [11,12] yielded the $\Delta H_f^0(298)$ values summarized in Table 2.

Estimation Methods

For the plutonium vapor species, $PuO_2F_2(g)$ and $PuO_2Cl_2(g)$, no thermodynamic data are available. Enthalpies of formation for these vapor species were estimated from known bond energies in uranium and plutonium vapor species. Hydroxide, chloride, and fluoride bond energies in $UO_2(OH)_2(g)$, $UO_2Cl_2(g)$, and $UO_2F_2(g)$ and hydroxide bond energies in $PuO_2(OH)_2(g)$ are given as

$$UO_2(OH)_2(g) = UO_2(g) + 2\ OH(g) \qquad \Delta H_r^0(298) = 813.3 \pm 11.4\ \text{kJ/mol} \qquad (3)$$

$$UO_2Cl_2(g) = UO_2(g) + 2\ Cl(g) \qquad \Delta H_r^0(298) = 775.9 \pm 5.5\ \text{kJ/mol} \qquad (4)$$

$$UO_2F_2(g) = UO_2(g) + 2\ F(g) \qquad \Delta H_r^0(298) = 1061.7 \pm 5.8\ \text{kJ/mol} \qquad (5)$$

and

$$PuO_2(OH)_2(g) = PuO_2(g) + 2\ OH(g) \qquad \Delta H_r^0(298) = 706.7 \pm 13.1\ \text{kJ/mol.} \qquad (6)$$

Assuming that the ratio of the chloride to hydroxide and fluoride to hydroxide bond energies are the same for U species as for Pu species, the bond energies in $PuO_2Cl_2(g)$ and $PuO_2F_2(g)$ are given as

$$PuO_2Cl_2(g) = PuO_2(g) + 2\ Cl(g) \qquad \Delta H_r^0(298) = 675.1\ \text{kJ/mol} \qquad (7)$$

and

$$PuO_2F_2(g) = PuO_2(g) + 2\ F(g) \qquad \Delta H_r^0(298) = 923.6\ \text{kJ/mol.} \qquad (8)$$

From these bond energies, $\Delta H_f^0(298)$ values for $PuO_2Cl_2(g)$ and $PuO_2F_2(g)$ were calculated and are given in Table 2. The $\Delta H_f^0(298)$ values for $UO_2(g)$ and $PuO_2(g)$ were taken from Green [13] and Cordfunke and Konings [10], respectively. The $\Delta H_f^0(298)$ values for OH(g), Cl(g), and F(g) were taken from Gurvich [14].

A number of mixed actinide vapor species are possible and are likely to be important vapor species in thermal treatment processes. These include all species with the general formula $AnO_2XY(g)$ where An = U, Pu, or Am and X and Y are any combination of OH, Cl, and F where $X \neq Y$. The thermodynamics of these vapor species are estimated from the thermodynamics of their counterpart species. For a reaction of the type

$$1/2\ AnO_2X_2(g) + 1/2\ AnO_2Y_2(g) = AnO_2XY(g), \tag{9}$$

the free energy of reaction at any temperature is taken to be

$$\Delta G_r^0 = RT\ln 2. \tag{10}$$

This assumes that ΔH_r^0 is zero and that ΔS_r^0 is dependent only on the symmetry numbers of the reactant and product species. This assumption has been used to calculate thermodynamics for mixed chromium vapor species and is known to be a good assumption to calculate the vapor pressure of $CrO_2ClF(g)$ from the vapor pressures of $CrO_2F_2(g)$ and $CrO_2Cl_2(g)$ [15].

Summary of Data

Derived and estimated $\Delta H_f^0(298)$ values of actinide gaseous species are combined with the calculated thermal functions for the vapor species and known thermal functions for the actinide oxides [10] and reactive gases [14] to yield free energy changes as a function of temperature for the various volatilization reactions over a temperature range from 800 to 1800 K. The data are summarized as follows:

$$1/3\ U_3O_8(s) + 1/6\ O_2(g) = UO_3(g) \tag{11}$$

$$\Delta G^0 = 371.32 - 144.86(T/1000) \pm 4.5, \text{ kJ/mol}$$

$$1/3\ U_3O_8(s) + 1/6\ O_2(g) + H_2O(g) = UO_2(OH)_2(g) \tag{12}$$

$$\Delta G^0 = 217.70 - 28.59(T/1000) \pm 11.0, \text{ kJ/mol}$$

$$1/3\ U_3O_8(s) + 1/6\ O_2(g) + 2\ HCl(g) = UO_2Cl_2(g) + H_2O(g) \tag{13}$$

$$\Delta G^0 = 113.56 - 6.70(T/1000) \pm 4.0, \text{ kJ/mol}$$

$$1/3\ U_3O_8(s) + 1/6\ O_2(g) + 2\ HF(g) = UO_2F_2(g) + H_2O(g) \tag{14}$$

$$\Delta G^0 = 106.0 - 6.29(T/1000) \pm 4.5,\ kJ/mol$$

$$PuO_2(s) + 1/2\ O_2(g) = PuO_3(g) \tag{15}$$

$$\Delta G^0 = 473.62 - 119.47(T/1000) \pm 6.5,\ kJ/mol$$

$$PuO_2(s) + 1/2\ O_2(g) + H_2O(g) = PuO_2(OH)_2(g) \tag{16}$$

$$\Delta G^0 = 267.94 - 3.23(T/1000) \pm 9.0,\ kJ/mol$$

$$PuO_2(s) + 1/2\ O_2(g) + 2\ HCl(g) = PuO_2Cl_2(g) + H_2O(g) \tag{17}$$

$$\Delta G^0 = 159.06 + 18.62(T/1000),\ kJ/mol$$

and

$$PuO_2(s) + 1/2\ O_2(g) + 2\ HF(g) = PuO_2F_2(g) + H_2O(g) \tag{18}$$

$$\Delta G^0 = 188.65 + 19.08(T/1000),\ kJ/mol.$$

A few experiments were conducted on 2% AmO_2/PuO_2 samples which suggested that the volatility of AmO_2 is about the same as the volatility of PuO_2 [11]. Thus, the same equations as used for the Pu species were used to estimate volatility for AmO_2 where the activity of AmO_2 is taken to be equal to its concentration in PuO_2. Vapor pressures of the various mixed species were calculated from estimated free energies given by equation (10) for reactions of the type given in equation (9).

Application to Thermal Treatment Processes

The thermodynamic data are now applied to various thermal treatment processes. Temperatures are taken to range from 800 to 1800 K. The operational temperatures for the RFP

FBU, the molten salt oxidizer, and an incinerator are taken to be 823, 1173, and 1373 K, respectively. Other process parameters are assumed to be the same for purposes of this treatment. In each process, the actinides are taken to be present as the oxides, $U_3O_8(s)$, $PuO_2(s)$, and $AmO_2(s)$ where activities of $U_3O_8(s)$ and $PuO_2(s)$ are taken to be unity and the activity of $AmO_2(s)$ is taken to be 0.1, i.e. 1000 ppm AmO_2 in PuO_2. The oxygen and water vapor pressures are each taken to be 0.1 atm. Acid gas vapor pressures, HCl(g) and HF(g), are taken to be a maximum of 0.1 atm and a minimum of 0.001 atm for an incinerator and are assumed to be negligible in the RFP FBU and the molten salt oxidizer. Chlorine and fluorine in the waste react with Na_2CO_3 to form NaCl and NaF resulting in very small quantities of HCl(g) and HF(g). Actual pressures of the reactive gases will be highly dependent upon the waste feed composition, waste feed rate, and the amount of excess air used. More accurate treatments could be obtained by including these factors. However, the parameters used herein are taken slightly on the conservative side and such that calculated actinide vapor pressures should be slightly on the high side.

As a function of temperature, the calculated vapor pressures of $UO_2(OH)_2(g)$, $UO_3(g)$, $PuO_2(OH)_2(g)$, and $PuO_3(g)$ are plotted in both Figures 4 and 5. The vapor pressures of $UO_2Cl_2(g)$ and $PuO_2Cl_2(g)$ as a function of temperature are plotted in Figure 4. The upper oxychloride curves are for conditions where the HCl(g) pressure is 0.1 atm and the lower oxychloride curves are for conditions were the HCl(g) pressure is 0.001 atm. The vapor pressures of $UO_2F_2(g)$ and $PuO_2F_2(g)$ as a function of temperature are plotted in Figure 5. The upper oxyfluoride curves are for conditions where the HF(g) pressure is 0.1 atm and the lower oxyfluoride curves are for conditions were the HF(g) pressure is 0.001 atm. Figures 4 and 5 show that if HCl(g) or HF(g) is present in the off-gas, the actinide volatility in the form of oxychlorides and oxyfluorides is increased. In addition, smaller amounts of HCl(g) and HF(g) are required at lower temperatures than at higher temperatures to enhance actinide volatility.

For a thermal oxidation processor with an assumed off-gas flow rate of 40 kmol/h and pressures of HCl(g) and HF(g) equal to 0.01 and 0.002 atm, respectively, the rate of volatilized U, Pu, and Am are calculated as a function of temperature and shown in Figure 6. U oxide volatility varies from very low levels at 800 K of 2.0×10^{-3} g/h to significant levels of 1.6×10^{3} g/h at 1800K. Pu oxide volatility is almost 5 orders of magnitude less than U oxide volatility and Am oxide volatility is about three orders of magnitude less than Pu oxide volatility. This agrees with simulated incineration tests by Vincent, et al. [16] which show that <0.1% U, <0.001% Pu, and <0.01% Am from the incineration waste feed is volatilized.

Taking temperatures representative of the RFP FBU, a molten salt oxidizer, and an incinerator total U, Pu, and Am volatilities are calculated and summarized in Table 3. For the RFP FBU and the molten salt oxidizer partial pressures of HCl(g) and HF(g) were taken to be zero. For an incinerator three cases are taken p(HCl) = 0.01 and p(HF) = 0.002 atm, p(HCl) = 0.10 and p(HF) = 0.002 atm, and p(HCl) = 0.01 and p(HF) = 0.10 atm. The contribution of the mixed vapor species like $UO_2ClOH(g)$ is also considered. Although, the vapor pressures of the actinide species are highest for an incinerator because of the higher operating temperature and the presence of acid gases, the actinide oxide volatilities are small considering that an air pollution control system will remove at least 99.97% of the particulates from the off-gas.

Conclusions

In conclusion, the volatilities of U oxides are low but significant and volatilities of Pu and Am oxides are very low. Oxyfluorides and oxychlorides are not expected to form in the RFP FBU or in a molten salt oxidizer because HF(g) and HCl(g) are removed from the off-gas by Na_2CO_3 present in the system. In an incinerator, however, the vapor pressures of the oxyfluorides and oxychlorides are significant relative to the vapor pressures of the oxides and oxyhydroxides.

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Table 1. Free energy functions, -(G^0 - H^0(298))/T, for actinide vapor species. (p^0 = 1 bar)

T (K)	$UO_3(g)$ (kJ/mol)	$UO_2(OH)_2(g)$ (kJ/mol)	$UO_2Cl_2(g)$ (kJ/mol)	$UO_2F_2(g)$ (kJ/mol)	$PuO_3(g)$ (kJ/mol)	$PuO_2(OH)_2(g)$ (kJ/mol)	$PuO_2Cl_2(g)$ (kJ/mol)	$PuO_2F_2(g)$ (kJ/mol)
800	334.14	410.12	386.76	360.17	343.80	419.82	396.50	369.86
900	339.82	419.15	394.35	367.57	350.00	429.36	404.60	377.78
1000	345.26	427.80	401.58	374.65	355.91	438.49	412.32	385.34
1100	350.43	436.08	408.47	381.40	361.54	447.22	419.65	392.53
1200	355.36	443.98	415.00	387.82	366.88	455.53	426.60	399.36
1300	360.05	451.53	421.22	393.92	371.96	463.47	433.20	405.86
1400	364.52	458.75	427.13	399.74	376.78	471.05	439.48	412.04
1500	368.78	465.65	432.76	405.30	381.38	478.30	445.44	417.93
1600	372.85	472.28	438.13	410.60	385.77	485.24	451.14	423.55
1700	376.74	478.63	443.26	415.66	389.96	491.89	456.57	428.92
1800	380.47	484.73	448.18	420.52	393.98	498.28	461.77	434.06

Table 2. Enthaplies of formation for relevant U and Pu vapor species.

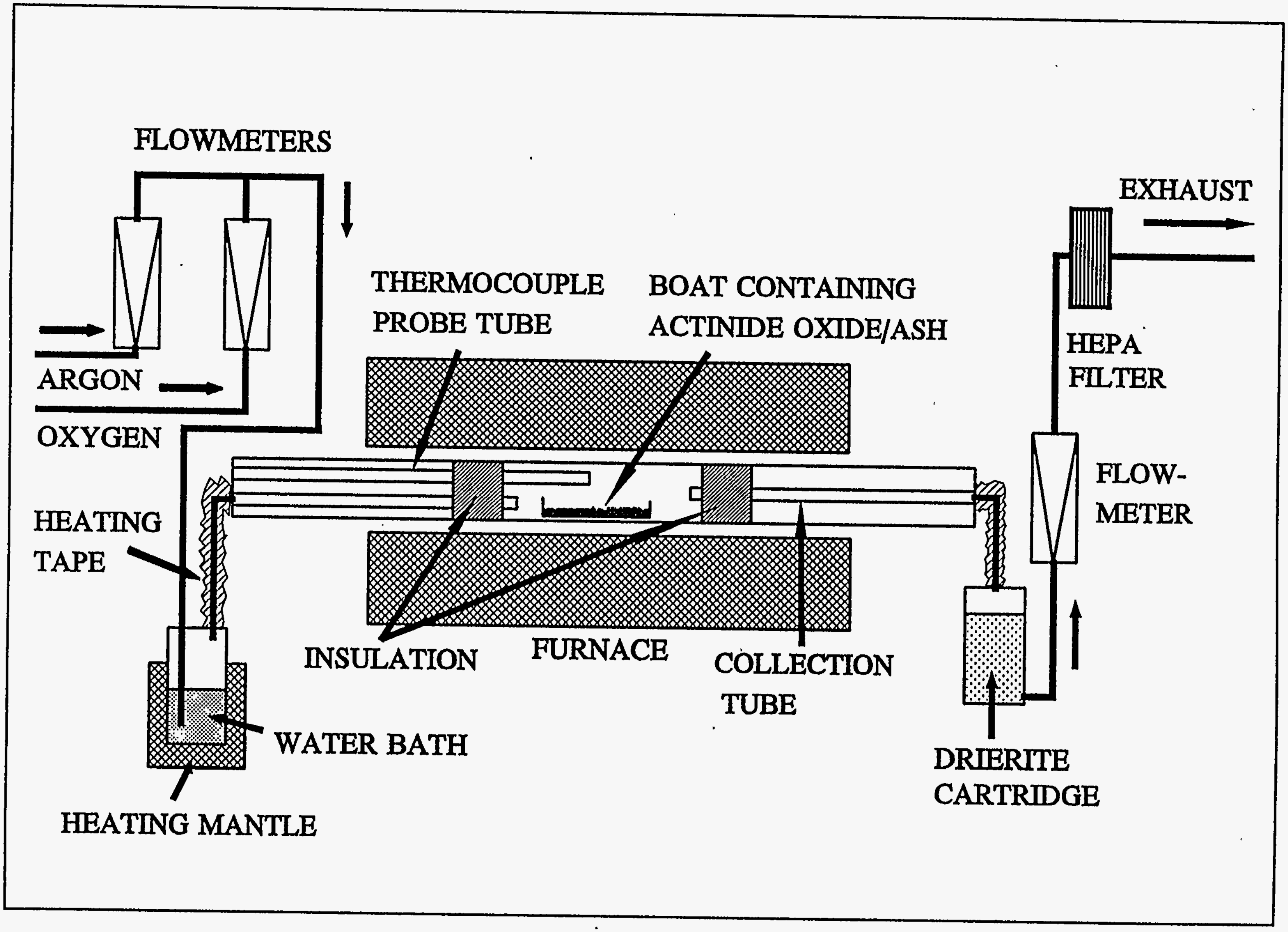
species	$\Delta H_f^0(298)$ (kJ/mol)
$UO_2(g)$	-466.30 ± 5.0
$UO_3(g)$	-796.74 ± 3.52
$UO_2(OH)_2(g)$	-1199.94 ± 10.25
$UO_2Cl_2(g)$	-999.64 ± 2.40
$UO_2F_2(g)$	-1369.22 ± 2.87
$PuO_2(g)$	-410.00 ± 20.0
$PuO_3(g)$	-562.75 ± 4.95
$PuO_2(OH)_2(g)$	-1018.15 ± 5.94
$PuO_2Cl_2(g)$	-822.45
$PuO_2F_2(g)$	-1154.88

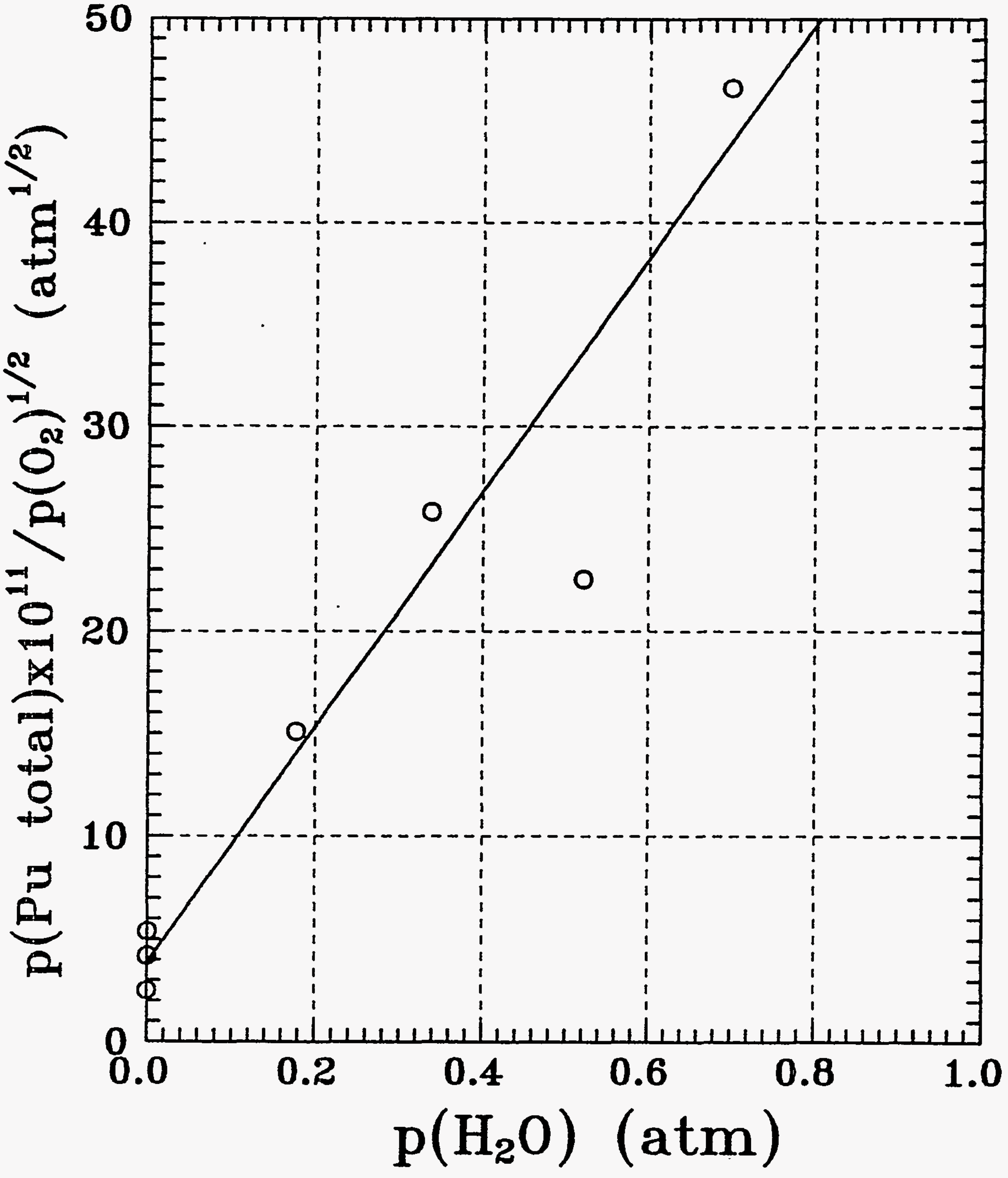
Table 3. Summary of actinide volatility data. Pressures of O_2(g) and H_2O(g) are taken to be 0.10 atm. Gaseous flow rate out of the processor is taken to be 40 kmol/h.

processor	p(HCl) (atm)	p(HF) (atm)	T (°C)	actinide	p(total) (atm)	volatility gU, Pu, or Am/h	major species
RFP FBU							
	0.0	0.0	550	U	2.80×10^{-14}	0.267×10^{-6}	$UO_2(OH)_2$
				Pu	4.05×10^{-19}	3.87×10^{-12}	$PuO_2(OH)_2$
				Am	4.05×10^{-22}	3.91×10^{-15}	$AmO_2(OH)_2$
molten salt oxidizer							
	0.0	0.0	900	U	1.27×10^{-9}	0.0121	UO_3, $UO_2(OH)_2$
				Pu	5.83×10^{-14}	0.557×10^{-6}	$PuO_2(OH)_2$
				Am	5.83×10^{-17}	0.562×10^{-9}	$AmO_2(OH)_2$
incinerator							
	0.01	0.002	1100	U	4.20×10^{-7}	4.00	UO_3, UO_2Cl_2
				Pu	8.04×10^{-11}	0.769×10^{-3}	PuO_2Cl_2, PuO_2ClOH
				Am	8.04×10^{-14}	0.775×10^{-6}	AmO_2Cl_2, AmO_2ClOH
	0.10	0.002	1100	U	9.11×10^{-6}	86.8	UO_2Cl_2
				Pu	3.59×10^{-9}	34.3×10^{-3}	PuO_2Cl_2
				Am	3.59×10^{-12}	34.6×10^{-6}	AmO_2Cl_2
	0.01	0.10	1100	U	1.76×10^{-5}	168	UO_2F_2
				Pu	5.04×10^{-10}	4.82×10^{-3}	PuO_2F_2, PuO_2FCl
				Am	5.04×10^{-13}	4.86×10^{-6}	AmO_2F_2, AmO_2FCl

Figure 1.

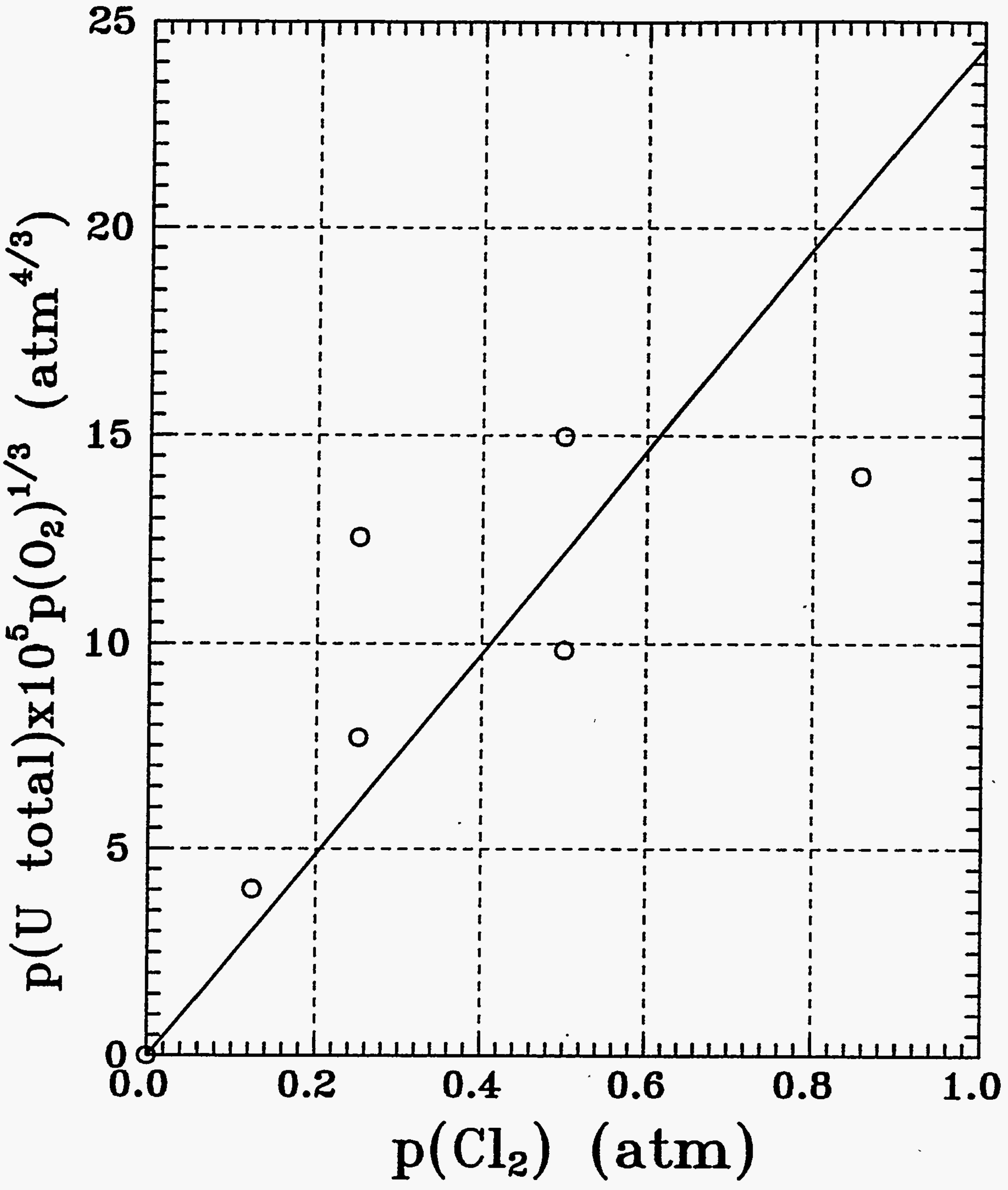
Transpiration Experiments in the Presence of Oxygen and Water Vapor





Plot of $p(\text{Pu total})/p(O_2)^{1/2}$ versus $p(H_2O)$ at 1475 K. The plot increases linearly which indicates that $PuO_2(OH)_2(g)$ is formed in the vapor.

Figure 2

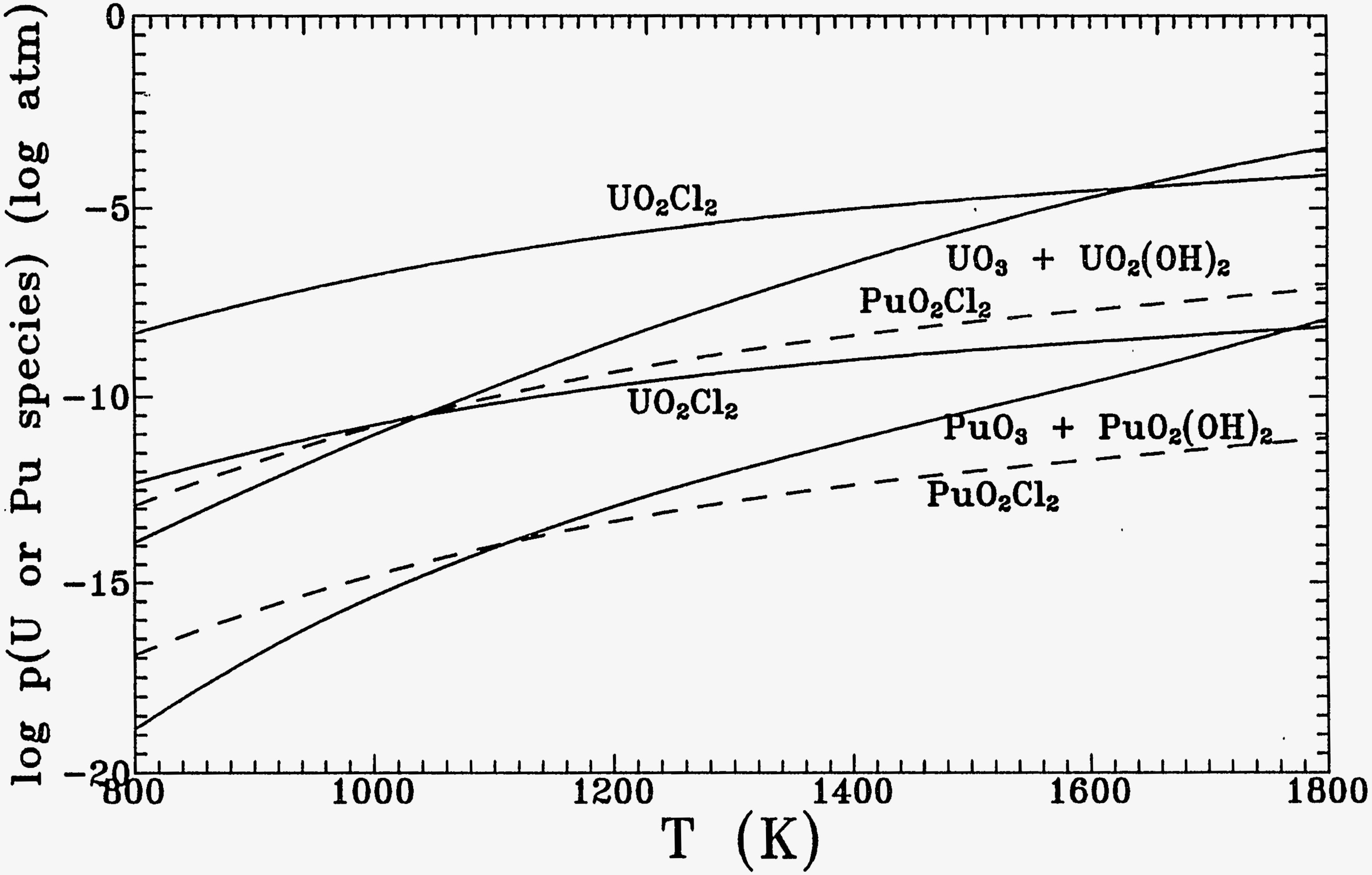


Plot of $P(U\ total)p(O_2)^{1/3}$ versus $p(Cl_2)$ at 1175 K. The plot increases in a linear fashion which indicates that $UO_2Cl_2(g)$ is formed in the vapor.

Figure 3.

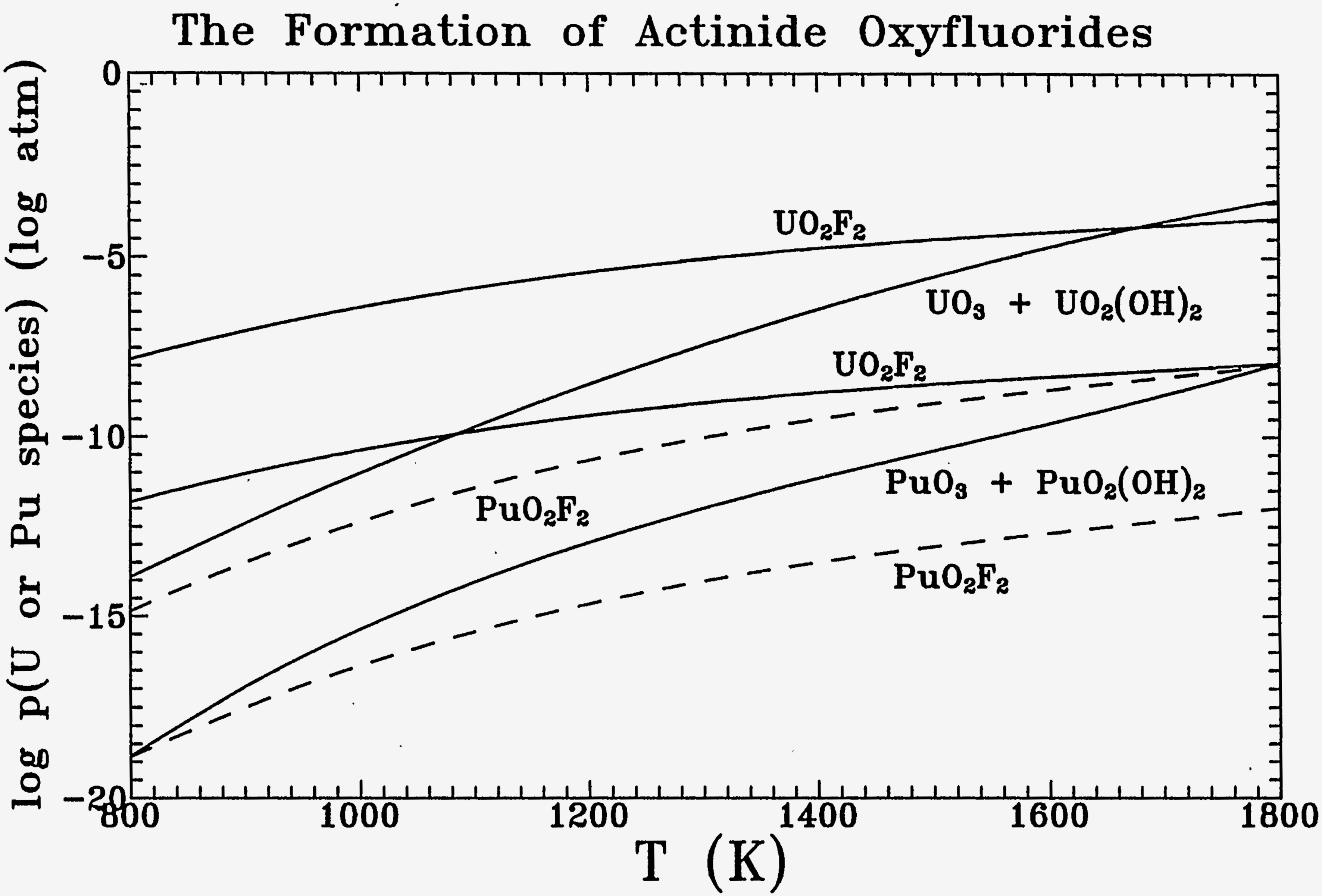
Figure 4

The Formation of Actinide Oxychlorides

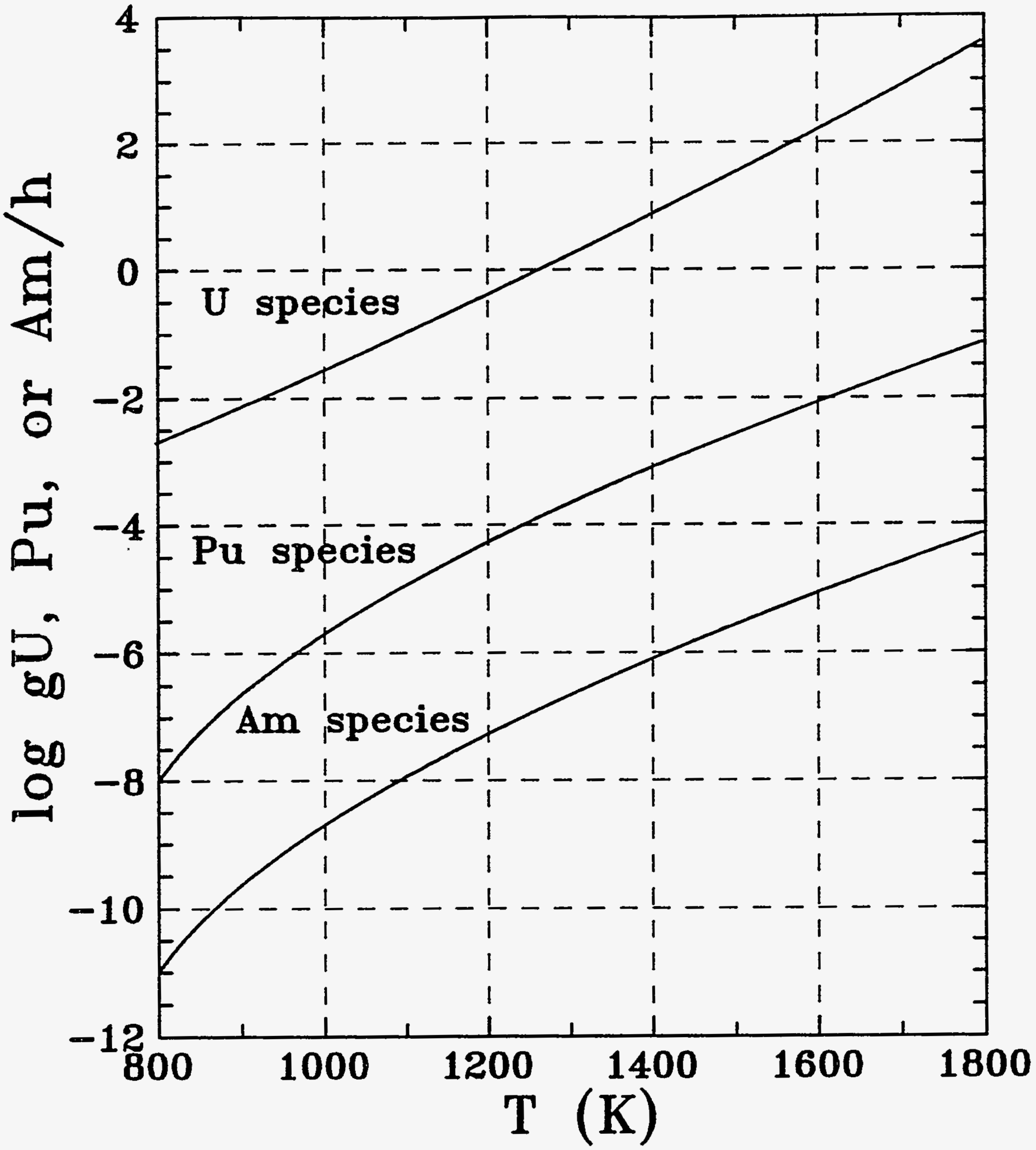


Plot showing log p(U species) and log p(Pu species) as a function of temperature where uranium is taken to be present as U_3O_8(s) and plutonium is taken to be present as PuO_2(s) with $p(O_2) = 0.10$ atm, $p(H_2O) = 0.10$ atm, and $p(HCl) = 0.10$ and 0.001 atm.

Figure 5



Plot showing log p(U species) and log p(Pu species) as a function of temperature where uranium is taken to be present as U_3O_8(s) and plutonium is taken to be present as PuO_2(s) with p(O_2) = 0.10 atm, p(H_2O) = 0.10 atm, and p(HF) = 0.10 and 0.001 atm.



Plot showing log gU, Pu, and Am/h volatilized as a function of temperature where uranium and plutonium are taken to be present as $U_3O_8(s)$ and $PuO_2(s)$. $AmO_2(s)$ is taken to be present at 1000 ppm in $PuO_2(s)$. The $O_2(g)$, $H_2O(g)$, HCl(g), and HF(g) pressures are taken to be 0.10, 0.01, 0.01, and 0.002 atm, respectively, and the offgas flow rate is taken to be 40 kmol/h.

Figure 6