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Review of Thermodynamic and Kinetic Data
for the Molten-Tin Process

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FOR THE MOLTEN TIN PROCESS

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ABSTRACT

This report gives a brief description of the Molten Tin Process for nuclear fuel reprocessing, and summarizes the available data on thermodynamics and kinetics that pertain to the process. The two main reactions of concern in the process are illustrated by:

where M represents U or some other element in an oxide fuel. It is especially important for the Molten Tin Process to have information on the chemical activities of metals dissolved in tin at temperatures in the vicinity of 1900K. Sufficient thermodynamic and kinetic information is presented in this report to show that the various steps in the Molten Tin Process are scientifically feasible, but more information will need to be experimentally determined to work out a detailed process flow sheet.

INTRODUCTION

The purpose of this report is to summarize the thermodynamic and kinetic data that pertain to the Molten Tin Process for nuclear fuel reprocessing. I have taken a twofold approach: (1) to survey the literature and summarize those aspects that describe the thermodynamic and kinetic behavior in the various steps of the Molten Tin Process, and (2) to estimate data when reasonable estimates can be made to fill in the gaps where data are lacking. Also, I have indicated some of the key areas where future data measurements would be useful for better evaluating the process.

Before discussing the types of data needed, I will give a brief description of the Molten Tin Process in order to define the areas where data are needed. The Molten Tin Process was originally conceived by Parlee and Anderson and studied by them with various coworkers.¹⁻³ During the past year, under the sponsorship of the DOE program on Pyrochemical and Dry Processing Methods (PDDM) we have taken a more general look at the concept of using a molten tin solvent system with the primary objective of developing a process within the frame of nonproliferation. Also, as the program has developed, the goals have been directed to concentrate on applications to breeder fuels. The process, as we currently envision it, still retains the two major steps defined by Parlee and Anderson. These steps are carried out in a molten tin bath contained in graphite at ~1900K, and for an oxide fuel may be illustrated by:

where M represents uranium and other typical dioxide formers. Similar reactions can also be written for metals with other valences in the fuel. For fuel forms such as carbide or metallic fuels, the first step of the process would be a simple dissolution in the tin melt rather than step (1) above.

In the illustration above, in step (1) the oxide fuel is reduced by carbon dissolved from the graphite container and present in low concentrations in the molten tin. This reduction process is known as a carbothermic reduction. The products of the reduction are CO gas, which is pumped off, and a metallic solution of the fuel constituents in molten tin. The metallic solutions in tin are sufficiently stable that solid carbides generally do not form under these conditions, in spite of the presence of graphite. In step (2) above, the actinide nitrides are precipitated out of the molten tin solution by pressurizing with nitrogen at ~1 atm. The fission products generally are expected to remain behind in the molten tin because of the relatively lower stability of their nitrides compared to their affinity for tin. Some, however, will carry over with the actinide nitrides, and it is one of the goals of this project to evaluate which do and to what extent. A selective amount of carryover would actually be desirable in the process as it can provide a deterrent to theft if it produces a high level of gamma radiation.

The current version of our approach to the Molten Tin Process is illustrated further by means of schematic flow diagrams in Figs. 1 and 2. Thus, the fuel is first deoxidized and introduced directly into molten tin at ~1900K using about a 5:1 weight ratio of tin to fuel. If the fuel is oxide, it is then carried through the carbothermic reduction step. Gaseous CO and radio-nuclides such as I_2 , Kr, Xe, and HT are removed through a cooled reflux condenser above the carbothermic reactor. Upon completion of the carbothermic

Fig. 1. Schematic Flow Diagram of the Molten Tin Process.

Figure 2. Portion of flow diagram of the Molten Tin Process showing Mass Flow through the Fission Product Volatization Step. Estimated percentage of fission products removed are given for distillation of 25% and 10% of the tin solvent, respectively.

reaction, about 10-25 percent of the tin is removed by distillation, and carries with it the volatile fission product metals as shown in Fig. 2. These volatile metals include Cs, Sr, and Sm, which are the main decay heat producers in nuclear wastes in the 10-1000y period. Tin is separated from the fission products by as yet an unspecified process, and the tin is sent back to the carbothermic reactor.

Nitriding is then carried out in two stages to obtain a fuel-enriched and a fuel-depleted actinide phase when working with breeder fuels; otherwise, if fuel enrichment is not required, it is done in one step. It is anticipated that proper selection of nitriding conditions such as nitrogen pressure, temperature, and catalysts will allow preferential enrichment of fuel actinides in the nitride phase in the first stage followed by removal of most of the remaining actinides in a second stage using more intense nitriding conditions.

After nitriding, the melt is cooled down to about 700-900K to allow precipitation of any residual U as USn_3 , plus Mo, Nb, and possibly Tc and Ru as insoluble tin compounds. The remaining tin solution is further processed by as yet an unspecified process to recover most of the fission product wastes for disposal, and the tin is recycled back into the carbothermic reactor.

From the description above, I can now define the main areas requiring thermodynamic and kinetic data. These are as follows:

- Carbothermic reduction of oxides in molten tin at ~1900K, e.g.,
 $MO_2(s) + 2C(\text{in Sn sol'n}) \rightarrow M(\text{in Sn sol'n}) + 2CO(g).$
- Volatilities of fission products from molten tin, e.g., $Cs(\text{in Sn sol'n}) \rightarrow Cs(g).$

- Nitriding of actinide and fission product metals dissolved in molten tin, e.g., $M(\text{in Sn sol'n}) + 1/2 N_2(g) \rightarrow MN(s)$. We also need to understand the distribution ratios of elements between molten tin and nitride phases including fuel enrichment or depletion possibilities, and the fission product content of the actinide nitride phases.
- Solubilities of M-Sn compounds in molten tin at lower temperatures, e.g., solubility of USn_3 in molten tin at 700-900K. Also phase diagram data that pertains to separation processes for Sn from fission products.

These four areas will be discussed in turn in this report, and thermodynamic data of general interest to the four areas will be summarized in an appendix at the end of the report.

CARBOTHERMIC REDUCTION OF OXIDES

There is only a limited amount of work available on the carbothermic reduction of oxides in molten tin saturated with graphite. Anderson and Parlee⁴ used experimentally measured activities of uranium in molten tin to calculate the equilibrium pressures of CO produced by the reaction:

Their calculated results (see Table I) gave CO pressures that were low by about a factor of three to ten and uranium activities that were high by one to two orders of magnitude as compared to later experimental data obtained by Bakshani, Parlee and Anderson.^{5,6} Nonetheless, they properly predicted that carbothermic reduction would occur.

Table 1. Experimentally determined activities of $U(a_U)$ in various U-Sn alloys, and calculated equilibrium CO pressure during carbothermic reduction.⁴

Temp. (K)		U concentration in wt% (mole fraction)		
		2% (0.0101)	9% (0.0471)	18% (0.0985)
1800	a_U^*	1.96×10^{-4}	5.40×10^{-4}	5.87×10^{-4}
	$p_{CO}(\text{atm})$	0.037	0.019	0.018
1900	a_U	3.12×10^{-4}	8.55×10^{-4}	9.30×10^{-4}
	$p_{CO}(\text{atm})$	0.105	0.063	0.060
2000	a_U	4.68×10^{-4}	12.9×10^{-4}	14.0×10^{-4}
	$p_{CO}(\text{atm})$	0.302	0.182	0.175

*Activity of uranium is based on an activity coefficient of 1 at a uranium mole fraction of 1.

I've summarized the results of Bakshani⁵ in Table II. I've also included in the table a calculated value of the equilibrium constant for reaction (3) based on data in the literature, i.e., $\Delta H_{f,298}^0$ for UO_2 and CO are from Brewer and Rosenblatt,⁷ free energy functions for UO_2 are from Schick,⁸ for C and CO from JANAF,⁹ and for U from Hultgren et al.¹⁰

Table II. Calculated equilibrium data for reaction (3) are compared with measured values of x_U and p_{CO} by Bakshani⁵ to obtain values of a_U and γ_U .

Series	Temp. (K)	$K_{eq}(\text{atm}^2)$ calc.	x_U meas.	$p_{CO}(\text{atm})$ meas.	a_U calc.	γ_U calc.
I	1723	1.07×10^{-8}	0.005	0.064	2.6×10^{-6}	5.1×10^{-4}
I	1768	4.84×10^{-8}	0.008	0.096	5.2×10^{-6}	6.6×10^{-4}
I	1803	1.49×10^{-7}	0.011	0.134	8.3×10^{-6}	7.6×10^{-4}
I	1863	9.23×10^{-7}	0.025	0.316	9.2×10^{-6}	3.7×10^{-4}
II	1723	1.07×10^{-8}	0.009	0.059	3.0×10^{-6}	3.4×10^{-4}
II	1768	4.84×10^{-8}	0.020	0.089	6.0×10^{-6}	3.0×10^{-4}
II	1803	1.49×10^{-7}	0.040	0.177	4.8×10^{-6}	1.2×10^{-4}
II	1863	9.23×10^{-7}	0.054	0.276	1.2×10^{-5}	2.2×10^{-4}

Bakshani ran two series of experiments. In series I, he reacted UO_2 with carbon and tin, while in series II he used a mixture of U and UO_2 for the reaction with carbon and tin. I've calculated the activity of uranium (see Table II) from the calculated K_{eq} and the measured CO pressure using the relation, $K_{eq} = a_U p_{CO}^2$. Also, since $a_U = \gamma_U x_U$, I've calculated the activity coefficient for uranium (γ_U) from the measured mole fractions of uranium (x_U). The very low values for γ_U indicate a very strong interaction between uranium and molten tin. It is this strong interaction that reduces the temperature required for the carbothermic reduction of UO_2 , and also prevents formation of uranium carbides.

Bakshani⁵ has also given approximate data on the kinetics of the carbothermic reduction process. He found the times to reach the equilibrium CO level-off pressures to be 145 min. at 1773K, 170 min. at 1823K, 105 min. at 1863K and 25 min. at 1933K. At higher temperatures, the data were complicated

by the evaporation of tin. Uranium concentrations attained at the equilibrium point were 1.76, 3.61, 4.97, and 5.45 wt.%, respectively, for the above runs.

Some experiments were also conducted at the Lawrence Livermore Laboratory (unpublished work) to obtain approximate kinetic data on the carbothermic reduction of UO_2 . At Livermore, we used 50g of tin and 10g of UO_2 microspheres (150-210 μm in dia.) for each run. The rate of the reaction was found to be linear in time and quite slow at 1873K, i.e., 3 percent conversion per hour. We repeated the experiment using 4.7g of cobalt added to the tin as a catalyst and obtained an initial conversion rate of 20%/h, which increased as the reaction proceeded to 50%/h. We believe that cobalt (and we would expect iron and nickel as well) is an effective catalyst for this reaction because it promotes the solubility of carbon in tin, and hence the continuous supply of carbon to the Sn- UO_2 interface. As the reaction progresses, we believe that the uranium dissolved in tin will also promote the solubility and migration of carbon in the tin.

There are no experimental data currently available on the carbothermic reduction in molten tin of oxide components of fuel elements other than for UO_2 . Estimates can be made of the behavior of other oxides based upon the free energy of formation of the oxide and of the free energy of solution of the metal in molten tin. Free energy data on oxides are generally available (e.g., see appendix), but not for the metallic solutions in molten tin (see next section). I would expect, however, that since UO_2 is among the most stable of the oxides, that the balance of the fuel constituents will also be reduced under the conditions required to reduce UO_2 . Reduction of PuO_2 should be possible at a somewhat lower temperature, and for ThO_2 at a somewhat higher temperature, than for UO_2 considering the relative stabilities of these oxides.

The kinetics of the carbothermic reduction should be controlled by the behavior of the major fuel constituent, i.e., UO_2 , PuO_2 or ThO_2 , and I expect that the PuO_2 and ThO_2 reduction kinetics will not differ greatly from that for UO_2 .

VOLATILITIES OF METALS FROM TIN

The volatilities of fission product elements dissolved in molten tin are dependent upon their respective partial pressures. The partial pressures are determined from the relation $p_M = a_M p_M^0$, which is equivalent to $p_M = \gamma_M x_M p_M^0$. Here p_M is the desired partial pressure of element M, a_M is its chemical activity, p_M^0 is the vapor pressure of pure element M, x_M is the mole fraction, and γ_M the activity coefficient. The reference state for M is taken to be the pure liquid metal for which by definition $\gamma_M = 1$. Generally, the vapor pressures for the pure elements are known and the mole fractions of the elements in tin can be determined, so that if we can obtain information on the activity coefficients, γ_M , then we can calculate the required partial pressures. Therefore, the goal in this section is to examine the available literature for information on activity coefficients of fission product elements in dilute solutions in tin.

In addition to the volatilization process, activity coefficients are also of concern in (1) determining the driving force for the carbothermic reduction step, (2) setting the conditions required for the nitriding step, and (3) establishing the equilibrium distribution of fission product and fuel elements between the molten tin and solid nitride phases.

Direct activity coefficient data on fission product elements in tin is very limited. Some information has been obtained by Fuwa and coworkers¹¹⁻¹⁵ on Y, Pr, and Gd at our temperatures of interest, and information is available for Ag and La at lower temperatures. However, even though the direct activity coefficient data is limited, there is extensive enthalpy of solution data for elements in tin, and estimates can be made of the activity coefficients by estimating the balance of the thermodynamic data required. We should emphasize that although estimation techniques should be of value to our understanding of the molten tin process, they are not a substitute for actual experiments that are needed to measure such effects as metal volatilities, carbothermic and nitriding reactions, and partitioning behavior.

The basic expression relating activity coefficient to the other thermodynamic parameters is:

$$(4) \quad RT \ln \gamma_M = \Delta \bar{H}_M - T \Delta \bar{S}_M^E = \Delta \bar{G}_M^E,$$

where γ_M is the activity coefficient of the solute referred to the pure liquid solute element with unit activity, $\Delta \bar{H}_M$ is the enthalpy of solution of the solute, $\Delta \bar{S}_M^E$ is the excess entropy of solution of the solute, and $\Delta \bar{G}_M^E$ is the excess free energy of solution of the solute. The superscript bars indicate partial molal quantities. Once $\Delta \bar{H}_M$ of solution is known, the only thermodynamic parameters that need to be estimated are the $\Delta \bar{S}_M^E$ above, and ΔC_p for formation of the solution. Values of ΔC_p are needed to determine the temperature dependence of $\Delta \bar{H}_M$ and $\Delta \bar{S}_M^E$. The major portion of the numerical value that determines the sum $\Delta \bar{H}_M - T \Delta \bar{S}_M^E$ in Eq. (4)

above is provided by $\bar{\Delta H}_M$. Hence, since $\bar{\Delta H}_M$ is known for most of the systems, it should be possible to obtain reasonable first estimates of γ_M .

Detailed comments will be given next on the individual fission product elements in tin, grouped according to valence or position in the periodic table. Whenever possible, I will summarize the data for infinitely dilute solutions, since concentrations of fission products in tin are very low in the Molten Tin Process.

Ag, Rb, and Cs in Sn:

Hultgren et al.,¹⁰ give the following data for the Ag-Sn system:

$$\begin{aligned} 900K: \quad \bar{\Delta G}_{Ag}^E &= 0.542 \text{ kcal/mol}, \quad \bar{\Delta H}_{Ag} = 1.046 \text{ kcal/mol}, \\ &\text{and } \bar{\Delta S}_{Ag}^E = 0.560 \text{ cal/mol-K} \end{aligned}$$

$$1250K: \quad \bar{\Delta G}_{Ag}^E \approx -4.160 \text{ kcal/mol}$$

The $\bar{\Delta G}_{Ag}^E$ value at 1250K corresponds to an activity coefficient of 0.187 for Ag in dilute solutions in tin. The trend in $\bar{\Delta G}_{Ag}^E$ with temperature is actually quite large, between 900 and 1250K, and indicates that γ_{Ag} at our working temperature of 1900K will be ~0.1.

I have not been able to find any thermodynamic data on the Rb-Sn and Cs-Sn systems. Compounds such as RbSn and CsSn have been reported,¹⁶ from which I can infer that attractive bonding forces exist in solutions of Rb-Sn and Cs-Sn. Further, drawing on the analogy of known thermodynamic data in the Na-Sn, Na-Pb, and K-Pb systems,¹⁰ I estimate γ_{Rb} and γ_{Cs} in liquid Sn to be about 10^{-2} at 1900K.

Sr and Ba in Sn:

King and Kleppa¹⁷ and Guadagno et al.,¹⁸ have measured the $\bar{\Delta H}_M$ of solution of Sr and Ba in liquid Sn at temperatures of ~700K. The data for infinitely dilute solutions are as follows.

	King	Guadagno	Ave.
$\bar{\Delta H}_{Sr}$	$-38.57 \pm 0.3 \text{ kcal/mol}$	$-37.00 \pm 0.4 \text{ kcal/mol}$	-37.8 kcal/mol
$\bar{\Delta H}_{Ba}$	$-43.78 \pm 0.6 \text{ kcal/mol}$	$-43.26 \pm 0.4 \text{ kcal/mol}$	-43.5 kcal/mol

There are no data available on $\bar{\Delta G}_M^E$ or $\bar{\Delta S}_M^E$ for these systems. However, I would expect $\bar{\Delta S}_M^E$ to be of the order of -10 cal/mol-K by analogy with Hultgren's data on Ca¹⁰ with the additional assumption that ΔC_p is close to zero for the Ca-Sn system. With these assumptions, the activity coefficients, γ_{Sr} and γ_{Ba} , would be expected to be in the region of 10^{-2} - 10^{-3} at 1900K.

Y, La, and Rare Earths in Sn:

Bayanov¹⁹ has summarized the $\bar{\Delta H}_M$ of solution data for La and the rare earths, and additional data is given by Guadagno et al.²⁰ on La, by Pratt and Morris²¹ on Nd and Sm, and by Bacha et al.²² on Eu. No $\bar{\Delta H}_M$ values have been reported for Y. In order to convert the literature data for this group of metals to a common reference state of pure liquid metal, information is needed on the transition energies going to higher temperature structures and for the enthalpies of fusion. The required data were obtained from Hultgren et al.,¹⁰ and are as follows:

	ΔH_{tr} (kcal/mol)	ΔH_{fus} (kcal/mol)	$\Delta H_{tr} + \Delta H_{fus}$ (kcal/mol)
Y	1.193	2.724	3.917
La	0.746	1.481	2.227
Ce	0.715	1.305	2.020
Pr	0.757	1.646	2.403
Nd	0.724	1.707	2.431
Sm	0.744	2.060	2.804
Eu	-	2.202	2.202
Gd	0.935	2.403	3.338

From the available data along with an estimate for Pm, I obtain the following best values for $\bar{\Delta H}_M$ of solution at infinite dilution in tin at 800K:

	$\bar{\Delta H}_M$ (kcal/mol)
La	-66.7 ± 0.6
Ce	-70.4 ± 0.6
Pr	-63.7 ± 0.4
Nd	-60.0 ± 1.5
Pm	est. - 58.6
Sm	-57.3 ± 2.5
Eu	-42.6 ± 2.0
Gd	-54.7 ± 2.6

There is sufficient data on the $\bar{\Delta H}_M$ of solution for La^{20,21} to obtain a temperature trend, and thus I estimate ΔC_p of solution to be 15 cal/mol-K. Furthermore, Matigorova and Bayanov³⁴ using an e.m.f. cell with low La concentrations in Sn at 673-973K, obtained values for $\bar{\Delta G}_{La}^E$. Combining the available data, I obtain as a best fit:

$$(5) \quad \bar{\Delta H}_{La} = -68,500 + 15(T-673) \text{ cal/mol}$$

$$(6) \quad \bar{\Delta S}_{La}^E = -28.00 + 15 \ln(T/673) \text{ cal/mol-K}$$

$$(7) \quad \bar{\Delta G}_{La}^E = -68,500 + 28,000T + 15(T-673) - 15T \ln(T/673) \text{ cal/mol}$$

Comparing these relations with the observed data gives the following for $\bar{\Delta H}_{La}$.

$T(K)$	$\bar{\Delta H}_{La}$ (cal/mol) calc.	$\bar{\Delta H}_{La}$ (cal/mol) meas.	Reference
632	-69,115	-68,467 $\pm$ 600	21
725	-67,720	-68,927 $\pm$ 400	20
750	-67,345	-67,727 $\pm$ 700	20
775	-66,970	-66,227 $\pm$ 1,100	20

For $\bar{\Delta G}_{La}^E$, the comparison with the measurements of Matigorova and Bayanov²³ is as follows:

$T(K)$	$\bar{\Delta G}_{La}^E$ (cal/mol) calc.	$\bar{\Delta G}_{La}^E$ (cal/mol) meas.
673	-49,656	-48,580 $\pm$ 1,400
773	-46,964	-47,820 $\pm$ 1,400
873	-44,461	-44,590 $\pm$ 1,400
973	-42,137	-41,950 $\pm$ 1,400

Extrapolating Eq. (7) to a working temperature of 1900K for the Molten Tin Process and applying Eq. (4) gives an activity coefficient of $\gamma_{La} = 9 \times 10^{-4}$.

The activity coefficients of Y, Pr, and Gd can also be indirectly derived from the experimental data of Fuwa et al.¹¹⁻¹⁴ in which they determined the nitrogen pressure for the onset of solid nitride formation for each of the above metals in molten Sn. Thus, for the reaction

the equilibrium constant is $K_{\text{eq}} = a_{\text{MN}}/a_{\text{M}}p_{\text{N}_2}^{1/2}$, or since the activity of solid MN ≈ 1 , and $a_{\text{M}} = \gamma_{\text{M}}x_{\text{M}}$, $\gamma_{\text{M}} = 1/K_{\text{eq}}x_{\text{M}}p_{\text{N}_2}^{1/2}$. By using the available thermodynamic data to calculate K_{eq} along with the measured values of Fuwa et al. for x_{M} and p_{N_2} , we can calculate values of γ_{M} . Fuwa et al., by using a combination of literature and estimated data for the nitrides, obtained the γ_{M} values summarized in Table III for 1800 and 1900K. The free

TABLE III. Values of γ_{M} for Y, Pr, and Gd in Dilute Solution in Tin at 1800 and 1900K based on the Experimental Data of Fuwa et al. 11-14 A comparison is given between values derived by Fuwa et al. and the author using different thermo- dynamic data for the nitrides.

Temp(K)	γ_{Y}		γ_{Pr}		γ_{Gd}	
	<u>Fuwa et al.</u>	<u>this work</u>	<u>Fuwa et al.</u>	<u>this work</u>	<u>Fuwa et al.</u>	<u>this work</u>
1800	0.0032	0.0019	0.025	0.0062	0.024	0.00023
1900	0.0065	0.0038	0.044	0.0123	0.043	0.00045

energy expressions for reaction (2) that I used (see appendix for references) are as follows:

$$(8) \Delta G_{f,T}^0(\text{YN}) = -73,480 + 21.20T \text{ cal/mol}$$

$$(9) \Delta G_{f,T}^0(\text{PrN}) = -78,900 + 22.93T \text{ cal/mol}$$

$$(10) \Delta G_{f,T}^0(\text{GdN}) = -74,660 + 19.43T \text{ cal/mol}$$

Uncertainties in the data for YN and GdN are about $\pm 5,000$ cal/mol, and for PrN $\pm 10,000$ cal/mol. The available information thus indicates that the activity coefficients for Y, La, and the rare earths in molten Sn will be of the order of 10^{-2} to 10^{-4} .

Other Elements in Sn:

Based on the foregoing information on the activity coefficients of group 1, 2, and 3 type elements in tin, and upon information available in Hultgren et al.¹⁰ some qualitative observations can be made for the remaining fission product elements. I would expect Cd and Sb to behave as nearly ideal solutions with $\gamma_M \approx 1$. In probably has a higher activity coefficient than the rare earths. Mo should have $\gamma_M \approx 1$ as it is relatively inert to reaction with Sn. I would expect some interaction of Nb and Tc with Sn with $\gamma_M \approx 0.1$. Ru, Rh and Pd should be more interactive with Sn and γ_M is probably $\sim 10^{-2}$. Zr is probably about like the rare earths, and Eu like Sr and Ba. Se and Te should be quite reactive with Sn as well as with carbon, the actinides, and yet other melt constituents. It is likely however that they will form volatile gaseous compounds. Br should form SnBr_4 which is very volatile.

Summary of Metal Volatilities:

Using the estimated γ_M values discussed above and the expression for partial pressures, $p_M = \gamma_M x_M p_M^0$, I have summarized partial pressure estimates in Table IV for a typical LWR fuel²⁴ dissolved in molten tin.

Although an LWR fuel is used for illustration here, use of a breeder fuel composition would not significantly alter the conclusions within the very approximate nature of the available data. Table IV can be used to make an initial assessment of the volatilities of the fission products relative to Sn.

Assume, for example, that 10 percent of the Sn is removed at 1873K by vacuum distillation in the molecular flow region, i.e., below a vapor pressure of $\sim 10^{-2}$ atm. Since Sn has a vapor pressure of 1.31×10^{-3} atm, a comparable percentage of a fission product with a mole fraction of 10^{-4} would be removed

Table IV. Summary of Estimated Partial Pressures of Fission Product Metals at 1873K above a Tin Melt Containing 0.666 wt% Non-Gaseous Fission Products, 16.6 wt% Actinide, and the Balance Tin.

Element M	Mol Frac (x_M)	Act. Coef. (γ_M)	P_M (atm) for	P_M (atm) above
			Pure M	Molten Tin
Ag	0.000014	0.1	2.30×10^{-2}	3×10^{-8}
Ba	0.000279	0.003	2.82×10^{-1}	2×10^{-7}
Br	0.000005	forms $\text{SnBr}_4(\text{g})$	(B.P. = 332K)	volatile
Cd	0.000019	1	(B.P. = 1040K)	$\sim 10^{-2}$
Ce	0.000462	0.0005	2.00×10^{-6}	5×10^{-13}
Cs	0.000499	0.01	(B.P. = 944K)	$\sim 10^{-2}$
Eu	0.000030	0.002	1.01	1×10^{-7}
Gd	0.000020	0.001	1.59×10^{-5}	3×10^{-13}
In	0.000003	0.003	4.90×10^{-2}	4×10^{-10}
La	0.000233	0.0009	1.69×10^{-6}	4×10^{-13}
Mo	0.000928	1	2.19×10^{-11}	2×10^{-14}

Table IV. (cont.)

Element M	Mol Frac (x_M)	Act. Coef. (γ_M)	P_M (atm) for	P_M (atm) above
			Pure M	Molten Tin
Nb	0.000004	0.1	6.05×10^{-13}	2×10^{-19}
Nd	0.000716	0.001	3.03×10^{-4}	2×10^{-10}
Pd	0.000323	0.01	7.48×10^{-5}	2×10^{-10}
Pm	0.000012	0.001	est. 5×10^{-3}	6×10^{-11}
Pr	0.000217	0.001	3.50×10^{-5}	8×10^{-12}
Rb	0.000100	0.01	(B.P. = 961K)	$\sim 10^{-3}$
Rh	0.000092	0.01	2.35×10^{-8}	2×10^{-14}
Ru	0.000549	0.01	1.00×10^{-10}	5×10^{-16}
Sb	0.000003	1	$1.07(\text{Sb}_2)$	$2 \times 10^{-6}(\text{Sb})$
Se	0.000017	forms SnSe(g)	(B.P. = 958K)	volatile
Sm	0.000142	0.001	3.65×10^{-1}	5×10^{-8}
Sn	0.000011	1	1.31×10^{-3}	1×10^{-8}
Sr	0.000254	0.003	3.50	3×10^{-6}
Tc	0.000216	0.1	9.06×10^{-12}	2×10^{-16}
Te	0.000113	forms SnTe(g)	(B.P. = 1261K)	volatile
Y	0.000135	0.001	8.05×10^{-6}	1×10^{-12}
Zr	0.001033	0.001	1.73×10^{-10}	2×10^{-16}

if it has a vapor pressure of $10^{-4} \times (1.31 \times 10^{-3}) = 1.31 \times 10^{-7}$ atm, or essentially all of the fission product would be removed if it has a vapor pressure of 1.31×10^{-6} atm. This, of course, assumes that kinetic factors

will not provide a barrier towards vaporization. Thus, Table IV indicates that the elements Cd, Cs, Rb, Sb, and Sr should be removed essentially completely by volatilizing off 10 percent of the Sn, and the elements Ag, Ba, Eu, and Sm should undergo partial removal. The elements Br, Se, and Te should also be removed completely because they form volatile gaseous species with Sn. This volatility behavior is illustrated in Fig. 2 for 10 and 25 percent volatilization of Sn, although numerically the values may not be in agreement with Table IV. I should emphasize again that the calculations given here, although strongly indicative, are not a substitute for the experimental measurements that are needed to determine the actual volatilities.

NITRIDING REACTIONS IN TIN

The existing information on the nitriding behavior of the fission products Y, Pr and Gd in Sn is described in the previous section, and will not be repeated here. There is also unpublished work without specific details on the nitriding of Pr, Sm, Nb and Zr in Sn mentioned in reference 2. The thermodynamics and kinetics of nitriding reactions for U in Sn are described in several references,^{1,2,3,25,26} and thermodynamic information on nitriding is also given for the ternary system U-Gd-Sn.^{11,27} Fuwa¹¹ describes some limited work on the U-Pr-Sn system, and on a simulated fuel consisting of 9.50 U, 0.10 percent each of Ce and Pr, and 0.05 percent each of Zr, Nb, Mo and Ru (all wt%) and the balance Sn. Anderson¹ also describes some limited work on the U-Zr-Sn system. In addition to the above literature work, studies are currently underway at the Lawrence Livermore Laboratory on the relative rates of nitriding of U, Th, and Pu in Sn, and of mixtures of Th-U and U-Pu in Sn.

The thermodynamics of nitriding of U in Sn to form solid UN were investigated by Anderson and coworkers^{1,2,3} at temperatures of 1793-1883 and compositions of 2, 5, 9 and 18 wt% U in Sn. The square roots of the measured equilibrium nitrogen pressures for the onset of nitriding are summarized in Table V, and the free energy change for precipitating UN(s) from Sn solutions is given by:

$$(11) \Delta G_T^0 \approx -35,250 + 9.4T \text{ cal/mol.}$$

Table V. Summary of the Square Root of the Equilibrium Nitrogen Pressures (in $\text{Atm}^{1/2}$) for Onset of Nitriding of Uranium in Tin.¹

Temp(K)	U concentration in wt% (mole fraction)			
	2% (0.0101)	5% (0.0256)	9% (0.0471)	18% (0.0985)
1793		0.326		
1810		0.360		
1816		0.375		
1825			0.282	
1835			0.305	
1840	0.850	0.412	0.315	0.290
1845		0.420		
1858		0.455		
1863			0.355	
1883			0.395	

As was discussed earlier for the Y, Pr and Gd systems, γ_M can be calculated from the relation $\gamma_M = 1/K_{eq} x_M p_{N_2}^{1/2}$ which applies to the nitriding reaction

Anderson¹ used the relation from the literature

$$(12) \quad \Delta G_{F,T}^0(UN) = -65,900 + 19.0T$$

for the free energy of formation of UN(s) to determine K_{eq} and derived the following expression for γ_U in Sn:

$$(13) \log \gamma_U = -6,700/T + 2.08 - 6.1 x_U.$$

The final term in this expression indicates that the activity coefficient of U decreases as its concentration in Sn increases. This is surprising behavior, since in liquid systems that show strong attractive forces, γ_M generally decreases with decreasing rather than increasing concentration of solute.

I have recalculated Anderson's γ_M expression using the most recent data on $\Delta G_{f,T}^0$ for UN (see appendix for references), which is given by the relation

$$(14) \Delta G_{f,T}^0 (UN) = -74,740 + 21.76 T,$$

which gives for γ_U

$$(15) \log \gamma_U = -8630/T + 2.687 - 5.9 x_U.$$

I believe that equation (15) is to be preferred for calculating the activity coefficients. Thus, for comparison purposes, values of γ_U from equation (14) are as follows:

γ_U for various mole fractions U

Temp. (K)	0.005	0.010	0.050	0.100
1700	0.004	0.004	0.002	0.001
1800	0.007	0.007	0.004	0.002
1900	0.013	0.012	0.007	0.004

Referring back to Table II, to the values of γ_U in Sn during the carbo-thermic reduction of UO_2 , we can see that the γ_U values during nitriding appear to be about an order of magnitude higher. Two possible explanations appear likely. Either, (1) gaseous CO and N_2 are influencing the behavior of γ_U in Sn, or (2) the uncertainties in the thermodynamic data preclude an accurate calculation of K_{eq} values.

The kinetics of nitriding of U solutions in Sn were studied by Schicks and coworkers,^{25,26} who found that times of the order of 10-30 hours were required to reach the final conversion yields of UN(s) in induction heated systems. By working with a fixed heating configuration and sample size, they were able to evaluate the necessary engineering and chemical parameters to quantitatively describe nitriding kinetics. The rate equation for nitriding is given by:

$$(16) \quad R\alpha = \frac{k_1 k_L \alpha C_S (C_U - C_U^*)}{k_1 C_U + k_L \alpha}$$

where:

R is the rate of absorption of nitrogen per unit of surface area (moles/cm²·s);

α is defined as A/V , cm²/cm³, i.e., the interfacial area between the gas phase and the liquid on a unit volume basis (A is interfacial area and V is volume of the melt);

k_L is the mass transfer coefficient of nitrogen in the liquid (cm/s);

k_1 is the forward chemical rate constant (cm³/mole-s);

C_U is the uranium concentration at time t (mole/cm³);

C_U^* is the equilibrium concentration of uranium (mole/cm³);

C_S is the concentration of dissolved nitrogen at the liquid interface (moles/cm³), in equilibrium with the gas at the interface.

This equation was successfully used to determine the mass transfer coefficient k_L and the chemical rate constant k_1 as a function of temperature. The constant k_L is influenced by the hydrodynamics of the system. These rate constants are essentially independent of all other variables. The temperature effect on the chemical rate constant k_1 can be summarized by the following Arrhenius-type equation

$$k_1 = 5.03 \times 10^{13} \exp(-108,000 \pm 12,000/RT) (\text{cm}^3/\text{mole-s}).$$

The influence of temperature on the mass transfer coefficient k_L is described by

$$k_L = 1.62 \exp(-18,300 \pm 6,500/RT) (\text{cm/s}).$$

From Schicks' studies and equation (16) above, it is apparent that the reaction kinetics are markedly dependent upon C_S , the nitrogen solubility (which is very low), and upon k_L , the mass transfer coefficient for nitrogen. Regarding the latter, Schicks found that stirring of the melt with a

larger induction coil greatly enhanced k_L . At LLL, we have found that addition of ~2 wt% Ca to the melt acts as a catalyst and reduces the time required for nitriding to 1-2 hours. We believe that the effect of the Ca is to promote the solubility of nitrogen in the Sn melt.

Schicks also found that the initial rates of nitriding of U were independent of temperature. It was only as the final degree of conversion to UN(s) was approached that temperature had a large effect. Final conversion yields of 100 percent could only be achieved at temperatures of about 1800-1840K. Above these temperatures, the yields dropped off to values of 80 percent at ~1870K, 60 percent at ~1920K, and 40 percent at ~2050K. Higher nitrogen pressures should shift the 100 percent conversion point to higher temperatures.

Fuwa and coworkers,^{11,27} in thermodynamic studies of nitriding in the U-Gd-Sn system found that Gd additions to the Sn melt raised the activity of U, and consequently lowered the temperature at which nitriding first occurred. The effect is negligible for the low fission product concentrations that we are concerned with in the Molten Tin Process, however it does suggest that a non fission product could be added to the melt to either lower the nitriding temperature or increase the degree of conversion.

In current nitriding studies in molten Sn at LLL, we have found that U nitrides at a more rapid rate than either Th or Pu at 1900K and 0.9 atm N_2 pressure. A nitriding run with a mixture of 8.0g U, 1.74g Pu and 1.5g Ca in 50g Sn for 2 hours gave a nitride phase with a U/Pu weight ratio of 10.14 compared with 4.88 in the initial mix. Th in molten Sn requires 5-6 hours for nitriding, as compared with 1-2 hours for U catalyzed with Ca (Ca does not seem to catalyze the nitriding of Th).

An experiment conducted by Fuwa¹¹ to simulate nitriding of a fuel/fission product mixture in Sn (9.5 percent U, 0.1 percent Ce, 0.1 percent Pr, 0.05 percent Zr, 0.05 percent Nb, 0.05 percent Mo, and 0.05 percent Ru) indicates that the UN(s) can be precipitated without detectable (less than ~1 percent of each of the fission product additives) coprecipitation of the fission products as determined by emission spectroscopy. The fission products appear to remain in solution in the Sn and solidify as tin intermetallics in the tin region upon cooldown, while the UN(s) precipitate settles to the bottom of the reaction container. More work is certainly needed in this area -- particularly in determining distribution coefficients for actinides and fission products between the Sn melt and nitride phases.

SOLUBILITIES OF M-SN COMPOUNDS IN SN

The liquidus curves (solubilities) for the Sn-rich compounds of U and the fission product elements in contact with liquid Sn are summarized in Fig. 3, and the Sn-rich compounds in equilibrium with the liquidus at the lowest temperatures are listed in Table VI. These data were taken from the available literature on binary diagrams,^{28,29,30} and where data were not available they were estimated. Estimated values in Fig. 3 are shown as dashed curves.

Fig. 3. Liquidus curves (solubilities) of the Sn-rich compounds of U and the fission product elements in contact with liquid Sn are depicted for temperatures of 200-1100°C. Estimated values are shown as dashed curves.

Table VI. Sn-Rich Compounds or Phases in
Contact with Sn Liquid at the Liquidus.

Ag ₃ Sn	Mo	Sb sol'n in β -Sn
BaSn ₅	NbSn ₂	SeSn
Cd sol'n in β -Sn	NdSn ₃	SmSn ₃
CeSn ₃	PdSn ₄	SrSn ₄
prob. CsSn ₄	prob. PmSn ₃	prob. Tc ₃ Sn
prob. EuSn ₃	PrSn ₃	TeSn
prob. GdSn ₃	prob. RbSn ₄	prob. Y ₂ Sn ₃
In sol'n in β -Sn	RhSn ₄	ZrSn ₂
LaSn ₃	Ru ₃ Sn ₇	USn ₃

Figure 3 shows that at temperatures below $\sim 600^\circ\text{C}$, the solubility of USn₃ in molten Sn falls to a very low level, while nearly all of the fission products remain in solution. Precipitation of USn₃ can therefore be used as a separation step to remove any residual U remaining after the nitriding step, and Th and possibly Pu could be expected to behave in similar fashion to the U. Fission products that would likely precipitate out with the U would be Mo, Nb, and possibly Tc and Ru.

Purification processes have not yet been developed for recovering the Sn for recycle after removing the actinides. Sn needs to be recycled because it would be too costly to discard it after use. Two metals that deserve consideration as additives to extract the fission products from Sn, are Al and Si. Neither of these metals forms compounds with Sn, nor shows any solid

solubility in Sn. Yet, these metals are prolific compound formers, and should extract the fission products from Sn as either aluminides or silicides. Thermodynamic data³¹ are not available to make an assessment of the relative stabilities of aluminides, silicides, or stannides in all cases, but generally it appears that the aluminides are most stable for the group 2 metals, and silicides for the balance of the fission product elements (the group 1 metals would have been removed by volatilization in an earlier step). Al and Si are relatively abundant and cheap compared to Sn, and aluminides and silicides should provide a corrosion resistant form in which to store radioactive wastes. Experimental work is needed to evaluate this approach.

APPENDIX - SUMMARY OF THERMODYNAMIC DATA

A general survey is given in this appendix of either references or partial tabulations of the thermodynamic data on metals, oxides, carbides, and nitrides that pertain to the fission product or actinide elements discussed in this report.

Metals and Gaseous Elements

Information on the vapor pressures and thermal data for the metals is generally from Hultgren et al.,¹⁰ with supplementary information by Honig and Kramer,³² and Brewer and Rosenblatt.⁷ Data on the gaseous elements is taken from JANAF.⁹

Oxides

The enthalpies of formation at room temperature are given by Brewer and Rosenblatt,⁷ and are summarized for the elements of interest in Table A-1. There is no convenient single literature source for the thermal functions for oxides, and it is considered beyond the scope of this report to summarize that information here. Such detailed information, when needed, is given in the text.

Table A-1. Enthalpies of Formation of Oxides of Interest to Nuclear Fuel Materials.⁷

Oxide	$\Delta H^0_{f,298}$ (kcal/mol)	Oxide	$\Delta H^0_{f,298}$ (kcal/mol)
Ag ₂ O	-7.3 ± 0.1	Rb ₂ O	-81 ± 2
BaO	-132.1 ± 2	Rh ₂ O ₃ ³³	-71.1 ± 9
CdO	-61.7 ± 0.5	RuO ₂	-72 ± 1
Ce ₂ O ₃	-429.3 ± 0.7	Sb ₂ O ₃ (cub)	-172.2 ± 1.5
Cs ₂ O	-81 ± 2	SeO ₂	-53.86
Eu ₂ O ₃	-394 ± 1	Sm ₂ O ₃	-433.9 ± 0.5
Gd ₂ O ₃	-433.9 ± 0.9	SnO ₂	-138.8 ± 0.1
In ₂ O ₃	221.3 ± 0.4	SrO	-140.5 ± 0.5
La ₂ O ₃	423.6 ± 0.2	TcO ₂	-103.7 ± 3
MoO ₂	-140.8 ± 0.2	TeO ₂	-77.1 ± 0.7
Nb ₂ O ₅	-454.7 ± 1	Y ₂ O ₃	-455.5 ± 0.5
Nd ₂ O ₃	-432.1 ± 0.2	ZrO ₂	-263.0 ± 0.5
PdO	-27.6 ± 0.8	PuO ₂	-252.9 ± 0.4
Pm ₂ O ₃	est. -433.0 ± 1	ThO ₂	-293.2 ± 0.4
Pr ₂ O ₃ (cub)	-436.8 ± 1.6	UO ₂	-259.0 ± 0.6

Carbides

Thermodynamic data on the carbides is of secondary interest to the Molten Tin Process to determine whether or not carbides of nuclear fuel materials can form in the presence of Sn. Carbide formation generally is not likely because of the higher stabilities of the Sn compounds or solutions in Sn. Data for the enthalpies of formation of some of the carbides are available in the

compilation of Kubaschewski and Alcock,³¹ and are summarized in Table A-II. In addition, it should be noted that Ag, Cd, In, Pd, Sb, and Sn are not expected to form carbides; Cs, Rb, Rh, Ru, and Tc under some conditions may form carbides of marginal stability; and Se and Te would be expected to form gaseous species such as CSe_2 . Thermodynamic data for the dicarbides of Y, La, and the rare earths are expected to be similar to those for CeC_2 and SmC_2 which have been listed in Table A-II.

Table A-II. Enthalpies of Formation of Oxides of Some Carbides of Interest to Nuclear Fuel Materials.³¹

Carbide	ΔH_f^0 (kcal/mol) f,298	Carbide	ΔH_f^0 (kcal/mol) f,298
BaC ₂	-17.7 ± 3.0	SrC ₂	-20.2 ± 4.0
CeC ₂	- 23.2 ± 1.7	ZrC _{0.96}	-48.27 ± 0.6
Mo ₂ C	-11.0 ± 0.7	Pu ₂ C ₃	-26.4 ± 2.0
NbC	- 33.0 ± 1.0	ThC _{1.94}	-28.0 ± C ₂
SmC ₂	-23.4 ± 2.0	UC _{1.9}	-23.0 ± 2.0

Nitrides

The enthalpies of formation for fission product and actinide elements that form stable nitrides are summarized in Table A-III. The data are from Kubaschewski and Alcock³¹ unless otherwise referenced. I have also summarized free energy functions in Table A-IV for the nitrides of Y, La, rare earths through Gd, and U. I do not anticipate nitride formation for the elements Ag, Cd, Pd, Rh, Ru, Sb, Se, Sn, Tc, or Te.

Table A-III. Enthalpies of Formation of Nitrides of Interest to Nuclear Fuel Materials. Data are from reference 31 unless otherwise indicated.

Nitride	$\Delta H_{f,298}^0$ (kcal/mol)	Nitride	$\Delta H_{f,298}^0$ (kcal/mol)
Ba_3N_2	-81.5 ± 7.5	PmN*	est -78
CeN	-78.0 ± 6.0	PrN*	est -78
Cs_3N^*	est. -20	Rb_3N^*	est -20
EuN^{34}	-46.5 ± 2.8	SmN	-77.2 ± 3.7
GdN^{34}	-73.4 ± 5.0	Sr_3N_2	-93.4 ± 5.0
InN	-33.0 ± 2.5	YN	-71.5 ± 5.0
LaN	-71.5 ± 5.0	ZrN	-88.0 ± 0.6
Mo_2N	-16.6 ± 0.5	PuN	-71.5 ± 1.6
Nb_2N	-59.4 ± 1.5	ThN	-90.5 ± 2.5
NdN*	est. -78	UN ³⁵	-72.4 ± 0.9

*These values were estimated by the author.

Table A-IV. Free Energy Functions
for Some Group 3 Nitrides and UN.

Nitride	$-(G_T^0 - H_{298}^0)/T$ (cal/mol-K) at T (K)			
	298	1800	1900	2000
YN*	12	23.62	24.19	24.77
LaN ³⁶	14.73	26.35	26.92	27.50
CeN ³⁶	16.49	28.79	29.44	30.06
PrN ³⁶	17.20	29.89	30.52	31.13
NdN ³⁶	17.85	29.92	30.55	31.15
SmN ³⁶	17.98	30.54	31.17	31.78
EuN ³⁶	20.76	32.24	32.80	33.34
GdN ³⁶	19.32	31.25	31.85	32.42
UN ³⁷	14.97	27.12	27.77	28.41

*Free energy functions for YN are derived by the author by estimating $S_{298}^0 = 12$ cal/mol-K, and that C_p is the same as that for LaN as given by Viksman et al.³⁶

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