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EQUATION-OF-STATE FOR ADVANCED FUELS

Interim Report

by

A. Sheth and L. Leibowitz

U OF C-AUA-USAEL

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

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ABSTRACT

A preliminary examination has been made of some existing physical property data for uranium and plutonium carbides and nitrides. A set of recommended values has been prepared for the compounds UC, UN, PuC, PuN, (U,Pu)C, and (U,Pu)N. The properties that have been evaluated are heat capacity, enthalpy, vapor pressure, melting point, heat of vaporization, and heat of fusion.

This preliminary evaluation is a prelude to a more extensive critical study of existing property data for candidate advanced fuels. The data presented should be considered an interim set until the rigorous critique, now in progress, is completed.

INTRODUCTION

The operation of breeder reactors is necessary to meet increasing electric demand and minimize electrical costs. Although an oxide-fueled breeder reactor has been under development for some time, fuels other than oxide fuels must be developed if the performance of the breeder reactor is to be improved. The advanced fuels being considered are carbides and nitrides of uranium and plutonium. These fuels not only have neutronic properties more favorable to breeding, but also have thermal conductivities that are about five times that of the oxide. These properties permit operation of fuel pins at higher linear power ratings and allow enough flexibility in design to optimize breeding ratio and minimize fabrication cost and fissile-material inventory. As a part of the recently initiated research program on advanced fuels, a report, ANL/CEN/AF-100, has been issued giving a detailed bibliography of property data on uranium and plutonium carbides and nitrides.

A more critical evaluation of the thermophysical properties of these materials will be made in the near future. However, in the interim, this report lists some recommended values for heat capacity, enthalpy, vapor pressure, melting point, and heats of fusion and vaporization for some selected advanced fuel candidates.

As a word of caution, this is a preliminary report and all the literature has not been thoroughly reviewed nor has the available data been critically analyzed. Extrapolations should be carefully made and due care should be exercised in using these values for accident analyses or any other work.

The compounds considered in this report are UC, UN, PuC, PuN, (U,Pu)C, and (U,Pu)N. References for the data used in this report are given at the end; however, a detailed bibliography may be found in ANL/CEN/AF-100.

Equation of State for Advanced Fuels

Evaluations were made of data on heat capacity, enthalpy, vapor pressure, melting point, heat of fusion, and heat of vaporization for UC, UN, PuC, PuN, (U,Pu)C and (U,Pu)N. In most of the cases, the emphasis was placed on the most recent experimental work or literature assessment. In a few cases, where the estimated or experimental data were not available, the estimation was made using linear interpolation or standard methods. To supplement the data that are presented in tabular form best fitting equation(s) were developed by fitting standard forms of equations by means of polynomial regression. No attempt was made to determine the optimum form of the equation. The preliminary recommended sets of properties are given below.

UC. The heat capacity and enthalpy of UC has been studied in the temperature range of 298 to 2800 K by experimental as well as analytical methods. The recent evaluation by Oetting¹ agrees with the available experimental data, and is recommended for general use. These values are given in Table 1. The best fitting equations, of the form shown, are as follows:

$$C_p^\circ = 14.7315 - 5.4072 \times 10^{-4} T + 1.02 \times 10^{-6} T^2 - \frac{2.38719 \times 10^5}{T^2} \quad (1)$$

$$H_T^\circ - H_{298}^\circ = - 5176.046 + 14.7315 T - 2.7036 \times 10^{-4} T^2 + 3.4 \times 10^{-7} T^3 + \frac{2.38719 \times 10^5}{T} \quad (2)$$

where C_p° = heat capacity in cal/mol-K

H_T° = enthalpy at temperature T in cal/mol

H_{298}° = enthalpy at 298 K in cal/mol

T = absolute temperature in K

TABLE 1. Heat Capacity and Enthalpy of UC

Temperature, K	Heat Capacity (C_p°), cal/mol-K	Enthalpy ($H_T^\circ - H_{298}^\circ$), cal/mol
298	11.98	0
300	12.00	24
400	13.19	1290
500	13.76	2641
600	14.11	4036
700	14.37	5461
800	14.58	6908
900	14.78	8376
1000	14.97	9864
1100	15.18	11371
1200	15.39	12899
1300	15.61	14449
1400	15.85	16022
1500	16.11	17621
1600	16.39	19245
1700	16.68	20899
1800	16.99	22582
1900	17.32	24298
2000	17.68	26048
2100	18.05	27834
2200	18.44	29658
2300	18.85	31522
2400	19.28	33428
2500	19.73	35378
2600	20.20	37374
2700	20.69	39418
2800	21.20	41512
2823	21.33	42012

The available data on vapor pressure of UC are not sufficient to evaluate critically and derive a single set of values. The vapor pressure varies with stoichiometry as well as the method of measurement. Nikol'skii and Levina^{1a} used Storms^{1b} data to derive theoretical equations linking uranium vapor pressure, carbon activity, and temperature and composition of UC solid solution. These equations are in a reasonable agreement with the experimental values given by Vozzella and coworkers^{2,3} for UC_{1.1}. Hence, for preliminary purposes one may use the values presented by Vozzella and coworkers in the range of 2200–2500 K; however, it must be borne in mind that their data represents a lower limit. These data are given in Table 2. The satisfying equations are as follows:

$$\log P_U \text{ (atm)} = 8.191 - \frac{3.624 \times 10^4}{T} \quad (3)$$

$$\log P_C \text{ (atm)} = 8.341 - \frac{3.608 \times 10^4}{T} \quad (4)$$

where P_U is partial pressure of uranium at temperature T in atmospheres and P_C is partial pressure of carbon at temperature T in atmospheres. Extrapolation of these equations should be done with great care. Changes in vapor species and heat capacity can cause marked deviations. In addition, a correction for the heat of fusion is needed above the melting point. Such effects will be explored in a more detailed report.

TABLE 2. Vapor Pressure of UC^a

Temperature, K	P_U , atm	P_C , atm
2190	4.3×10^{-9}	7.3×10^{-9}
2200	5.2×10^{-9}	8.7×10^{-9}
2300	2.71×10^{-8}	4.5×10^{-8}
2400	1.23×10^{-7}	2.03×10^{-7}
2500	4.96×10^{-7}	8.11×10^{-7}
2525	6.89×10^{-7}	1.13×10^{-6}

^aFor UC_{1.1}

Reavis⁴ studied the melting behavior of (U,Pu)C solid solutions using differential thermal analysis and metallographic techniques. He reported solidus and liquidus temperatures of UC as 2520 and 2540°C, respectively. These values are somewhat higher than other literature values, compiled by Burdi,⁵ which range from 2280 ± 50 to 2590 ± 50°C. For the present, however, the recommended value for the melting point of UC is 2530 ± 10°C, as suggested by Reavis⁴.

For the heat of vaporization, many discrepancies exist in the available values, which range from 235.1 kcal/mol reported by Vozzella and coworkers^{2,3} to 321.7 kcal/mol reported by Tetenbaum and Hunt⁶. Since the latter work is more recent and shows good internal consistency (varying from 322.4 to 321.9 kcal/mol in the temperature range from 2155 to 2455 K), the value of

321.7 kcal/mol is recommended as heat of vaporization of UC until a more thorough analysis is performed.

Considerable uncertainty also exists about the heat of fusion of UC. No direct measurements have been made and only estimations exist. The estimations are usually made by assuming a constant entropy of fusion; however, the values used for the entropy of the fusion vary from 6.8 to 4 eu. Reavis⁴ assumed 20 kcal/mol as a heat of fusion of UC to satisfy the melting behavior of (U,Pu)C, which is very high. Chasanov²⁸ suggested using 4.2 eu as the entropy of fusion. The use of the value of 4.2 eu and a melting point of 2530°C yields 11.8 kcal/mol as a heat of fusion of UC. This value is recommended until more work is carried out.

UN. A reasonable amount of work has been done on the heat capacity and enthalpy of UN in the temperature range from 298 to 3000 K. Tagawa⁷ has recently evaluated heat capacity data of UN; these can be used until a more critical analysis is made. His evaluated data are given in Table 3 and the satisfying equations are as follows:

$$C_P^\circ = 12.942 + 5.4509 \times 10^{-4} T + 1.045 \times 10^{-6} T^2 - \frac{1.62823 \times 10^5}{T^2} \quad (5)$$

$$H_T^\circ - H_{298}^\circ = -4436.52 + 12.942 T + 2.72545 \times 10^{-4} T^2 + 3.4833 \times 10^{-7} T^3 + \frac{1.62823 \times 10^5}{T} \quad (6)$$

where the terms have the same meanings and dimensions as were given earlier.

The available literature values on vapor pressure or decomposition pressure of UN are not sufficient to warrant critical evaluation. Vaporization occurs incongruently by preferential loss of nitrogen, forming the two-phase system comprising nitrogen-saturated liquid uranium and uranium-saturated nonstoichiometric uranium mononitride. Because the vapor pressure depends on the stoichiometry of the initial sample, comparison of different data is difficult. The recent evaluation made by Tagawa⁷ may be used until more data are collected and further evaluation is made. His data are given in Table 4 and the satisfying equations are as follows:

$$\log P_U \text{ (atm)} = 5.805 - \frac{26010}{T} \quad (7)$$

$$\log P_{N_2} \text{ (atm)} = 9.849 - \frac{31980}{T} \quad (8)$$

In this case the overriding pressure at high temperature is due to nitrogen and, hence, species changes may not be too important in influencing extrapolation of Eq. 8. Above melting, of course, a correction due to heat of fusion would still be needed.

TABLE 3. Heat Capacity and Enthalpy of UN

Temperature, K	Heat Capacity (C_p°), cal/mol-K	Enthalpy ($H_T^\circ - H_{298}^\circ$), cal/mol
298	11.37	0
300	11.39	21
400	12.31	1211
500	12.82	2470
600	13.19	3771
700	13.50	5106
800	13.79	6471
900	14.08	7865
1000	14.37	9287
1100	14.67	10739
1200	14.99	12222
1300	15.32	13737
1400	15.67	15286
1500	16.04	16872
1600	16.43	18495
1700	16.83	20157
1800	17.26	21862
1900	17.71	23610
2000	18.17	25403
2100	18.66	27245
2200	19.17	29136
2300	19.69	31079
2400	20.24	33075
2500	20.81	35128
2600	21.40	37238
2700	22.01	39408
2800	22.64	41641
2900	23.29	43937
3000	23.97	46300

TABLE 4. Vapor Pressure of UN

Temperature, K	P_U , atm	P_{N_2} , atm
1600	3.55×10^{-11}	7.22×10^{-11}
1700	3.0×10^{-10}	1.0×10^{-9}
1800	2.2×10^{-9}	1.22×10^{-8}
1900	1.3×10^{-8}	1.04×10^{-7}
2000	6.31×10^{-8}	7.23×10^{-7}
2100	2.62×10^{-7}	4.17×10^{-6}
2200	9.6×10^{-7}	2.06×10^{-5}
2300	3.13×10^{-6}	8.81×10^{-5}
2400	9.27×10^{-6}	3.34×10^{-4}
2500	2.52×10^{-5}	1.14×10^{-3}

Usually the melting point and the decomposition pressure of UN are measured simultaneously. Olson and coworkers⁸ carried out a detailed study while observing the apparent melting point of UN as a function of N_2 pressure. An empirical equation was fitted to their data such that the curve asymptotically approaches the change in free energy line (ΔF°) as the temperature decreases. This equation fails to satisfy the data of other workers; however, since the melting point does depend on the N_2 pressure, the value of $2860 \pm 30^\circ\text{C}$, which was suggested by Weber,⁹ should be used as the apparent melting point of UN in the nitrogen-pressure range from 2.5 to 6 atm.

In studying heat of vaporization of UN, Gingerich¹⁰ considered the following reactions:

and its partial reactions

Using the above sets of reactions and the derived values of Gingerich for the enthalpies of transformations, one can calculate 199.6 kcal/mol as the heat of vaporization of UN when reduced to 298 K. This value agrees very well with the value of 199 ± 1 kcal/mol at 10^{-3} to 1.0 Torr N_2 pressure given by Hoenig¹¹. A combination of these two sets of data yields the recommended value of 199 kcal/mol for the heat of vaporization of UN.

No data are available on the heat of fusion of UN. Since the melting point is a function of N_2 pressure, the heat of fusion cannot be estimated by standard methods. Assuming a melting point of 2860°C and an entropy of fusion of 4.2 eu yields a heat of fusion value of 13.2 kcal/mol.

PuC. The data on heat capacity and enthalpy of PuC are very scarce. In the limited work in the literature, the stoichiometry is found to vary from $\text{PuC}_{0.82}$ to PuC, and this seems to affect the values of heat capacity and enthalpy. It is suggested that the experimental data collected by Kruger¹² should be used. He measured the enthalpy of PuC using an isothermal drop calorimeter in the range from 298 to 1300 K. These data have been extensively extrapolated up to 1900 K by various authors. In view of this, until more experimental data are collected, one should continue using the data extrapolated from Kruger's work. The data covering the entire extrapolated range are given by Oetting¹³ and are represented here in Table 5. The satisfying equations are as follows:

$$C_P^\circ = 13.08 + 11.44 \times 10^{-4} T - \frac{3.232 \times 10^5}{T^2} \quad (9)$$

$$H_T^\circ - H_{298}^\circ = -5035 + 13.08 T + 5.718 \times 10^{-4} T^2 + \frac{3.232 \times 10^5}{T} \quad (10)$$

Literature on the vapor pressure of PuC deals with two types of systems. The first is single phase PuC, in which the partial pressure of plutonium over PuC is measured. The second system is in the diphasic region of PuC and Pu_2C_3 , which involves the decomposition reaction

In any case, the data are very scanty and more complete work covering a wide range of temperature and pressure is required. In the meantime, one may use the data of Olson and coworkers¹⁴ for the diphasic system and single-phase data collected at Argonne National Laboratory¹⁵. Tables 6 and 7 give the data for single-phase and diphasic systems, respectively. The satisfying equations are as follows:

$$\text{Pu in PuC}_{1-x}: \log P_{\text{Pu}} (\text{atm}) = (8.05 \pm 0.43) - \frac{24050 \pm 462}{T} \quad (11)$$

$$\text{Pu in PuC} + \text{Pu}_2\text{C}_3: \log P_{\text{Pu}} (\text{atm}) = (5.30 \pm 0.17) - \frac{19160 \pm 260}{T} \quad (12)$$

The same caution mentioned in connection with UC should be exercised in extrapolation of these equations.

The available data on the melting point of PuC seems to agree very well. Very little effect of stoichiometry on the melting point is observed; however, this may be due to insufficient characterization of the samples used. In any case, one may use 1654°C as the melting point of $\text{PuC}_{0.85}$. This value is presented from Oetting's recent review¹³ of thermochemical data of plutonium compounds.

The limitations cited for evaluating vapor pressure data for PuC also apply to the heat of vaporization. From a study involving the diphasic region, Olson and coworkers¹⁴ reported 87.6 kcal/gfw as the heat of vaporization; Oetting¹³ reported 235 ± 35 kcal/mol at 1806 K and 105 kcal/mol at 1900 K. However, a number of uncertainties in the data exist. In consideration of these facts, until more work is done, one should use 87.6 kcal/gfw in the diphasic region and 235 ± 35 kcal/mol in the single-phase region as the heat of vaporization of PuC.

TABLE 5. Heat Capacity and Enthalpy of PuC

Temperature, K	Heat Capacity (C_P°), cal/mol-K	Enthalpy ($H_T^\circ - H_{298}^\circ$), cal/mol
298	9.785	0
300	9.88	18
400	11.52	1095
500	12.36	2292
600	12.87	3554
700	13.22	4860
800	13.49	6196
900	13.71	7556
1000	13.90	8936
1100	14.07	10335
1200	14.23	11750
1300	14.38	13181
1400	14.52	14626
1500	14.66	16085
1600	14.79	17557
1700	14.92	19043
1800	15.04	20541
1900	15.16	22051
1927	15.19	22461

TABLE 6. Vapor Pressure of PuC

Temperature, K	P_{Pu} , atm
900	2.0×10^{-19}
1000	9.7×10^{-17}
1100	1.53×10^{-14}
1200	1.02×10^{-12}

TABLE 7. Vapor Pressure of PuC (PuC + Pu₂C₃)

Temperature, K	P _{Pu} , atm
1366	1.8x10 ⁻⁹
1450	1.21x10 ⁻⁸
1550	8.69x10 ⁻⁸
1650	4.88x10 ⁻⁷
1750	2.24x10 ⁻⁶
1835	7.23x10 ⁻⁶

The same problems exist in evaluating the heat of fusion of PuC as were mentioned for UC. By the same type of calculation used for UC, one obtains a value of 8.1 kcal/mol as the heat of fusion of PuC.

PuN. Most of the work on heat capacity and enthalpy of PuN in the literature involves only estimations. Therefore, the latest estimation made by Kent and coworkers¹⁶, is recommended. Their values are in reasonable agreement with the values given by other workers and shows the proper trend. Until more work is done and more experimental data are collected, one should use their data, which are given in Table 8. The satisfying equations are as follows:

$$C_P^\circ = 14.3959 + 7.149 \times 10^{-4} T + 4 \times 10^{-8} T^2 - \frac{4.81804 \times 10^5}{T^2} \quad (13)$$

$$H_T^\circ - H_{298}^\circ = -5938.87 + 14.3959 T + 3.5745 \times 10^{-4} T^2 + 1.333 \times 10^{-8} T^3 + \frac{4.81804 \times 10^5}{T} \quad (14)$$

The data on vapor pressure of PuN, although not complete, are very consistent. However, not all workers give partial pressure of N₂ and the temperature range covered is usually very small. In order to arrive at a recommended set of values, the data of Kent¹⁶, Battelle Memorial Institute,^{17,18} and Rand¹⁹ were combined. The best fitting equations were obtained by polynomial regression. The raw data are given in Table 9 and the best fitting equations with average errors are as follows:

$$\log P_{Pu} \text{ (atm)} = 5.9863 - \frac{2.1056 \times 10^4}{T} \quad (15)$$

$$\text{(Average Error } \approx \pm 12.5\%) \quad (16)$$

$$\log P_{N_2} \text{ (atm)} = 5.2125 - \frac{2.0967 \times 10^4}{T}$$

$$\text{(Average error } \approx \pm 12.8\%)$$

TABLE 8. Heat Capacity and Enthalpy of PuN

Temperature, K	Heat Capacity (C_P°), cal/mol-K	Enthalpy ($H_T^\circ - H_{298}^\circ$), cal/mol
298	9.19	0
400	11.67	1009
600	13.50	3631
800	14.24	6413
1000	14.67	9307
1200	14.98	12274
1400	15.23	15294
1600	15.44	18362
1800	15.64	21470
2000	15.87	24615

TABLE 9. Vapor Pressure of PuN

Temperature, K	P_{Pu} , atm	P_{N_2} , atm	References
1658	1.59×10^{-7}		16
1800	1.76×10^{-6}		
1900	7.73×10^{-6}		
1976	2.15×10^{-5}		
1400	1.0×10^{-9}	2.0×10^{-10}	17
1600	7.0×10^{-8}	1.0×10^{-8}	
1800	2.2×10^{-6}	3.8×10^{-7}	
2000	3.2×10^{-5}	5.5×10^{-6}	
2200	3.4×10^{-4}	5.8×10^{-5}	
2400	1.5×10^{-3}	2.6×10^{-4}	
1885	4.89×10^{-6}	1.0×10^{-6}	18
1920	8.15×10^{-6}	1.7×10^{-6}	
1925	1.16×10^{-5}	2.5×10^{-6}	
1995	2.64×10^{-5}	5.6×10^{-6}	
2055	5.3×10^{-5}	1.1×10^{-5}	
2130	1.09×10^{-4}	2.3×10^{-5}	
1873	6.25×10^{-6}		19
1973	2.41×10^{-5}		
2073	8.16×10^{-5}		

Extreme caution should be exercised here, too, in any extrapolation of these equations.

As in the case of UN, the melting behavior of PuN is affected by the N₂ pressure. In the literature, apparent melting points or decomposition temperatures are given at widely varying nitrogen pressures. In view of this, values given by Spear²⁰ should be used. He has reported an apparent melting point of $2570 \pm 30^\circ\text{C}$ at 1 atm nitrogen pressure and has estimated a value of $2830 \pm 50^\circ\text{C}$ at 50 ± 20 atm nitrogen pressure.

No data are available in the literature on the heat of vaporization or heat of fusion of PuN. Owing to the clearcut effect of N₂, it is difficult to estimate these values; however, using 2570°C as melting point and assuming an entropy of fusion of 4.2 eu, we find a heat of fusion of 11.9 kcal/mol.

(U,Pu)C. No work has been found in the literature in which heat capacity and enthalpy of (U,Pu)C have been measured. Therefore, an attempt was made to use a linear interpolation between data for UC and PuC to obtain an estimate for (U,Pu)C. Before doing this, the approach was tested by interpolating data for UN and PuN, and comparing the results with published values for the heat capacity of (U,Pu)N. The estimated data from UN and PuN and recommended values for (U,Pu)N were in good agreement (Maximum deviation of 10% near 2000 K). Kerrisk²⁹ has used a similar approach to calculate heat capacity of (U_{0.8}Pu_{0.2})C_{0.97} and has reported a maximum uncertainty of 10% in the vicinity of melting point. Following the same procedures, values for the heat capacity and enthalpy for (U_{0.8}Pu_{0.2})C were estimated using linear interpolation and recommended data for UC and PuC. The results are given in Table 10. The satisfying equations are as follows:

$$C_p^\circ = 14.3951 - 1.9279 \times 10^{-4} T + 8.1 \times 10^{-7} T^2 - \frac{2.54754 \times 10^5}{T^2} \quad (17)$$

$$H_T^\circ - H_{298}^\circ = -5143.20 + 14.3951 T - 9.6395 \times 10^{-5} T^2 + 2.7 \times 10^{-7} T^3 + \frac{2.54754 \times 10^5}{T} \quad (18)$$

As in the case of heat capacity and enthalpy, very few reliable data are available on vapor pressure of (U,Pu)C. The upper limit of the partial pressure of plutonium given by Ainsley and coworkers²¹ in 1963 is the only set of consistent data available. These data are given in Table 11 and the satisfying equation is as follows:

$$\log P_{\text{Pu}} (\text{atm}) = 5.47 - \frac{23000}{T} \quad (19)$$

The melting point of (U,Pu)C appears to be affected by composition to a greater extent than that of the other compounds discussed previously. In the literature, one can find measurements using 5 to 20% Pu. There is also a distinct effect of oxygen and nitrogen incorporated as impurities. Some workers have also reported a slight effect from dissolved sesquicarbide. In view of this, until more work is done and a more thorough analysis is performed, the melting point values given in Table 12 are suggested.

Using the estimated values for the heat of fusion of UC and PuC, and the linear interpolation method used by Reavis^{4,23} the value obtained for the heat of fusion of (U_{0.8}Pu_{0.2})C is 11.1 kcal/mol.

TABLE 10. Heat Capacity and Enthalpy of (U,Pu)C^a

Temperature, K	Heat Capacity (C _p ^o), cal/mol-K	Enthalpy (H _T ^o - H ₂₉₈ ^o), cal/mol
298	11.54	0
300	11.58	23
400	12.86	1251
500	13.48	2571
600	13.86	3940
700	14.14	5341
800	14.36	6766
900	14.57	8212
1000	14.76	9678
1100	14.96	11164
1200	15.16	12669
1300	15.36	14195
1400	15.58	15743
1500	15.82	17314
1600	16.07	18907
1700	16.33	20528
1800	16.60	22174
1900	16.89	23849

^aEstimated for (U_{0.8}Pu_{0.2})C from data for UC and PuC using linear interpolation.

TABLE 11. Vapor Pressure of (U,Pu)C^a

Temperature, K	P _{Pu} , atm
1703	9.2x10 ⁻⁹
1773	3.14x10 ⁻⁸
1873	1.55x10 ⁻⁷
1973	6.5x10 ⁻⁷
2073	2.37x10 ⁻⁶

^aFor (U_{0.85}Pu_{0.15})C

TABLE 12. Melting Point of (U,Pu)C

Compound	Solidus Temperature	Liquidus Temperature	Reference
(U _{0.95} Pu _{0.05})C _{0.98}	2500 $\pm$ 20°C	2535 $\pm$ 20°C	22
(U _{0.8} Pu _{0.2})C	2275 $\pm$ 20°C	2485 $\pm$ 20°C	23

No data are available in the literature about the heat of vaporization of (U,Pu)C.

(U,Pu)N. Regarding the heat capacity and enthalpy of mixed nitride, the only work that is available in the literature is by Alexander and coworkers.²⁴ They give values for the heat capacity and enthalpy of (U_{0.8}Pu_{0.2})N in the range from 298 to 2400 K; however, the values for the last 600 K are extrapolated. These data are presented in Table 13 and the satisfying equations are as follows:

$$C_P^\circ = 10.84 + 2.6 \times 10^{-3} T \quad (20)$$

$$H_T^\circ - H_{298}^\circ = -3345.77 + 10.84 T + 1.3 \times 10^{-3} T^2 \quad (21)$$

TABLE 13. Heat Capacity and Enthalpy of (U,Pu)N^a

Temperature, K	Heat Capacity (C _P [°]), cal/mol-K	Enthalpy (H _T [°] - H ₂₉₈ [°]), cal/mol
298	11.61	0
400	11.88	1198
600	12.40	3626
800	12.92	6158
1000	13.44	8794
1200	13.96	11534
1400	14.48	14378
1600	15.00	17326
1800	15.52	20378
(2000)	(16.04)	(23534)
(2200)	(16.56)	(26794)
(2400)	(17.08)	(30158)

^aFor (U_{0.8}Pu_{0.2})N; values in parentheses are extrapolated.

Only a very limited amount of work has been done on the vapor pressure of mixed nitrides. Moreover, only Alexander and coworkers²⁴ have given partial pressures of each individual species. Their data are in good agreement, however, with the work of Potter²⁵ and Keller.¹⁸ Since there was no best-fitting equations available for Alexander's data, they were fitted to the standard form using polynomial regression. The data are given in Table 14 and the equations with their average errors are as follows:

$$\log P_U \text{ (atm)} = 7.6619 - \frac{3.0416 \times 10^4}{T} \quad (22)$$

(Average error $\approx$ 20.4%)

$$\log P_{Pu} \text{ (atm)} = 5.2505 - \frac{2.0893 \times 10^4}{T} \quad (23)$$

(Average error $\approx$ 8.5%)

$$\log P_{N_2} \text{ (atm)} = 4.5797 - \frac{2.1089 \times 10^4}{T} \quad (24)$$

(Average error $\approx$ 6.9%)

As with the other nitride fuels, the melting point or dissociation temperature depends upon the nitrogen pressure; however, the data in the literature are very sparse. In view of this, the values reported by Huebotter²⁶ and Nightingale²⁷ should be used. These data, which are for $(U_{0.8}Pu_{0.2})N$, are given in Table 15.

TABLE 14. Vapor Pressure of $(U,Pu)N^a$

Temperature, K	P_U , atm.	P_{Pu} , atm.	P_{N_2} , atm.
1400	1.0×10^{-14}	2.0×10^{-10}	3.0×10^{-11}
1600	3.0×10^{-12}	1.5×10^{-8}	2.5×10^{-9}
1800	6.3×10^{-10}	5.1×10^{-7}	8.8×10^{-8}
2000	4.0×10^{-8}	6.7×10^{-6}	1.1×10^{-6}
2200	7.0×10^{-7}	5.8×10^{-5}	1.0×10^{-5}
2400	8.1×10^{-6}	3.1×10^{-4}	5.5×10^{-5}

^aFor $(U_{0.8}Pu_{0.2})N$

TABLE 15. Melting Point (Dissociation Temperature) of $(U,Pu)N$

Compound	Dissociation Temperature, °C	Nitrogen Pressure, atm	Reference
$(U_{0.8}Pu_{0.2})N$	2360	< 1 atm	26
$(U_{0.8}Pu_{0.2})N$	2780 ± 20	> 1 atm	27

No data are available for the heats of vaporization and fusion of (U,Pu)N; however, using linear interpolation and estimated heat of fusion values for UN and PuN, one can calculate the heat of fusion of (U_{0.8}Pu_{0.2})N to be 12.9 kcal/mol.

It should be reemphasized that extrapolation of vapor-pressure equations should be done with great caution. Changes in the vapor species may produce major changes in vapor pressure. Large errors may result if important species that are not adequately represented in the lower temperature equations are present at higher temperatures. In addition, any extrapolation through the melting point must be corrected for the heat of fusion, and variations in relevant heat capacities must be allowed for, if necessary. These effects will be considered in more detail in the more complete study currently being performed.

CONCLUSIONS

This report presents a recommended set of thermophysical property values for candidate advanced fuels which may reasonably be used until a more thorough critique of the available data, now in progress, is completed. When no data were available, values were estimated, if possible, using standard estimation methods. Literature data, in some cases, were fitted to standard equations with little or no attempt to optimize the form of the equations. For these reasons, care should be exercised in extrapolating the values given. This preliminary survey of the existing data has revealed many serious gaps in the necessary information. Both experimental work and analysis are needed to rectify that situation.

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