**PHASE EQUILIBRIA AND MELTING POINT DATA
FOR ADVANCED FUEL SYSTEMS**

by

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Chemical Engineering Division

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PHASE EQUILIBRIA AND MELTING POINT DATA FOR ADVANCED FUEL SYSTEMS

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ABSTRACT

Thermodynamic and phase equilibria data on UC, PuC, (U,Pu)C, UN, PuN, and (U,Pu)N systems and on these systems plus fission product elements are presented as a basis for predicting the chemical state of irradiated mixed carbide or mixed nitride fuel. Melting point data for the systems listed above are also given.

INTRODUCTION

Free energy data for various reactions that may occur during irradiation of fast reactor fuels and information on the phase relationships that exist between fission-product elements and the fuel form the basis for predicting the chemical state of irradiated fuel. This information is also needed for interpreting data obtained in postirradiation studies of the fuel. In this report, available data on free energy and phase relationships of the (U,Pu)C-fission product and (U,Pu)N-fission product systems are discussed and used to predict the chemical state of irradiated actinide carbides and nitrides. The report also discusses the effect of low concentrations of oxygen on both the carbide and nitride fuel. Melting points for UC, PuC, (U,Pu)C, UN, PuN, and (U,Pu)N systems are given in the Appendix.

PHASE EQUILIBRIA FOR IRRADIATED FUELS

The free energy data available on the reactions of fission product elements to form carbides, alloys, or compounds with uranium and/or plutonium, and to form alloys or compounds with cladding materials are shown in Table 1 and Fig. 1. Table 1 also includes the melting points and boiling points of fission-product elements to allow easy assessment of the possibility of transport of these elements in the vapor phase. The fission yields from ^{235}U and ^{239}Pu are listed so that their relative importance to the chemistry of carbide fuels may be more readily assessed. The free energy data available in the literature were fitted to a linear temperature dependence of the form

$$\Delta G = -A + BT \quad (1)$$

where ΔG is in cal/mol, A is (10^3 cal)/mol, B is cal/mol-deg, and T is temperature in K. The temperature range over which the analytical expression was derived for the free energy of reaction is also given. Unless otherwise stated, the ΔG value listed in Table 1 is the standard free energy of formation of the compound shown (*i.e.*, the free energy of the reaction by which the listed compound is formed from its elements, when all the reactants and products are in the standard states in the given temperature range). Also

TABLE 1. Free Energy for the (U,Pu)C-Fission Product System

Element	M.P., K ^a	B.P., K ^a	Fission Yield, ^b %		Reaction (std. reaction of formation unless stated otherwise)	$\Delta G(\text{cal}) = -A + BT$			Ref.
			235	239		A 10 ³ cal mol	B cal mol-deg	Temp. Range, K	
Ag	1234	2223	0.03	1.2					
Ba	1123	1800	6.7	5.9	Ba(g) + 2C(s) → BaC ₂ (s)	56.1	14.4	1300-1650	1
					Ba(l) + 2C(s) → BaC ₂ (s)	19.7	-2.7	1300-1650	1,2
Cd	594	1040	0.19	0.9	→ PuCd ₁₁	45.9	35.7	631-679	3
					→ PuCd ₆	39.27	25.86	679-904	3
					→ UCd ₁₁	27.3	36.4	573-746	4
Ce	1088	2700	14 ^c	12 ^c	→ CeC	27.9	8.2	815-940	5
					Ce(l) + 2C(s) → CeC ₂ (s)	36.2	4.4	1700-2200	6,2
Cr	2200	2750	d	d	→ Cr ₃ C ₂	13.3	-4.15	885-1098	7
					→ Cr ₇ C ₃	29.45	-7.03	880-1023	7
					→ Cr ₂₃ C ₆	77.0	-18.3	1150-1300	8
Cs	302	943	19.4	21.0	Cs(g) + C(s) → CsC ₃ (s)	33.8	23.8	720-1020	9
					Cs(g) + C(s) → CsC ₁₀	31.3	18.9	720-1020	9
					Cs(g) + C(s) → CsC ₂₄	34.0	18.2	720-1020	9
Fe	1805	3270	d	d	→ Fe ₃ C	-2.68	-2.62	1000-1420	10
					→ Fe ₂ C	-2.5	-2.5	450-650	10
					→ PuFe ₂	12.3	2.27	790-1106	11
					→ UFe ₂	16.68	2.54	903-1043	12
					→ UFeC ₂	33.0	3.46	995-1051	13
					→ UFeC ₂	35.0	5.19	1051-1084	13
					→ UFe ₂	17.58	3.23	1043-1153	12
I	386	457	2.0	1.5	→ UI ₃	131.2	50.4	470-670	14
					→ UI ₄	134	37	779-1030	15
In	429	1723	0.02	0.0 [*]	→ UIn ₃	26.7	13.7	626-950	4,16
					→ UIn ₃	23.0	11.3	1093-1314	16
Kr	117	121	3.9	2.0					

TABLE 1. Free Energy for the (U,Pu)C-Fission Product System (cont'd.)

Element	M.P., K ^a	B.P., K ^a	Fission Yield, ^b %		Reaction (std. reaction of formation unless stated otherwise)	$\Delta G(\text{cal}) = -A + BT$		Temp. Range, K	Ref.
			235	239		A 10^3 cal mol	B cal mol-deg		
La	1193	3743	6.5	5.7	$\text{La(l)} + 2\text{Cs(s)} \rightarrow \text{LaC}_2(\text{s})$	20.3	-2.8	1700-2300	2,6
Mn	1490	2420	d	d	$+ \text{Mn}_3\text{C}$	3.33	-0.26	298-1000	17
					$+ \text{Mn}_3\text{C}$	5.24	1.65	1000-1173	17
					$+ \text{Mn}_7\text{C}_3$	30.5	9.0	900-1100	18
					$+ \text{Mn}_5\text{C}_2$	21.6	6.4	900-1100	18
					$+ \text{Mn}_{23}\text{C}_6$	92.0	33	900-1100	18
Mo	2893	4800	25.0 ^d	22.9 ^d	$+ \text{Mo}_2\text{C}$	12.0	-1.44	600-1400	19
					$+ \text{MoC}_{1-x}$	2.2	-2.55	1900-2200	20
					$+ \text{Mo}_3\text{C}_2$	4.68	-1.15	1650-2300	21
					$+ \text{Mo}_7\text{C}_3$	2.4	-1.0	1650-2300	21
					$+ \text{Mo}_{23}\text{C}_6$	1.3	-0.7	1650-2300	21
Na	370	1156	e	e	$+ \text{Na}_2\text{C}_2$	-8.375	-3.75	900-1100	22
Nd	1297	3300	18.1	15.1	$\text{Nd(l)} + 2\text{C(s)} \rightarrow \text{NdC}_2(\text{s})$	18.4	-5.7	1500-2300	2,6
Ni	1730	3000	d	d	$+ \text{Ni}_3\text{C}$	-8.11	-1.7	298-1000	17
					$+ \text{UNi}_5$	67.65	22.9	1070-1320	23
Pd	1820	2473	1.5	15	$+ \text{UPd}_3$	90.6	13.1	1370-1770	42
Pm	1350	2370	2.2	1.9					
Pr	1208	3400	6.1	5.7	$+ \text{PrC}$	30.4	10.8	870-950	5
					$\text{Pr(l)} + 2\text{C(s)} \rightarrow \text{PrC(s)}$	38.9	6.2	1600-2100	2,6, 24-26
Pu	913	3500	f	f	$\text{Pu(l)} + 0.9\text{C(s)} \rightarrow \text{PuC}_{0.9}$	14.06	1.60	920-1060	27
					$+ \text{PuC}_{0.9}$	11.49	-0.74	1450-1850	27
					$2\text{PuC} + \text{C} \rightarrow \text{Pu}_2\text{C}_3$	4.2	-3.48	900-1900	26,27
Rb	312	973	3.9	1.8	$\text{Rb(g)} + \text{C(s)} \rightarrow \text{RbC}$	28.8	13.3	620-1020	28
					$\text{Rb(g)} + \text{C(s)} \rightarrow \text{RbC}$	27.5	18.5	620-1020	28
					$\text{Rb(g)} + \text{C(s)} \rightarrow \text{RbC}$	30.6	17.6	620-1020	28

TABLE 1. Free Energy for the (U,Pu)C-Fission Product System (cont'd.)

Element	M.P., K ^a	B.P., K ^a	Fission		Reaction (std. reaction of formation unless stated otherwise)	ΔG(cal) = -A + BT			Ref.
			Yield, ^b %			A	B	Temp. Range, K	
			235	239		10 ³ cal mol	cal mol-deg		
Rh	3440	6200	3.4	5.6	+ URh ₃ + URh ₃ C _x + U ₂ RhC ₂	61.37 57.04 75.67	-1.1 -5.5 7.75	1000-1150 870-1100 1000-1200	29 29 30,31
Ru	2723	4423	12.5 ^g	22.0 ^g	+ URu ₃ + URu ₃ C _x + PuRu ₂ + U ₂ RuC ₂	58.8 53.1 7.90 -13.7	8.4 -7.0 1.11 -43.7	1000-1140 860-1070 900-1100 1600-1800	32 32 33 42
Sb	904	1650	0.1	0.2					
Sm	1345	2173	1.9	3.2	Sm(l) + 2C(s) + SmC ₂ (s)	21.0	-3.5	1400-2000	2,6
Sn	505	2573	0.1	0.03	+ USn ₃	40.8	1.4	636-950	4
Sr	1047	1633	9.1	3.7	Sr(g) + 2C(s) + SrC ₂ (s) Sr(l) + 2C(s) + SrC ₂ (s)	54.2 20.3	17.1 -3.3	1200-1500 1200-1500	1 1,2,34
Tc	2445	5150	5.8	6.0					
Te	725	1663	2.0	2.0					
Xe	16.1	166	20.6	22.7					
U	1405	4090	f	f	+ UC _{1,0} + UC _{1,0} 2UC + C + U ₂ C ₃ 2UC + C + U ₂ C ₃	24.08 25.96 3.04 0.88	-1.27 0.0 5.19 1.62	1000-1350 1350-2000 800-1100 1100-2000	30 30 50 30
Y	1797	3600	4.7	1.7	+ YC ₂ + YC + Y ₂ C ₃	23.9 15.36 29.98	-6.1 0.0 0.0	1600-2000 1700 1700	35 35 35
Zr	2130	3170	30.7	21.3	+ ZrC	53.8	7.9	800-2000	2,36, 37

^a"Handbook of Chemistry and Physics," 46th Ed.,
Chemical Rubber Company (1965).

^bCalculated from data by M. E. Meek and B. F. Rider,
APED-5398-A (1968).

^c25% ¹⁴⁴Ce, 75% ¹⁴⁴Nd.

^dComposition of Type 316 stainless steel cladding:
Fe, 65%; Cr, 17%; Ni, 13%; Mo, 2.2%.

^eFor consideration in sodium bonded fuel elements.

^fThe fuel matrix.

^g40% ¹⁰⁶Ru, 60% ¹⁰⁶Pd.

Fig. 1. Free Energy for the (U,Pu)C-Fission Product System

listed are some standard reactions such as the following

for which ΔG data were not directly taken from the literature. For reaction (2), ΔG was determined from ΔG values for

and

The data from Table 1 are plotted in Fig. 1 in temperature range 400 to 2100 K. Differences between Fig. 1 and similar figures^{38,39} previously published are difficult to assess. Prior work did not include references for the free energy data that were plotted.

Phase Equilibrium in Irradiated Uranium Carbide

Phase equilibria in the uranium-carbon system were recently reviewed by the IAEA Panel on Thermodynamic Properties,³⁰ who recommend the phase diagram shown in Fig. 2. The recommended U-C phase diagram is consistent with a large number of experimental observations, thereby indicating that phase equilibria in the uranium-carbon system are well known.

The free energy data and phase relationships of the individual fission products with uranium and carbon are best considered in a number of groups of chemically similar elements:

- (a) Elements from lanthanum to gadolinium
- (b) Yttrium, zirconium, and niobium
- (c) Barium and strontium
- (d) Molybdenum, technetium, ruthenium, rhodium, and palladium
- (e) Selenium and tellurium
- (f) Bromine, iodine, cesium, and rubidium
- (g) Krypton and xenon
- (h) Silver, cadmium, indium, tin, and antimony

(a) Lanthanum to Gadolinium. The systems comprising uranium and carbon and one of the elements lanthanum,⁴⁰⁻⁴⁴ cerium,⁴⁰⁻⁴⁶ praseodymium,⁴⁰ neodymium,⁴⁰⁻⁴² and gadolinium^{40,47} have been studied. The lanthanide-carbon systems are characterized by two compounds, the sesquicarbide and the dicarbide. The lanthanide sesquicarbide and dicarbides are isomorphous with the corresponding uranium compounds. However, the lanthanide sesquicarbides and dicarbides are immiscible with the corresponding uranium compounds. The lanthanides do not form a monocarbide phase similar to uranium carbide. Samarium and gadolinium do form the lanthanide (Ln) carbide, LnC_x , where $0.35 < x < 0.17$.⁴⁸ Lanthanide monocarbides can be stabilized by solubility in uranium carbide. The limits of solubility of the lanthanides in the $\text{LnC}_2 + \text{U}_{1-x}\text{Ln}_x\text{C} + (\text{U}_{1-x}\text{Ln}_x)_2\text{C}_3$ phase field have been determined using a Vegard's law relationship between UC and hypothetical LnC lattice parameters.⁴⁰⁻⁴² The solubility data are shown in Table 2. Table 2 indicates

TABLE 2. Solubility Limits of Lanthanides in the Uranium-Lanthanide-Carbon System

Element	Temp., °C	Maximum Solubility, mol % "Lanthanide Monocarbide"	
		Ref. 40	Ref. 41 & 42
La	1250	0.2-0.4	0.5
Ce	1600	~4	~1
Pr	1400	3.3	- ^a
Nd	1400	3.9	0.8
	1000	3.9	-
Gd	1000-1450	16.5	-

^aNot determined.

that the solubility of fission product lanthanides in UC will not be exceeded during burnup. Thus, the chemical state of the lanthanide fission products in irradiated UC is predicted to be "LnC", although Fig. 1 shows that the lanthanide dicarbides are more stable than UC. The implicit assumption in this prediction is that the solubility of each lanthanide element is independent of the presence of the others in the UC matrix. The validity of this assumption has yet to be determined.

(b) Yttrium, Zirconium, and Niobium. The systems of uranium and carbon with yttrium,^{40,45,49,50} zirconium,^{45,50,51} and niobium^{45,49,50} have been studied. The yttrium-carbon system contains monocarbide, sesquicarbide, and dicarbide phases. As shown in Fig. 1, YC₂ is more stable than UC. Relative stability may be less important than the solubility of YC in UC. Complete miscibility is observed between YC and UC. Similarly, NbC and ZrC are completely miscible with UC. Zirconium and niobium do not form higher carbides, in contrast to yttrium. The chemical state of yttrium, zirconium, and niobium in irradiated UC is predicted to be YC, ZrC, and NbC. The effect of fission products yttrium, zirconium, and niobium on the solubility of the lanthanides in the UC matrix is yet to be determined.

(c) Barium and Strontium. Barium and strontium form dicarbides that are only slightly less stable than UC (see Fig. 1). The systems of uranium and carbon with barium and strontium have not been studied. Because of the lack of information on the U-Ba-C and U-Sr-C systems, predictions on the chemical state of barium and strontium in irradiated UC fuel are difficult to make.

(d) Molybdenum, Technetium, Ruthenium, Rhodium, and Palladium. The systems of uranium and carbon with molybdenum^{45,50} technetium,⁵² ruthenium,^{32,45} rhodium,^{29,45} and palladium^{32,53} have been studied. Ternary carbides of the form UMoC₂, UTcC₂, U₂RuC₂, and U₂RhC₂ are observed in three-phase regions with UC and U₂C₃. The compounds UTcC₂ and UMoC₂ are isomorphous, as are

U_2RuC_2 and U_2RhC_2 , and the two latter compounds are completely miscible in each other. The miscibility of $UTcC_2$ in $UMoC_2$ has not been determined. There is no ternary compound in the U-Pd-C system. There is a narrow UC + UPd_3 phase region along a tie line between UC and UPd_3 . There is a three-phase region UC + U_2C_3 + UPd_3 adjacent to the two-phase UC + UPd_3 region. A $U_2(Ru,Rh,Pd)C_2$ phase has been observed in a U-C-Ru-Rh-Pd system.⁵⁵ The solubility limit of palladium in $U_2(Ru_xRh_{1-x})C_2$ has not been determined. A prediction of the chemical state of these fission products must therefore include $UMoC_2$ and $UTcC_2$ as separate phases or as $U(Tc,Mo)C_2$, and palladium as UPd_3 or included in $U_2(Rh_xRu_{1-x})C_2$.

(e) Selenium and Tellurium. The systems of uranium and carbon with tellurium⁵⁴ and selenium⁵⁵ have been studied. A ternary carbide of the form U_2TeC_2 exists in a three-phase region with UC and U_2C_3 . A similar ternary compound does not exist in the U-Se-C system. Uranium and selenium form binary compounds of the form USE , U_3Se_4 , and U_3Se_5 , among others. The solubility of selenium in U_2TeC_2 has not been measured. The chemical states of selenium and tellurium in irradiated UC are predicted to be ternary carbides of the form U_2TeC_2 . It is not important to the overall carbon balance within the fuel pin if selenium instead forms a binary compound with uranium. Selenium is a low yield fission product.

(f) Bromine, Iodine, Cesium, and Rubidium. These elements do not form carbides. Their common property of a low boiling point suggests that considerable redistribution is possible within the fuel rod by vapor transport of the elemental form. UI_3 and UI_4 are more stable than UC, as shown in Fig. 1. Bromides and iodides of cesium and rubidium are well-known compounds and are the predicted chemical states in irradiated UC.

(g) Krypton and Xenon. Krypton and xenon will remain as gases.

(h) Silver, Cadmium, Indium, Tin, and Antimony. This group of elements are present in low concentration (as fission products) and, consequently, have not been investigated in systems with uranium and carbon. Therefore, no predictions are made of the chemical state of these elements in irradiated uranium carbide.

Phase Equilibrium in Irradiated Plutonium Carbide

Phase equilibria in the plutonium-carbon system were recently reviewed by the IAEA Panel on Thermodynamic Properties,^{56,57} who recommend the phase diagram shown in Fig. 3. However, considerably more experimental work needs to be done before firm phase boundary lines can be drawn in the Pu-C system. The free energy data and phase relationships of the individual fission products with plutonium and carbon will be considered in the same groups as were used for uranium and carbon, namely,

- (a) Elements from lanthanum to gadolinium
- (b) Yttrium, zirconium, and niobium
- (c) Barium and strontium
- (d) Molybdenum, technetium, ruthenium, rhodium, and palladium
- (e) Selenium and tellurium
- (f) Bromine, iodine, cesium, and rubidium
- (g) Krypton and xenon
- (h) Silver, cadmium, indium, tin, and antimony

Fig. 3. Phase Diagram of the Pu-C System⁵⁷

(a) Lanthanum to Gadolinium. The systems of plutonium and carbon with lanthanum,⁴⁰ cerium,^{40,45} praseodymium,⁴⁰ and neodymium⁴⁰ have been studied. As shown in Fig. 1, the lanthanide dicarbides are more stable than PuC. Solubility of the lanthanides in the PuC matrix, as shown in Table 3, is perhaps more important than the relative stability of lanthanide dicarbides and PuC. The solubility limits of the lanthanides in PuC will not be exceeded during burnup. Thus, the chemical state of the lanthanide (Ln) fission products in irradiated PuC is predicted to be "LnC", which means that monocarbides of the lanthanides will be dissolved in the PuC matrix. The implicit assumption in this prediction is the same as that for UC, namely, that the solubility of each lanthanide element is independent of the presence of the others in the PuC matrix. The validity of this assumption has yet to be determined.

TABLE 3. Limits of Solubility of Lanthanides in the Plutonium-Lanthanide-Carbon System

Element	Temp., °C	Maximum Solubility, mol % "Lanthanide Monocarbide" ⁴⁰
La	950-1450	~2
Ce	800-1450	~4
Pr	800	~2.5
Nd	850	3.5-4.0

(b) Yttrium, Zirconium, and Niobium. The systems of plutonium and carbon with yttrium, zirconium, and niobium have been studied.⁴⁵ YC, ZrC, and NbC are completely miscible with PuC. The chemical state of yttrium, zirconium, and niobium in irradiated PuC is predicted to be YC, ZrC, and NbC dissolved in PuC. The effect of fission products yttrium, zirconium, and niobium on the solubility of the lanthanides in the PuC matrix has yet to be determined.

(c) Barium and Strontium. Barium and strontium form dicarbides which are more stable than plutonium carbide (see Fig. 1). There are no data on the systems of plutonium and carbon with barium and strontium. The chemical states of barium and strontium in irradiated PuC fuel are, therefore, difficult to predict.

(d) Molybdenum, Technetium, Ruthenium, Rhodium, and Palladium. The systems of plutonium and carbon with molybdenum, ruthenium, rhodium, and palladium have been studied.^{40,45,58} Molybdenum forms a ternary compound, PuMoC₂, which exists in a three-phase region with PuC and Pu₂C₃. PuMoC₂ is isomorphous with UMoC₂. The ternary phase diagrams of plutonium and carbon with ruthenium, rhodium, and palladium are complex because a large number of binary intermetallic compounds are formed with plutonium. There are no ternary compounds analogous to U₂RuC₂ and U₂RhC₂. Ternary compounds of the type PuRu₃C and PuRh₃C are observed in the transition-metal-rich

region. Three-phase regions exist containing $\text{PuC} + \text{Pu}_2\text{C}_3$ plus PuRu_2 or PuRh_3 or PuPd_3 . The chemical states of ruthenium, rhodium, and palladium in irradiated PuC are strongly dependent on the initial composition of the fuel.

(e) Selenium and Tellurium. There are no data on the systems of plutonium and carbon with tellurium and selenium.

(f,g,h) Remaining Elements. The predictions for the elements listed in items f, g, and h, namely, Br, I, Cs, Rb, Kr, Xe, Ag, Cd, In, Sn, and Sb, are the same as the predictions made for these elements in the discussion of the phase equilibria of these elements with uranium and carbon.

Phase Equilibrium in Irradiated Uranium-Plutonium Carbide

Phase equilibria in the uranium-plutonium-carbon system has been reviewed by the IAEA Panel on Thermodynamic Properties.⁵⁹ The bulk of the experimental data is below 650°C or above 2000°C . More experimental work needs to be done in the temperature range of 650 to 2000°C . A tentative isothermal section of the U-Pu-C system at 1600°C is shown in Fig. 4. There is little additional information on phase relationships of individual fission-product elements with systems of carbon and mixed uranium and plutonium. The data are limited to the U-Pu-Ru-C system. Preliminary studies indicate that U_2RuC_2 can accommodate Pu up to $(\text{U}_{0.8}\text{Pu}_{0.2})_2\text{RuC}_2$.⁴⁰ More data are needed on the solubility limits of Rh and Pd in $(\text{U,Pu})_2\text{RuC}_2$. Because the data base of (uranium and plutonium)-carbon-fission product systems is limited, predictions of the chemical states of the fission-product elements in irradiated uranium-plutonium carbide are limited to extrapolations of the predictions made earlier for the UC- and PuC -fission product systems.

Fig. 4. Tentative Isothermal Section in the System U-Pu-C at 1600°C ⁴⁵

Predictions of the chemical state of fission products in irradiated uranium-plutonium carbide are given in Table 4. The distribution of fission products for a 10% burnup of $(U_{0.8}Pu_{0.2})C_{1.004}$ and a 50-day cooling time was taken from Ref. 40. The reference column lists where the phase predicted in the stoichiometry column have been observed in analyses of a limited number of fuel pins with low burnups and out-of-pile experiments on carbide fuels containing simulated fission products. As indicated in the review, "Chemical Compatibility Between Cladding Alloys and Advanced Fuel" (ANL-AFP-9, May 1975), predictions of the chemical state of fission products in irradiated fuel allow calculation of the variation of the C/M ($M = U + Pu$) ratio during burnup. The variation in the C/M ratio during burnup has been calculated for three different predictions of stoichiometries.

For Prediction A, the lanthanide fission products are assumed to form dicarbides. For Prediction A, the at.% C required for the formation of the fission product carbides (in the stoichiometries shown) are listed. The sum of the carbon required is 7.15 at.%. The resultant C/M ratio is 0.948, a decrease from the original C/M of 1.004. Carbon has a higher affinity for fission-product elements than for uranium and plutonium. This is in sharp contrast to the mixed oxide fuel system in which oxygen has a lower affinity for fission-product elements than for uranium and plutonium and the O/M ratio increases during irradiation. The prediction here that fission in the mixed carbide fuel consumes carbon is essentially the same as that made by Lorenzelli and Marcon³⁹ based on similar calculations.

Recent work by Haines and Potter⁴⁰ and Lorenzelli and Marcon^{41,42} leads to a vastly different prediction, Prediction B. The basis of the new prediction is the measurement of the solubilities of the fission-product lanthanides in the UC matrix and the PuC matrix. At 10% burnup, the solubility limit of the lanthanides is not exceeded in either the UC or the PuC matrix, and the lanthanide dicarbide phase does not form. The stoichiometries and at.% carbon used for Prediction B in Table 4 are the same as for Prediction A, except where noted. The symbol "CeC" represents Ce dissolved in the (U,Pu)C matrix. Moreover, (U,Pu)TcC₂ instead of (U,Pu)₂TcC₂ is chosen for Prediction B in accordance with the prediction of Haines and Potter.⁴⁰ The evidence in support of either stoichiometry is scanty. If the change in Tc stoichiometry is excluded from consideration for a moment, the effect of lanthanide solubility in the (U,Pu)C matrix is to require less carbon, namely, 5.06 at.%. The resultant C/M ratio is 0.996. Including the change in Tc stoichiometry from (U,Pu)₂TcC₂ to (U,Pu)TcC₂ requires an additional 0.29 at.% C for a total of 5.35 at.% carbon for Prediction B, yielding a C/M ratio of 0.990.

Prediction C is based on the premise that the solubility limits of Ba and Sr in mixed carbide fuel are not exceeded at 10% burnup. In Table 4, the notations, "BaC" and "SrC", represent, respectively, Ba and Sr dissolved in the (U,Pu)C matrix. All other stoichiometries and the atom percentages of carbon are the same as for Prediction B. Prediction C requires 4.92 at.% carbon, yielding a C/M ratio of 1.000. If the stoichiometry of Tc is changed from (U,Pu)TcC₂ to (U,Pu)₂TcC₂, 4.63 at.% carbon is required and the C/M ratio becomes 1.006.

TABLE 4. Estimated Change in the C/M Ratio at 10% Burnup for $(U_{0.80}Pu_{0.20})C_{1.004}$

Element	at.%	Prediction A		at.% C Used	Prediction B		Prediction C	
		Stoichiometry	Ref.		Stoichiometry	at.% C Used	Stoichiometry	at.% C Used
Ag	0.07	-						
Am	0.02	-						
Ba	0.31	BaC ₂		0.62			"BaC"	0.31
Br	0.01	Br, CsBr, RbBr						
Cd	0.04	-						
Ce	0.59	CeC ₂		1.18	"CeC"	0.59		
Cs	0.91	Cs, CsI, CsBr	39					
Eu	0.03	EuC ₂		0.06	"EuC"	0.03		
Gd	0.02	GdC ₂		0.04	"GdC"	0.02		
I	0.08	CsI	39					
In	<0.01	-						
Kr	0.08	Kr (gas)						
La	0.28	LaC ₂		0.56	"LaC"	0.28		
Mo	1.02	(U, Pu)MoC ₂	39, 55	1.02				
Nb	0.02	NbC	39	0.02				
Nd	0.69	NbC ₂		1.38	"NdC"	0.69		
Pd	0.65	(U, Pu) ₂ (Ru, Rh, Pd)C ₂	39, 55					
Pm	0.09	PmC ₂		0.18	"PmC"	0.09		
Pr	0.23	PrC ₂		0.46	"PrC"	0.23		
Rb	0.11	Rb, RbI, RbBr						
Rh	0.27	(U, Pu) ₂ (Ru, Rh, Pd)C ₂	39, 55, 60					
Ru	1.01	(U, Pu) ₂ (Ru, Rh, Pd)C ₂	39, 55, 60					
Sb	0.02	-						
Se	0.02	(U, Pu) ₂ SeC ₂						
Sm	0.16	SmC ₂		0.32	"SmC"	0.16		
Sn	0.04	-						
Sr	0.12	SrC ₂		0.24			"SrC"	0.12
Tc	0.26	(U, Pu) ₂ TcC ₂	60		(U, Pu)TcC ₂	0.29		
Te	0.15	(U, Pu) ₂ TeC ₂	39					
Xe	0.07	Xe (gas)						
Y	0.10	YC	39, 55	0.10				
Zr	0.97	ZrC	39, 55	0.97				
U	34.31							
Pu	8.49							
C	47.73							
		$\Sigma FPC = 7.15$		$\Sigma FPC = 5.35$		$\Sigma FPC = 4.92$		
		$(U, Pu)C_{0.948}$		$(U, Pu)C_{0.990}$		$(U, Pu)C_{1.000}$		

The results of Predictions A, B, and C are summarized in Table 5. Although the changes in the C/M ratio in Table 5 are small, small changes in the C/M ratio are thought (by analogy to the C/U ratio in UC fuel) to have a large effect in the fuel pin. As discussed in the review, "Chemical Compatibility Between Cladding Alloys and Advanced Fuel" (ANL-AFP-9), the carbon potential in UC is unaffected by the inclusion of fission products. The carbon potential is thus determinable from the C/U ratio as shown in Fig. 5. Although the changes in the C/M ratio in Table 5 are small, similar

TABLE 5. Summary of Changes in C/M Ratio at 10% Burnup^a

Initial C/M	Disposition of Lanthanides, Ba, Sr		Prediction ^b	Final C/M
	Soluble in (U,Pu)C	Dicarbide Phases		
1.004		Lanthanide, Ba, Sr	A	0.948
1.004	Lanthanides	Ba, Sr	B	0.996
1.004	Lanthanides, Ba, Sr		C	1.006

^a50-day cooling time.

^bWith (U,Pu)₂TcC₂ in all cases.

Fig. 5. Activity of Carbon as a Function of UC_x Composition⁶¹

changes in the C/U ratio radically alter the carbon potential (and tendency toward carburization) of the fuel. Because this prediction of the C/M ratio is based on a total carbon balance in the irradiated fuel, it is important to know accurately the chemical state of every fission product in the irradiated fuel.

Phase Equilibrium in Irradiated Uranium-Plutonium Nitride

Free energy data and phase relationships are a basis for the prediction of the chemical state of an irradiated nitride fuel. The available free energy data for the reactions of fission product elements to form nitrides is shown in Table 6 and Fig. 6. Phase equilibria in the uranium-nitrogen system have recently been reviewed by Tagawa⁶⁷ who recommends the phase diagram shown in Fig. 7. The recommended U-N phase diagram is consistent with a large number of experimental observations, which indicates that the uranium-nitrogen system is well known. Phase equilibrium in the plutonium-nitrogen system was reviewed by Holleck and Kleykamp⁶⁹ and by Tagawa.⁷⁰ Holleck⁴⁵ recommends the phase diagram shown in Fig. 8. More experimental work is required to determine the composition range of PuN as a function of nitrogen pressure and temperature. Phase equilibria in the uranium-plutonium-nitrogen system was calculated by Potter.⁷¹ The calculated U-Pu-N phase diagram is shown in Fig. 9. Experimental work needs to be done to determine the composition range of the mononitride region and the nature of the phase diagram in the sesquinitride region.

The free energy data and phase relationships of the individual fission products with uranium and nitrogen are best considered in a number of groups of chemically similar elements:

- (a) Elements from lanthanum to gadolinium
- (b) Yttrium, zirconium, and niobium
- (c) Barium and strontium
- (d) Molybdenum, technetium, ruthenium, rhodium, and palladium
- (e) Selenium and tellurium
- (f) Bromine, iodine, cesium, and rubidium
- (g) Krypton and xenon
- (h) Silver, cadmium, indium, tin, and antimony

(a) Lanthanum to Gadolinium. The systems of uranium and nitrogen with lanthanum, cerium, praseodymium, and neodymium have been studied.^{45,72-74} The lanthanide-nitrogen binary system is characterized by a single compound, the mononitride. The lanthanide mononitrides are completely miscible with UN. Similarly, complete solid solutions between lanthanide nitrides and PuN are expected, although this was confirmed only in the case of cerium.⁴⁵ The chemical state of the lanthanide elements in irradiated (U,Pu)N is predicted to be the lanthanide mononitride.

(b) Yttrium, Zirconium, and Niobium. The systems of uranium and nitrogen with yttrium,^{45,72-74} zirconium,^{45,74-76} and niobium^{45,74-76} have been studied. Yttrium, zirconium, and niobium form mononitrides that are completely miscible with UN. Similarly, ZrN is completely miscible with PuN.^{45,77} The chemical state of fission product elements yttrium, zirconium, and niobium in irradiated (U,Pu)N is predicted to be YN, ZrN, and NbN.

TABLE 6. Free Energy Data for the (U,Pu)N-Fission Product System

Element	Reaction (std. reaction of formation unless stated otherwise)	$\Delta G(\text{cal}) = -A + BT$		Temp. Range, K	Ref.
		$\frac{A}{10^3 \text{ cal}}$ mol	$\frac{B}{\text{cal}}$ mol-deg		
Pu	→ PuN	70.64	21.6	1600-2000	62
La	→ LaN	72.1	25.0	298-1000	63
Ce	→ CeN	78.0	25.0	298-1000	63
Pr	→ PrN	75.0	25.0	298-1000	64,65
Nd	→ NdN	71.0	25.0	298-1000	64,65
Y	→ YN	71.5	25.0	298-1000	63,65
Zr	→ ZrN	87.9	23.1	1135-1500	63
Nb	→ NbN	56.8	20.0	298-1000	63,65,66
Cr	→ Cr ₂ N	24.1	13.65	400-1400	63
U	→ UN	70.2	18.8	400-1000	67
	→ UN	72.3	20.85	1000-2100	67
	UN + 0.27N ₂ → UN _{1.54}	15.2	9.3	500-1600	67
Sr	→ Sr ₃ N ₂	77.0		298	68
Ba	→ Ba ₃ N ₂	90.7	57.5	298-1000	68
Mo	→ Mo ₂ N	15.9	14.0	298-800	68
B	→ BN	60.7	17.0	298-1200	68
Fe	→ Fe ₂ N	0.9	11.3	298-1200	68
	→ Fe ₄ N	2.9	11.9	298-1200	68

Fig. 6. Free Energy Data for the (U,Pu)N-Fission Product System

Fig. 7. Phase Diagram of the U-N System⁶⁷

Fig. 8. Phase Diagrams of the P-N System⁴⁵

- ϵ - PuN
- γ - PuN
- δ - PuN
- β - PuN
- δ - PuN
- ▲ α - PuN

Fig. 9. Calculated Isothermal Sections in the U-Pu-N System at 1000°C^{45, 71}

(c) Barium and Strontium. As shown by Table 6 and Fig. 6, Ba_3N_2 and Sr_3N_2 are more stable than U_2N_3 . There are no data on the stability of these compounds above 1000 K. Nevertheless, the chemical state of fission-product elements barium and strontium in irradiated (U,Pu)N is predicted to be Ba_3N_2 and Sr_3N_2 .^{74,78}

(d) Molybdenum, Technetium, Ruthenium, Rhodium, and Palladium. The binary molybdenum nitrides Mo_2N and MoN decompose above 850°C .⁷⁴ Consequently, the chemical state of fission-product element molybdenum in irradiated (U,Pu)N is predicted to be the elementary metal or metallic inclusions containing other fission-product elements. Although there are no data on the system composed of uranium, nitrogen, and technetium, the chemical state of technetium in irradiated (U,Pu)N is predicted to be the elementary metal or metallic inclusions containing other fission product elements by analogy to molybdenum. The metallic fission-product elements ruthenium, rhodium, and palladium do not form nitrides.⁷⁴ Free energy data in Table 1 show URu_3 , URh_3 , and UPd_3 to be very stable. Calculations show that $\text{U}(\text{Ru},\text{Rh},\text{Pd})_3$ would be thermodynamically stable in UN at the temperatures and nitrogen pressures expected in a UN fuel rod.⁷⁴ The analogous compounds with plutonium (PuRh_3 and PuPd_3) exist.⁴⁵ Plutonium forms a binary compound PuRu_2 with ruthenium. The predicted chemical state of fission-product elements ruthenium, rhodium, and palladium in irradiated (U,Pu)N is $(\text{U,Pu})(\text{Ru},\text{Rh},\text{Pd})_3$. Some fission product molybdenum and technetium may be contained in this metallic inclusion.

(e) Selenium and Tellurium. Although selenium and tellurium form nitrides SeN_x and Te_3N_4 , nothing is known of the stability of these compounds. Both of these nitrides probably decompose at low temperatures.⁷⁴ The predicted chemical state of fission product elements selenium and tellurium in irradiated (U,Pu)N is the elemental metal or in compounds with cesium.

(f,g,h) Remaining Elements. The predictions of the chemical state of the fission-product elements listed in items f, g, and h are the same for irradiated (U,Pu)N as for (U,Pu)C. Cesium and rubidium are expected to react with iodine and bromine to form bromides and iodides, with the remaining cesium and rubidium forming selenides or tellurides. Xenon and krypton are expected to remain as gases. Silver, cadmium, indium, tin, and antimony are present in low concentration as fission products. Therefore, no predictions are made of the chemical state of these elements in irradiated (U,Pu)N.

The predicted fission-product stoichiometries in irradiated (U,Pu)N are listed in Table 7. The distribution of fission products for a 10% burnup of $(\text{U}_{0.80}\text{Pu}_{0.20})\text{N}_{1.004}$ and a 50-day cooling time was taken from Ref. 40. Also shown in Table 7 are estimates of the nitrogen atoms transmuted as a result of the $^{14}\text{N}(\text{n},\alpha)^{11}\text{B}$ and $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$ reactions.^{78,79} As shown in Table 6 and Fig. 6, boron forms a stable nitride, BN. The predicted chemical state of boron in irradiated (U,Pu)N is BN. Carbon from the (n,p) reaction is present at the 130 ppm level. Since this is of the order of the carbon impurity initially in the fuel, the carbon from the (n,p) reaction will be treated as equivalent to nitrogen and will not affect the predicted nitrogen stoichiometries or the overall nitrogen balance in the system.

TABLE 7. Estimated Change in the N/(U + Pu) Ratio
at 10% Burnup for $(U_{0.80}Pu_{0.20})N_{1.004}$

Element	at. %	Stoichiometry	at. % N Used
Ag	0.07		
Am	0.02		
Ba	0.31	Ba_3N_2	0.02
Br	0.01	CsBr	
Cd	0.04		
Ce	0.59	CeN	0.59
Cs	0.91	Cs, CsI, $CsTe_x$, $CsSe_x$	
Eu	0.03	EuN	0.03
Gd	0.02	GdN	0.02
I	0.08	CsI, RbI	
In	<0.01		
Kr	0.08	Kr	
La	0.28	LaN	0.28
Mo	1.02	Mo	
Nb	0.02	NbN	0.02
Nd	0.69	NdN	0.69
Pd	0.65	(U, Pu) (Pd, Ru, Rh) ₃	-0.22
Pm	0.09	PmN	0.09
Pr	0.23	PrN	0.23
Rb	0.11	Rb, RbI	
Rh	0.27	(U, Pu) (Pd, Ru, Rh) ₃	-0.09
Ru	1.01	(U, Pu) (Pd, Ru, Rh) ₃	-0.34
Sb	0.02		
Se	0.02	Se, $CsSe_x$	
Sm	0.16	SmN	0.16
Sn	0.04		
Sr	0.12	Sr_3N_2	0.08
Tc	0.29	Tc	
Te	0.15	Te, $CsTe_x$	
Xe	1.07	Xe	
Y	0.10	YN	0.10
Zr	0.97	ZrN	0.97
B ^a	0.30	BN	0.30
U	34.31		
Pu	8.49		
N ^b	47.29		
C ^b	0.14		
			$\Sigma = 3.11$
			(U, Pu)N _{1.036}

^aFrom $^{14}N(n, \alpha)^{11}B$.

^bFrom $^{14}N(n, p)^{14}C$.

The at.% N required for the formation of the fission product (and boron) nitrides in the stoichiometries shown are listed in Table 7. The sum of the nitrogen required is 3.11 at.%. The resultant N/(U + Pu) ratio (with N = N + C as discussed above) is 1.036, an increase from the original ratio of 1.004. The increase in N/(U + Pu) ratio would be larger if molybdenum and/or technetium were included in the (U,Pu)(Ru,Rh,Pd)₃ phase or formed a separate binary phase with uranium or plutonium.

Nitrogen has a lower affinity for fission-product elements than for uranium and plutonium. The predicted behavior of mixed nitride fuel during irradiation is thus similar to mixed oxide fuel (in which the O/M ratio increases during burnup) but contrasts with mixed carbide fuel (in which the C/M ratio is predicted to remain constant or decrease during burnup). The prediction here that the nitrogen activity of mixed nitride fuel increases during burnup, with the consequent formation of the uranium sesquinitride phase, is in agreement with previous predictions.^{74,78,80} However, this prediction is based largely on observations of phase equilibria in ternary systems of uranium, nitrogen, and a single fission-product element. Further work needs to be done to examine phase equilibria in (U,Pu)N containing mixtures of fission-product elements. In addition, postirradiation examination data on the phases formed in irradiated fuel is needed as a check on the predicted chemical state of (U,Pu)N during burnup.

EFFECT OF LOW LEVEL OXYGEN CONTENT

Oxygen has a common effect on the behavior of mixed carbide fuel and mixed nitride fuel. Oxygen decreases the activity of carbon and nitrogen in these fuels. The carbon activity of UC is decreased by two orders of magnitude when the oxygen content is increased from 150 to ~2,000 ppm.⁸¹ The nitrogen activity of U₂N₃ is reduced by the addition of 2 to 3 wt % oxygen.^{82,83} Lowering of the carbon activity or nitrogen activity has an obviously beneficial effect with regard to carburization or nitriding of the cladding. Consequently, the pertinent phase relations have been examined to determine the extent of oxygen solubility in carbide and nitride fuels. *A priori* it is assumed that UO₂ and PuO₂ phases must be avoided both in the fuel during manufacture and in the fuel pin during burnup. More severe cladding attack is encountered with mixed urania and plutonia than is encountered with "oxygen free" carbide and nitride fuel.

The U-C-O ternary phase diagram at 1700°C is shown in Fig. 10.⁸⁴ The solubility of "UO" in UC (mol %) is 35% at point I over the temperature range 1100 to 2200°C, 10% at point II over the temperature range 1100 to 1700°C, and 6% at point III over the temperature range 1100 to 1700°C.⁸⁴ Oxygen is insoluble in the sesquicarbide phase. The two-phase region UC_{1.5} + UC_{1-x}O_x (0 < x < 0.06) is the region where oxycarbide fuels may possess advantages over carbide fuels.

The Pu-C-O ternary phase diagram at 1300°C is shown in Fig. 11.⁸⁴ The solubility of "PuO" in PuC (mol %) is 65% at point B over the temperature range 1000 to 1400°C and 35% at point A over the temperature range 1000 to 1400°C.⁸⁴ The regions where oxycarbide fuels may possess advantages over carbide fuels are the monoxycarbide region, PuC_{1-x}O_x (0 < x < 0.65) and the two-phase region PuC_{1.5} + PuC_{1-x}O_x (0 < x < 0.35).

The U-Pu-C-O system has usually been treated as a pseudo-ternary M-C-O system^{85,87} and the phase diagram proposed for it is similar to the U-C-O phase diagram shown in Fig. 10. Values of the solubility of "MO" in MC (point I) have ranged from 37 mol % in the temperature range 1400 to 1750°C⁸⁷ to 50 mol % in the temperature range 1100 to 1650°C.⁸⁵ The limit of oxygen solubility in the monocarbide in the presence of sesquicarbide (point III) has been reported as being 5 mol % "MO" at 1500°C⁸⁵ and 12 mol %⁸⁷ and 18 mol %⁸⁶ at 1600°C.

Discussion of the U-Pu-C-O system in terms of a pseudo-ternary phase diagram fails to account for U/Pu segregation. For example, in "oxygen-free" mixed carbide fuel with Pu/(U + Pu) = 0.20, the measured distribution ratio of actinide in (U,Pu)C to actinide in (U,Pu)₂C₃ was 1.20 for uranium and 0.45 for plutonium. These values were independent of temperature (1500 to 1700°C) and percent sesquicarbide (10 to 70%).^{88,59}

Less is known about oxynitrides than oxycarbides. Figure 12⁸⁹ shows a section of a proposed U-N-O ternary phase diagram at 1400°C. In Fig. 12, SS denotes the (body-centered cubic) solid solution of UO₂ and α-U₂N₃. At temperatures above ~1170°C, UO₂ and α-U₂N₃ are completely miscible.^{89,90} The shape of the miscibility gap below 1170 has not been determined.⁹⁰ Lowering the nitrogen pressure causes the solid solution to decompose. For example, at 1250°C and a N₂ pressure of 0.166 atm, the solid solution (with O/U = 0.5) decomposes into UN and UO₂. In Fig. 12, SS' denotes the UO₂-αU₂N₃ solid solution in equilibrium with β-U₂N₃. The maximum oxygen solubility of SS' is represented by UN_{1.22}O_{0.27} at 1400°C and UN_{1.33}O_{0.23} at 1200°C.⁸⁹ The β-U₂N₃ phase has little or no oxygen solubility. In Fig. 12, the β-U₂N₃ + UN two-phase region is too narrow to be shown. The oxygen solubility in UN has been reported as being 2 to 6 mol % "UO" in the temperature range 1900-2300°C,⁸⁹ 7 mol % in the temperature range 1600 to 1900°C,⁹¹ and 6 mol % in the temperature range 1200 to 1600°C.⁹²

Fig. 12. A Portion of the U-N-O Phase Diagram at 1400°C. SS denotes a solid solution of UO₂ and U₂N₃.⁸⁹

In the Pu-N-O system, experimental information is still too limited to allow a phase diagram to be constructed. The reported limit of "PuO" solubility in PuN is 14 mol % in the temperature range from 1400 to 1600°C.⁸⁷

Data are also insufficient for constructing a phase diagram of the U-Pu-N-O system. The reported solubility limit of "Mo" in MN [M = U + Pu with Pu/(U+Pu) = 0.20] is 7 mol % in the temperature range 1400 to 1600°C.⁸⁷ It is not yet clear that the U-Pu-N-O system can be adequately described as a pseudo-ternary M-N-O system.

CONCLUSIONS

The extent of change in the carbon/actinide or nitrogen/actinide ratio during irradiation can be predicted on the basis of a balance of the total carbon or nitrogen in the fuel. This approach requires accurate knowledge of the chemical state of each fission product. Consequently, further work needs to be done on both carbide and nitride fuels. For carbide fuels, the following information is needed:

(1) Data to place the Pu-C phase diagram on a firmer experimental basis and more information on U-Pu-C phase equilibria between 650 and 2000°C.

(2) Carbon activity in mixed uranium-plutonium carbide and the effect of the inclusion of varying amounts of fission-product elements and oxygen on the carbon activity.

(3) Terminal solubilities of selected fission-product lanthanide elements in the mixed carbide and the effect on lanthanide solubility of also dissolving other lanthanides or high-yield fission-product element zirconium, or oxygen in the carbide matrix.

(4) Pertinent phase equilibria relationships in systems containing uranium, plutonium, and carbon, together with selected mixtures of high-yield metallic fission product elements molybdenum, ruthenium, rhodium, and palladium.

(5) Pertinent phase equilibria relationships in systems containing uranium, plutonium, and carbon, along with alkaline earth elements, especially the terminal solubility of the alkaline earth elements in the mixed carbide matrix.

(6) Postirradiation examination data from carbide fuel pins showing pertinent phase equilibria relationships and the effects of fission product and carbon transport.

For nitride fuels, the following information is needed:

(1) The composition range of plutonium mononitride and uranium-plutonium mononitride and the nature of the phase diagram in the uranium-plutonium sesquinitride region.

(2) Nitrogen activity in mixed uranium-plutonium nitride and the effect on nitrogen activity of the inclusion of varying amounts of fission-product elements and oxygen.

(3) Additional free energy data for nitrides of fission-product elements, particularly for high-yield fission products.

(4) Pertinent phase relationships in systems containing uranium, plutonium, and nitrogen, along with selected high-yield fission products, particularly partially or completely simulated (U,Pu)N + fission-product systems.

(5) Postirradiation examination data from nitride fuel pins showing pertinent phase equilibria relationships and the effects of fission product and nitrogen transport.

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APPENDIX

Melting Point Data for Candidate Fuels

The melting points for various actinide carbides and nitrides are tabulated. The impurity levels for each material are also given.

TABLE A-1. Uranium Carbide (UC)

Temp., K	Composition C/U	Impurity (ppm)	
		O	N
2863 $\pm$ 50 ^a	1.0	- ^b	-
2763 $\pm$ 35 ^c	1.00 $\pm$ 0.06	280	60
2793 $\pm$ 20 ^d	1.0	-	-
2813 $\pm$ 25 ^e	1.0	<300	<300
Recommended Value ^f 2780 $\pm$ 25 K			

^aP. Chiotti, J. Amer. Ceram. Soc. 35, 123 (1952).^bUnspecified.^cR. Benz, C. G. Hofmann, and G. N. Rupert, High Temp. Sci. 1, 342 (1969).^dC. F. Knights and R. Perkins, J. Nucl. Mater. 39, 224 (1971).^eJ. G. Reavis, K. A. Johnson, and J. A. Leary, *Plutonium 1970*, The Metallurgical Society, AIMPE, New York, p. 791.^fE. K. Storms and R. J. Ackerman, IAEA Panel on the Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974.TABLE A-2. Uranium Sesquicarbide^a (U₂C₃)

Temp., K	Composition C/U	Impurity (ppm)	
		O	N
2110-2170 ^b	1.4	- ^c	-
2038-2093 ^d	1.48	200	36
2093 $\pm$ 25 ^e	1.5	290	40
Recommended Value ^f 2100 $\pm$ 25 K			

^aU₂C₃ $\rightarrow$ β -UC₂.^bR. Coninck, W. Van Lierde, and A. Gijss, J. Nucl. Mater. 46, 213 (1973).^cUnspecified.^dM. B. Sears and L. M. Ferris, J. Nucl. Mater. 32, 101 (1969).^eR. Benz, C. G. Hofmann, and G. N. Rupert, High Temp. Sci. 1, 342 (1969).^fE. K. Storms and R. J. Ackerman, IAEA Panel on the Thermodynamic Properties of the U-C, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974.

TABLE A-3. Plutonium Carbide (PuC)

Temp., K	Composition C/Pu	Impurity (ppm)	
		O	N
1873 $\pm$ 25 ^a	0.86	<300	<300
1933 $\pm$ 10 ^b	0.87	- ^c	-
1927 $\pm$ 20 ^d	0.85	-	-
Recommended Value ^e 1875 $\pm$ 25 K			

^aJ. G. Reavis, K. A. Johnson, and J. A. Leary, *Plutonium 1970*, The Metallurgical Society, AIMPE, New York, p. 791.

^bO. L. Kruger, *Nuclear Metallurgy* 10, 387 (1964).

^cUnspecified.

^dR. N. R. Mulford, F. H. Ellinger, G. S. Hendrix, and E. D. Albrecht, *Plutonium 1960*, Cleaver-Hume Press, London, p. 301.

^eM. H. Rand, IAEA Panel on Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974, revised March 1975.

TABLE A-4. Plutonium Sesquicarbide (Pu_2C_3)

Temp., K	Composition C/Pu	Impurity (ppm)	
		O	N
2323 ± 20 ^a	1.5	— ^b	—
2298 ± 50 ^c	1.5	100	—
2283 ± 25 ^d	1.47	—	—
Recommended Value ^e 2285 ± 25 K			

^aR. N. R. Mulford, F. H. Ellinger, G. S. Hendrix, and E. D. Albrecht, *Plutonium 1960*, Cleaver-Hume Press, London, p. 301.

^bUnspecified.

^cJ. T. Dalton, *Carbides in Nuclear Energy*, Vol. I, Macmillan, London, p. 77 (1964).

^dJ. G. Reavis, to be published.

^eM. H. Rand, IAEA Panel on Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974, revised March 1975.

TABLE A-5. Uranium-Plutonium Carbide (U,Pu)C
(see also Fig. A-1)

Temp., K		Composition	Impurity (ppm)	
Solidus	Liquidus		O	N
2700 ± 20^a	2753 ± 20^a	$(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}_{0.95}$	2000	200
2520 ± 25^b	2758 ± 25^b	$(\text{U}_{0.81}\text{Pu}_{0.19})\text{C}_{0.95}$	405	84

^aD. Stahl and A. Strasser, *Carbides in Nuclear Energy*, Vol. I, Macmillan, London, p. 373 (1964).

^bJ. G. Reavis, K. A. Johnson, and J. A. Leary, *Plutonium 1970*, The Metallurgical Society, AIMPE, New York, p. 791.

Fig. A-1. Solidus and Liquidus Temperatures for the UC-PuC Region

1. J. T. Dalton, unpublished results, AERE Harwell (unspecified oxygen and nitrogen content).
2. J. G. Reavis, K. A. Johnson, and J. A. Leary, *Plutonium 1970*, The Metallurgical Society, AIMPE, New York, p. 791 (see Table A-5).
3. D. Stahl and A. Strasser, *Carbides in Nuclear Energy*, Vol. I, Macmillan, London, p. 373 (1964) (see Table A-5).
4. M. H. Rand, IAEA Panel on Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974, revised March 1975.

TABLE A-6. Uranium-Plutonium Sesquicarbide (U,Pu)₂C₃

mol % Pu ₂ C ₃	at. % C	Temp., ^a K	
		Solidus	Liquidus
0	60.0	2675 ^b	2680 ^b
5	61.09	-	2590
10	-	-	2580
10	61.34	-	2580
15	59.37	2560	2610
15	61.48	-	2480
20	55.85	-	2490
20	59.86	-	2480
30	51.07	-	2520
30	59.75	2510	2570
40	55.81	-	2410
45	60.00	2370	2510
50	50.64	2370	2420
50	53.40	2350	2360
50	55.00	-	2370
50	57.31	-	2400
50	59.41	-	2390
50	59.86	-	2390
56	59.53	-	2420
60	56.68	-	2285
66	61.37	2410	2470
75	56.85	-	2220
75	57.92	-	2350
80	55.94	-	2170
85	59.71	-	2280
100	60.0	2285 ^c	2325 ^c

^aUnless specified otherwise, the data are from J. T. Dalton, *Carbides in Nuclear Energy*, Vol. I, Macmillan, London, p. 77 (1964). (Temperatures were accurate to ± 50 K. The samples were of unspecified oxygen and nitrogen content.)

^bRecommended value, E. K. Storms and R. J. Ackerman, IAEA Panel on the Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974.

^cRecommended value, M. H. Rand, IAEA Panel on Thermodynamic Properties of the UC, PuC, and (U,Pu)C Systems, Grenoble, France, May 1974, revised March 1975.

TABLE A-7. Uranium Nitride (UN at 1 atm N₂ Pressure)

Temp., K	Composition N/U	Impurity (ppm)	
		O	C
2923 ± 100 ^a	1.0	- ^b	-
3028 ± 85 ^c	1.0	-	-
3054 ± 30 ^d	1.0	-	-
3073 ± 50 ^e	1.0	470	55
2985 ± 30 ^f	1.0	500	-

Recommended Value 3035 ± 40 K

^aP. Chiotti, J. Amer. Ceram. Soc. 35, 123 (1952).

^bUnspecified.

^cD. F. Carroll, HW-SA-3370 (1964).

^dW. M. Olson and R. N. R. Mulford, J. Phys. Chem. 67, 952 (1963).

^eJ. Bugl and A. A. Bauer, J. Amer. Ceram. Soc. 47, 425 (1964).

^fR. Benz and W. B. Hutchinson, J. Nucl. Mater. 36, 135 (1970).

TABLE A-8. Uranium Sesquinitride (U₂N₃ at 1 atm N₂ Pressure)

Temp., K	Composition	Impurity (ppm)	
		O	C
1618 ± 50 ^a	U ₂ N ₃	- ^b	-
1625 ^c	U ₂ N ₃	-	-
1623 ± 40 ^d	N/U = 1.50	<700	-

Recommended Value 1623 ± 40 K

^aJ. Bugl and A. A. Bauer, J. Amer. Ceram. Soc. 47, 425 (1964).

^bUnspecified.

^cM. Katsura and T. Sano, J. Nucl. Sci. Technol. 4, 283 (1967).

^dR. Benz, G. Balog, and B. H. Baca, High Temp. Sci. 2, 221 (1970).

TABLE A-9. Plutonium Nitride (PuN at 1 atm N₂ Pressure)

Temp., K	Composition N/Pu	Impurity (ppm)	
		O	C
2829 ± 15 ^a	1.0	- ^b	-
2857 ± 30 ^c	0.95	-	450
Recommended Value ^d 2843 ± 30 K			

^aD. F. Carroll, HW-SA-3370 (1964).^bUnspecified.^cW. M. Olson and R. N. R. Mulford, J. Phys. Chem. 68, 1048 (1964).^dK. E. Spear and J. M. Leitnaker, ORNL-TM-2106 (1968).TABLE A-10. Uranium-Plutonium Nitride [(U,Pu)N at 1 atm N₂ Pressure]

Temp., K	Composition	Impurity (ppm)	
		C	O
3053 ± 20 ^a	(U _{0.8} Pu _{0.2})N _{0.99±0.01}	2400-3000	600-1100

^aE. T. Weber, BNWL-842, Section 6.1 (1968).