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A REPORT TO THE VIENNA PANEL (1968)
THE URANIUM-CARBON AND PLUTONIUM-CARBON SYSTEMS

by

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URANIUM-CARBON SYSTEM

1. Phase Relationship

I. Phase Diagram

A considerable effort has been made in recent years to determine the phase relationship in the U-C system. It is clear that this is a very difficult system to study and, as a result, there are areas of disagreement. Two problems are particularly troublesome; the proclivity to oxycarbide and carbonitride formation with the important influence these impurities have on the measured properties, and the unexpectedly slow reaction kinetics.

A discussion of observations in this system which were reported before early 1967 has been published by Storms (1967). A phase diagram, shown as Figure 1.1, is based upon this evaluation, and it summarizes much of the current knowledge of the system. However, there still are several areas of uncertainty which will be discussed in the following sections.

It is generally agreed that the formation of U_2C_3 is quite slow under normal pressures, even in the absence of oxygen and nitrogen impurity. For this reason, the conditions for its formation and its decomposition temperature are still in some doubt. Henney et al. (1963) argue that the presence of oxygen in concentrations above ~1000 ppm inhibits the formation of U_2C_3 and that in the presence of UO_2 its decomposition temperature is reduced to 1650°C (Henney, 1966). Henry et al. (1967) find U_2C_3 , UC_xO_y , and $U(CO)_2$ in equilibrium at 1700° (Figure 1.2) in agreement with the general observations of Anselin et al. (1964) and Brett et al. (1964). It would appear that an understanding of this compound will have to depend on more extensive studies of the oxycarbide system.

Once formed, U_2C_3 appears to be equally difficult to decompose. Neutron diffraction studies (Bowman, 1966) which have been carried into the miscibility gap (Figure 1.1) indicate that times over one hour are needed to produce partial decomposition. This is supported by anneal and quench experiments (Wittman and Bowman, 1963) so long as the temperature is not carried above the miscibility gap.

A range of temperatures for the decomposition reaction $2UC_2 = U_2C_3 + C$ has been observed. Oxygen stabilization of UC_2 should lead to a lower value. Thus, Henney et al. (1963) argue that this temperature is 1750° in the pure system rather than $\sim 1500^\circ$ as has been observed by others. The value chosen becomes rather important when the above reaction is used to add to the meager free energy values for U_2C_3 (Figure 2.10). Studies by Wittman (1967) and by Wallace et al. (1968) using material containing less than 100 ppm oxygen have given an average decomposition temperature of $1520 \pm 10^\circ$. If this small amount of oxygen is responsible for a 230° lowering of this temperature, then there is no hope for an accurate measurement. However, there has been no indication in any other direct measurement of this reaction that oxygen could have such a pronounced effect.

In the absence of U_2C_3 , the decomposition of UC_2 into $UC + C$ occurs below 1520° . On the basis of data given in Figures 2.4 and 2.12, this should happen near $1377^\circ C$. It is this reaction which accounts for the frequent observation of UC in slowly cooled $UC_2 + C$. Further studies of this metastable region would be very useful.

It is clear from the above comments that a further understanding of the pure U-C system will have to depend on studies of the ternary systems, U-C-O and U-C-N.

II. Crystal Structure:

The structures of the various phases in this system have been determined on a number of occasions and the excellent agreement leaves little doubt about the results. A summary of the structure and lattice parameters is listed in Table 1.1.

Table 1.1

STRUCTURE AND LATTICE PARAMETERS OF α -U, UC, AND α -UC ₂				
Phases present	Composition of first phase	Lattice parameter (Å)	Structure	Investigator
α -U	Pure	$a = 2.8539 \pm 0.0001$ $b = 5.8691 \pm 0.0001$ $c = 4.9554 \pm 0.0001$	$Cmcm D_{2h}^{17}$ Orthorhombic	Mueller and Hitterman (1960)
UC + U	UC _{0.93}	$a = 4.9563 \pm 0.0007$	fcc	Magnier and Accary (1964)
UC + UC ₂	UC _{1.0}	$a = 4.9605 \pm 0.0002$	fcc	Figure 1 * 3
U ₂ C ₃	U ₂ C ₃	$a = 8.0889 \pm 0.0009$	bcc	Witteman and Bowman (1963)
α -UC ₂ + C	UC _{1.89}	$a = 3.519 \pm 0.001$ $c = 5.979 \pm 0.002$	Tetragonal	Witteman and Bowman (1963)
α -UC ₂	UC _{1.94}	$a = 3.5241 \pm 0.0005$ $c = 5.9962 \pm 0.0008$	Tetragonal	Witteman and Bowman (1963)

Uranium metal has three crystal forms: orthorhombic, tetragonal, and body-centered cubic. Only the first is stable at room temperature and is seen in quenched material.

UC is fcc and has a very small composition range at low temperatures. However, at higher temperatures the lattice can accommodate not only vacancies in the carbon sublattice but C₂ groups can replace the single carbon atoms. In this way, the cubic lattice occurs between UC_{0.89} and UC_{1.0} at 2125°C. If the quenching rate is sufficiently rapid, the lattice can retain most of the carbon vacancies and a small fraction of the C₂ groups, depending of course on the stoichiometry of the sample. The lattice parameter of UC in U + UC or UC + UC₂ is consequently quite sensitive to the quenching rate. Whether vacancies and C₂ groups exist together at high temperatures near UC_{1.0} is uncertain, but probable.

Figure 1.3 shows the variation of lattice parameter and the effect of

Figure 1.3. Lattice parameter of UC as a function of composition.

various annealing times. This behavior is further complicated by the effect of dissolved oxygen. When oxygen replaces carbon in the lattice the gross effect is to lower the parameter. Small amounts of oxygen, in the presence of uranium, however, have been found to produce a maximum (Magnier et al., 1964; Anselin et al., 1964). This effect, shown in Figure 1.4 is apparently due to the presence of carbon atom vacancies in the lattice.

The vacancy concentration would depend on the ambient CO pressure and the heating temperature, and this would account for the rather scattered results in this region. Since the lattice parameter is occasionally used to indicate the stoichiometry and/or purity, a better understanding of this behavior should be sought.

Fig. 1. The variation of lattice parameter of $UC_{1-x}O_x$ with oxygen content.

U_2C_3 was found to be bcc ($I\bar{4}3d$) from x-ray (Mallett et al., 1952) as well as from neutron diffraction studies (Austin, 1959). A lattice parameter of $8.088\text{\AA}$ is usually found regardless of how it is prepared. The compound has a very narrow composition range as well as a low solubility for oxygen and nitrogen. Its formation has been suggested to result from a slight shift in the uranium positions (Gillam, 1962) with the movement of the carbon atoms by interstitial diffusion accounting for the slowness of formation. Magnier et al. (1964a) observed the phase to form from UC_2 by nucleation and growth. Its formation is facilitated by the application of stress and, indeed, the use of pressure can lead to a rapid conversion (Witteaman, 1966).

The structure of $\alpha\text{-}UC_2$ has been determined on several occasions by neutron diffraction (Atoji and Medrud, 1959; Austin, 1959; A. L. Bowman et al., 1966; Atoji, 1967). Each assigned the CaC_2 -type structure ($I4/mmm$). A. L. Bowman et al. (1966) examined the structure at 1700°C and Atoji (1967) extended the measurements from room temperature to 5°K . No structure change

or change in the magnetic properties was observed. Although no super-lattice due to vacancy ordering was observed, the sensitivity may not have been sufficient to see it. It is quite important to the thermodynamics of this phase to determine if such ordering occurs and a further study at low temperatures should be made using more sensitive techniques. The lattice parameters of this phase increase as the carbon content increases, but oxygen apparently has the opposite effect (Henney, 1966). As yet, a definite study of this behavior has not been reported.

Two conflicting structures for β -UC₂ had been suggested by several workers from indirect evidence, but until a neutron diffraction was used, this problem could not be resolved. A. L. Bowman et al. (1966) have made such a study at high temperatures and found a structure similar to KCN with the C₂ groups either as free rotators or randomly oriented along the (111) plane.

2. Thermochemical Properties

I. UC:

A. Low Temperature Heat Capacity

A number of low temperature heat capacity studies have been made but with some differences. Westrum et al. (1965) used massive pieces broken from an arc-melted button. Provided a surface oxide was not formed during handling, this sample should have been oxygen and nitrogen free, although no analyses were given for these elements. An average composition for the three buttons used is $UC_{1.039}$, which means a small amount of UC_2 must have been present. No correction was apparently made. The thermal values at 298.15° are listed in Table 2.1. Andon et al. (1964a) made a similar measurement using arc-melted UC containing 2.5 mole % UC_2 for which corrections were made. The analyzed oxygen content of 0.12 wt % is rather high, but its effect on the measurements is not known since its chemical form is unknown. These data are also listed in Table 2.1. The rather limited values given by deCombarieu et al. (1963) are significantly higher compared to the preceding studies, while the material was apparently much purer. For subsequent calculations, an average between the values reported by Andon et al. (1964a) and those of Westrum et al. (1965) will be used.

Table 2.1

A COMPARISON OF MEASURED LOW TEMPERATURE THERMAL VALUES FOR UC, U_2C_3 , AND UC_2 AT $298.15^\circ K$

C_p (cal/deg-mole)	S° (cal/deg-mole)	$H_{298.15}^\circ - H_0^\circ$ (cal/mole)	Assumed composition	Investigator
		UC		
12.11	14.28	2193	$UC_{1.0}$	Westrum et al. (1965)
11.84	14.03	2159	97.5 UC + 2.5 $UC_{1.9}$	Andon et al. (1964a)
		U_2C_3		
25.66	32.93	4829	U_2C_3	Farr et al. (1965)
26.55	32.91	4836	75.3 U_2C_3 + 10.6 UC + 4.1 $UC_{1.9}$ + 9.9 C	Andon et al. (1964b)
		α - UC_2		
14.46	16.30*	2513	72.05 $UC_{1.90}$ + 10.03 UC + 17.9 C	Westrum et al. (1965)
14.52	16.33*	2521	$UC_{1.94}$	Farr et al. (1965)
14.50	16.31*	2522	4.7 UC + 95.3 $UC_{1.91}$	Andon et al. (1964a)

* Entropy of mixing between random C_1 and C_2 groups is not included.

B. High Temperature Heat Content

Within a short time of one another, two measurements of the heat content of UC were reported, one at lower temperatures and the other to near the melting point, both in excellent agreement.* In the overlap region there is an average deviation from the least squares line of +1% and +0.4%, respectively, for the two studies as listed in Figure 2.1. Levinson's values clearly show an increasing slope, i.e., heat capacity, as the temperature is increased. The usual function which has been used to fit such data (Maier and Kelley, 1932) is inadequate. Consequently, Storms (1967) has chosen to use an equation of the form:

$$H_T - H_{298} = a + bT + cT^2 + dT^3 + e/T \quad (1)$$

and Leitnaker and Godfrey (1967) adopted the form

$$H_T - H_{298} = a + bT + cT^2 + dT^{5/2} + e/T. \quad (2)$$

Contrary to the experience of Leitnaker and Godfrey (1967), equation (1) gives the smaller deviation from the data. By combining the data and forcing C_p at 298.15° to agree with the low temperature measurements, the equation for $H_T^O - H_{298}^O$, as well as thermal functions shown in Tables 2.2 and 2.3 were obtained. The data and equation (1) are compared in Figure 2.1. The values obtained using the two equations differ only in the choice of C_p and S^O at 298.15° .

Because of this increasing heat capacity, particularly in the case of UC_2 , there has been a general reluctance to accept the data of Levinson. In defense of his data I would like to point out that he has measured the

*To adjust to a common reference temperature ($298^\circ K$), 300 cal were subtracted from the values of Harrington and Rowe (1964) and 170 cal were added to the values of Levinson (1964). When the former data were reported at the Harwell Conference, this correction was omitted.

heat content of six other carbide systems (TiC, ZrC, HfC, NbC, TaC and WC), and in each case, where comparison could be made with other measurements, the agreement has been excellent. Most of the carbide systems, however, show this rising C_p (TiC, ZrC, TaC) but not all (HfC, NbC, WC). If this effect were due to the apparatus used by Levinson, it is surprising that each of his studies do not show the same behavior. Indeed, if other heat content measurements which have been made by other workers in this temperature range (Nb, Mo, Ta) are fit by equation (1), a similar increase in C_p is found at high temperatures. The use of the Kelley equation in the past has hidden this behavior (Storms, 1967).

Table 2.2

THERMAL FUNCTIONS OF $UC_{1.0}$ ^a

T (°K)	$H_T^\circ - H_{298}^\circ$ (cal/mole)	C_p° (cal/mole-deg)	S_T° (cal/mole-deg)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/mole-deg)
298.15	0.0	11.98	14.15	14.15
300	22.18	12.00	14.22	14.15
400	1282	13.06	17.84	14.64
500	2618	13.59	20.82	15.58
600	3995	13.94	23.33	16.67
700	5402	14.19	25.50	17.78
800	6832	14.42	27.41	18.87
900	8285	14.64	29.12	19.91
1000	9760	14.86	30.67	20.91
1100	11260	15.08	32.10	21.87
1200	12780	15.32	33.42	22.77
1300	14320	15.58	34.66	23.64
1400	15890	15.85	35.82	24.47
1500	17490	16.13	36.92	25.26
1600	19120	16.44	37.98	26.03
1700	20780	16.77	38.98	26.76
1800	22470	17.11	39.95	27.46
1900	24200	17.48	40.88	28.15
2000	25970	17.86	41.79	28.81
2100	27780	18.27	42.67	29.45
2200	29620	18.69	43.53	30.07
2300	31520	19.14	44.37	30.67
2400	33450	19.61	45.20	31.26
2500	35440	20.10	46.01	31.83
2600	37470	20.60	46.81	32.39
2700	39560	21.13	47.59	32.94
2800	41700	21.68	48.37	33.48
2823	42200	21.81	48.55	33.60

^a $H_T^\circ - H_{298.15}^\circ = -49624 \times 10^3 + 14.315T - 1.5130 \times 10^{-4}T^2 + 3.5038 \times 10^{-7}T^3 + 2.0828 \times 10^5/T$ (cal/mole, 298°-2823°K, $\pm 0.4\%$).

Figure 2.1 . High temperature enthalpy of UC_{10} .

Table 2.3
High-temperature thermal functions of UO

Temperature (°K)	C_p (cal/mole-deg)	$H_T^0 - H_{298}^{0,5}$ (cal/mole)	S_T^0 (cal/mole-deg)	$(H_T^0 - H_{298}^{0,5})/T$ (cal/mole-deg)
298.15	12.11	0	14.28	-14.28
300.00	12.14	22	14.35	-14.28
400.00	13.08	1260	17.99	-14.77
500.00	13.57	2024	20.97	-15.72
600.00	13.89	3000	23.47	-16.81
700.00	14.15	4101	25.64	-17.92
800.00	14.38	5327	27.54	-19.01
900.00	14.61	6677	29.25	-20.05
1000.00	14.84	8149	30.80	-21.05
1100.00	15.08	9744	32.22	-22.00
1200.00	15.33	11465	33.55	-22.91
1300.00	15.59	13311	34.78	-23.78
1400.00	15.87	15284	35.95	-24.60
1500.00	16.17	17480	37.05	-25.40
1600.00	16.47	19918	38.11	-26.16
1700.00	16.80	22781	39.12	-26.89
1800.00	17.13	24278	40.09	-27.00
1900.00	17.49	24209	41.02	-28.28
2000.00	17.85	25976	41.93	-28.94
2100.00	18.23	27770	42.81	-29.58
2200.00	18.62	29622	43.66	-30.20
2300.00	19.03	31505	44.50	-30.80
2400.00	19.45	33428	45.32	-31.39
2500.00	19.88	35395	46.12	-31.96
2600.00	20.33	37495	46.91	-32.52
2700.00	20.78	39760	47.69	-33.07
2800.00	21.25	41700	48.45	-33.61

298.15°K-2481°K

$$H_T^0 - H_{298}^{0,5} = 14.430T - 1.074 \times 10^{-3}T^2 + 1.600 \times 10^{-5}T^3 \\ + 3.473 \times 10^{-7}T^4 - 1.001 \times 10^{-9}T^5$$

Average % error -0.84

In the absence of measurements, a number of estimations of the heat capacity have flourished. Two of the more widely used attempts are compared to several direct measurements and the results of the present treatment in Figure 2.2.

Figure 2.2 Heat Capacity of UC

C. Heat of Formation from Combustion Calorimetry

The heat of formation of UC has been measured by combustion calorimetry on three occasions. Farr et al. (1959) obtained -21.0 ± 1.0 kcal/mole after correcting for about 4% free uranium and 850 ppm oxygen. Droege et al. (1959) gave -20.0 ± 5.0 kcal/mole, after corrections were made for the 1450 ppm oxygen and the uranium metal present. If a common heat of formation for U_3O_8 is used, this value becomes -19.7 kcal/mole. A recent recalculation of the former measurement by Huber et al., (1963) has led to -21.7 ± 1.0 kcal/mole. This was subsequently accepted by the Vienna Panel (1963). Based on a better estimation of the stoichiometry, this becomes -21.1 ± 0.9 kcal/mole for $UC_{0.96}$ (Storms and Huber, 1967).

The vaporization study by Storms (1966) suggested that the heat of formation of carbon-deficient UC might be rather composition-sensitive. Since carbon-deficient material was used in both of the calorimetric studies, another combustion measurement was undertaken by Storms and Huber (1967) using $\text{UC}_{0.996}$ and $\text{UC}_{1.032}$. Values of -23.3 ± 0.9 kcal/mole and -23.0 ± 1.0 kcal/mole, respectively, were obtained for $\Delta H_f^\circ(298.15^\circ)$. The effect of stoichiometry is shown in Figure 2.3.

Figure 2.3. Heat of Formation of UC as a Function of Composition.

D. Free Energy Measurements

The various high temperature studies which give free energy values are compared in Figure 2.4. The shape of the curve is based on the thermal functions listed in Table 2.2 and its position has been adjusted to pass through the most reliable free energy value (1). Each of these measurements will be discussed individually in the order listed in the figure.

(1) The heat of formation from combustion calorimetry has been converted to the free energy of formation by using the following thermal functions:

	<u>-fef, cal/mole-deg</u>
UC _{1.0} (Table 2.2)	14.15
U (Flotow and Lohr, 1960)	12.00
C (JANAF Tables 1960)	1.36
Δfef (formation)	0.79

(2) By equilibrating a bismuth melt with a mixture of UC + UC₂ and determining the concentration of U in the melt, Craig obtained the activity of U in the carbide mixture. The same procedure was used to obtain the activity of U in UC₂ + C. In order to calculate ΔF_f for UC, the ΔF_f for UC₂ in equilibrium with carbon was assumed equal to ΔF_f for UC₂ in equilibrium with UC. This assumption will create an unknown error, but one which will make the calculated free energy of UC numerically too small. Since UC₂ is unstable at the temperature of this measurement, a partial decomposition into carbon and either UC or U₂C₃ could further increase the uncertainty in the free energy value.

(3) Robinson and Chiotti (1964) studied the equilibrium between UC and liquid Zn. The disappearance of UZn_{8.5} above ~700°C was used to obtain -22.7 kcal/mole (700°C) as the free energy for UC

through the relationship $\Delta G^{\circ}(\text{U}_2\text{C}_3) + \Delta G^{\circ}(\text{UZn}_{8.5}) - 3\Delta G^{\circ}(\text{UC}) = 0$. The absence of U_2C_3 in the system at room temperature was explained by assuming an oxygen stabilization of the UC phase which increased as the temperature was lowered, thereby causing the U_2C_3 to decompose. Since most of this work was done in a graphite crucible, unit carbon activity could have resulted. Under this condition, however, UC and U_2C_3 cannot exist together. In addition, the formation of U_2C_3 is so slow at this temperature that an equilibrium involving this phase would be unlikely. In the absence of proof that U_2C_3 actually formed at 700° , there is a serious doubt whether the claimed reaction actually occurred.

(4) Robinson and Chiotti (1964) have measured the free energy of various compositions within the oxycarbide system using the emf produced by the cell $\text{U/LiCl-KCl-UCl}_3/\text{UO}_{x_{1-x}}, \text{C}$. By extrapolating to zero oxygen content, they obtained $\Delta F^{\circ}_{(\text{UC})} = -16,915 - 1.9T$ (460° - 760°C) as an expression for the free energy of formation of pure UC. Unit carbon activity was assumed. Such a low free energy could result if unit carbon activity was not actually achieved at the oxycarbide- UCl_3 interface. According to the phase diagram and an extrapolation of vapor pressure studies, a very small change in the carbon content at this temperature can drastically alter the uranium activity. If this were the case, the above equation would give the partial free energy of uranium in UC_{1-x} , where x represents a very small but unknown defect in the carbon lattice.

(5) McIver (1966) measured the potential created by a cell having an electrolyte of LiCl/KCl containing UCl_3 , and electrodes of U and UC. A number of reasons for the low result can be suggested. The UC sample analyzed to be $\text{UC}_{0.971}$, but the lattice parameter ($4.9534\text{\AA}$) was too low

for this composition. Thus, either the material was impure or the stoichiometry was actually much lower, i.e., about $\text{UC}_{0.90}$. Since such a low composition for the UC phase cannot be quenched in, the former possibility is the more likely one. This creates two counter-acting sources of error. The low stoichiometry will raise the uranium activity, but oxygen stabilization of the phase might produce a lower value. The net result is bound to be very uncertain. The total free energy was then calculated assuming unit carbon activity, an impossibility under the circumstances.

(6) The $\text{UO}_2 + \text{UC}_2 + \text{UC} + \text{CO}$ equilibrium has been studied by several workers. Piazza and Sinnott (1962) measured the CO pressure between 1761° and 1953°K . Bazin and Accary (1967) extended the measurement from 1723° to 2073°K . They observed the same behavior whether the starting material was pure $\text{UC}_{1.0}$, $\text{U}(\text{C}_{0.9}\text{O}_{0.1})$, $\text{U}(\text{C}_{0.76}\text{O}_{0.24})$ or $\text{U}(\text{C}_{0.7}\text{O}_{0.3})$. Henry et al. (1967) determined the CO pressure as a function of composition at 1973° . At this temperature the UC phase contained 5 atomic percent oxygen. The pressures reported by these studies are in excellent agreement. The resulting free energy of formation of UC is shown in Figure 2.4. Apparently the dissolution of 5 at. % oxygen does not have much effect on the free energy of UC.

(7) A number of vapor pressure measurements have been made in this system with varying success. Indeed, if viewed on an equal basis, the measurements would lead to total uncertainty (Figure 2.5). However, sufficient experience has been accumulated that one can reasonably eliminate quite a few of the attempts solely on the basis of the described experimental procedure. For example, if a powder is used without a

Figure 2.5 Evaporation Rate of U_(g) from UC₂ + C and of Carbon from Graphite.

Table 2.5

Thermal Functions of $UC_{1.90}^*$

	Temperature °K	$H_T^O - H_{298}^O$ cal/mole	C_p^O cal/mole-deg	S_T^O cal/mole-deg	$-(H_T^O - H_{298}^O)/T$ cal/mole-deg
α -	298.15	0.00	14.52	16.33	16.33
	300	26.92	14.58	16.42	16.33
	400	1607.5	16.67	20.95	16.93
	500	3321.3	17.49	24.77	18.13
	600	5093.4	17.91	28.00	19.51
	700	6900.9	18.23	30.79	20.93
	800	8740.6	18.57	33.25	22.32
	900	10618.	18.99	35.46	23.66
	1000	12543.	19.52	37.48	24.94
	1100	14527.	20.187	39.37	26.17
	1200	16585.	20.99	41.16	27.34
	1300	18730.	21.94	42.88	28.47
	1400	20978.	23.05	44.55	29.56
	1500	23344.	24.30	46.18	30.62
	1600	25844.	25.72	47.79	31.64
	1700	28493.	27.29	49.40	32.64
	1800	31308.	29.03	51.01	33.61
	1900	34304.	30.92	52.62	34.57
	2000	37497.	32.98	54.26	35.51
	2038	38766.	33.80	54.89	35.87
β -	2038	41264.	29.44	56.12	35.87
	2100	43089.	29.44	57.00	36.48
	2200	46033.	29.44	58.37	37.45
	2300	48976.	29.44	59.68	38.39
	2400	51920.	29.44	60.93	39.30
	2500	54864.	29.44	62.14	40.19
	2600	57808.	29.44	63.29	41.06
	2700	60751.	29.44	64.40	41.90
	2800	63695.	29.44	65.47	42.72
α - UC_2	$H_T^O - H_{298}^O = 8.377 \times 10^3 + 23.40T - 5.752 \times 10^{-3}T^2 + 2.727 \times 10^{-6}T^3 + 5.487 \times 10^5/T$				
β - UC_2	$H_T^O - H_{298}^O = -1.873 \times 10^4 + 29.44T$				

*Randomization entropy not included.

prolonged purification about 2000°C, the presence of important amounts of evaporating $\text{UO}_{(g)}$ and of serious concentration gradients within the sample would be a certainty. The grinding of a sample between measurements, even if this is done in a dry box, is a very $\dots$ procedure. Without berating each measurement, there are several which I would expect to give trustworthy values. The resulting uranium pressures are compared in Figure 2.6, and the partial molar heats of vaporization are plotted in Figure 2.7.

Given this body of data, there remains the problem of interpretation. Because most measurements do not fall at compositions for which thermal data or heats of formation values are available, it is impossible to make thermodynamic calculations without assuming that the properties are independent of composition. Furthermore, it has been impossible to determine if the measured pressures and partial heats at the various compositions were internally consistent. The mass spectrometric study reported by Storms (1966) allows these isolated measurements to be compared and interpolated to more convenient compositions. Mass spectrometry is ordinarily given a rather high uncertainty because of several unknowns in the machine pressure calibration. However, the internal consistency of the data within a system should be very good. Therefore, I propose to adjust the pressure curve given by Storms (1966) so as to average the various absolute measurements at the various compositions. This requires an 8% increase in pressure. As a result, the pressures at all compositions have the benefit of four absolute measurements and, therefore, should be more certain than a single measurement. Other mass spectrometric studies at $\text{UC}_{1.04}$ (Pattoret et al., 1967) and $\text{UC}_2 + \text{C}$ (Norman and Winchell, 1964) are also in excellent agreement.

Figure 2.6 Pressure of $U_{(g)}$ over various Compositions in the Uranium-Carbon System.

Figure 2.7 Partial Molar Heat of Vaporization of Uranium as a Function of Composition.

In order to calculate the total free energy of UC it is also necessary to know the carbon activity and the heat of vaporization of uranium. These will be discussed in order.

The carbon activities at several compositions have been obtained by measuring the $UC_2(g)/U(g)$ intensity ratio in a mass spectrometer (Storms, 1966; Pattoret et al, 1967), from the vaporization behavior of the congruent composition (Pattoret et al, 1967; Vozzella, 1965), and from CH_4-H_2 equilibrium measurements (White and Juenke, 1967). These results are compared to a Gibbs-Duhem integration of the uranium pressures in Figure 2.8. The small extrapolation of the measured carbon activity, 1973° to 2000° in the case of White and Juenke (1967) and 2500 to 2400° for Pattoret et al, (1967) was made using the temperature coefficients reported by Storms (1966). For subsequent calculations, the Gibbs-Duhem values which are listed in Table 2.4, will be used.

The heat of vaporization of uranium is another problem, but one to which this system can make a contribution. There are three areas of the U-C system from which an estimate of the heat of vaporization of uranium can be obtained. A look at Figure 1.1 will help place these in context. The regions consist of liquid uranium which is saturated with carbon; a composition of $UC_{1.0}$ for which thermal data and a heat of formation value are known; and $UC_{1.9}$ which must be treated rather cautiously. I will discuss the first two here and UC_2 in a later section.

One would expect the dissolution of carbon to lower the pressure of uranium over the liquid, but by some unknown amount. Hence, the $U(g)$ pressure over this solution gives a lower limit to that for pure

Figure 2.8 Activity of Carbon as a Function of Composition in the Uranium-Carbon System.

Table 2.4
Activity of U and C, and ΔF_f^0 at 2000° and 2400°K

C/U Atom ratio	Uranium* activity 2000°K	Carbon activity	$-\Delta F_f^0$ kcal/mole	C/U Atom ratio	Uranium* activity 2400°K	Carbon activity	$-\Delta F_f^0$ kcal/mole
1.86	1.67×10^{-3}	1.0	25.41	1.90	3.35×10^{-3}	1.0	27.18
1.80	2.35×10^{-3}	8.30×10^{-1}	25.39	1.88	4.35×10^{-3}	8.71×10^{-1}	27.17
1.75	3.20×10^{-3}	6.97×10^{-1}	25.34	1.86	5.00×10^{-3}	8.08×10^{-1}	27.15
1.09	3.20×10^{-3}	6.97×10^{-1}	24.39	1.84	5.70×10^{-3}	7.53×10^{-1}	27.13
1.07	3.80×10^{-3}	5.95×10^{-1}	24.36	1.82	6.30×10^{-3}	7.13×10^{-1}	27.10
1.05	4.75×10^{-3}	4.82×10^{-1}	24.31	1.80	6.80×10^{-3}	6.84×10^{-1}	27.06
1.03	6.40×10^{-3}	3.62×10^{-1}	24.24	1.76	7.80×10^{-3}	6.33×10^{-1}	26.99
1.02	8.00×10^{-3}	2.91×10^{-1}	24.19	1.72	8.8×10^{-3}	5.90×10^{-1}	26.89
1.01	1.05×10^{-2}	2.22×10^{-1}	24.14	1.66	9.50×10^{-3}	5.64×10^{-1}	26.74
1.00	2.20×10^{-2}	1.07×10^{-1}	24.06	1.60	1.00×10^{-2}	5.47×10^{-1}	26.56
0.99	7.00×10^{-2}	3.33×10^{-2}	23.95	1.55	1.07×10^{-2}	5.24×10^{-1}	26.42
0.98	1.15×10^{-1}	2.01×10^{-2}	23.81	1.40	1.15×10^{-2}	4.99×10^{-1}	25.94
0.97	1.65×10^{-1}	1.39×10^{-2}	23.65	1.35	1.20×10^{-2}	4.84×10^{-1}	25.77
0.96	2.10×10^{-1}	1.08×10^{-2}	23.47	1.25	1.25×10^{-2}	4.69×10^{-1}	25.41
0.95	2.60×10^{-1}	8.65×10^{-3}	23.29	1.20	1.33×10^{-2}	4.45×10^{-1}	25.23
0.94	3.10×10^{-1}	7.18×10^{-3}	23.09	1.10	1.75×10^{-2}	3.50×10^{-1}	24.80
0.93	3.60×10^{-1}	6.12×10^{-3}	22.89	1.05	2.35×10^{-2}	2.66×10^{-1}	24.51
0.92	4.20×10^{-1}	5.18×10^{-3}	22.69	1.03	2.80×10^{-2}	2.25×10^{-1}	24.37
0.915	4.50×10^{-1}	4.81×10^{-3}	22.58	1.01	3.60×10^{-2}	1.76×10^{-1}	24.22
				1.00	4.50×10^{-2}	1.41×10^{-1}	24.13
				0.99	7.00×10^{-2}	9.03×10^{-2}	24.03
				0.98	1.00×10^{-1}	6.29×10^{-2}	23.91
				0.97	1.35×10^{-1}	4.62×10^{-2}	23.77
				0.96	1.70×10^{-1}	3.64×10^{-2}	23.62
				0.95	2.10×10^{-1}	2.92×10^{-2}	23.45
				0.94	2.50×10^{-1}	2.43×10^{-2}	23.28
				0.93	2.80×10^{-1}	2.15×10^{-2}	23.10
				0.92	3.20×10^{-1}	1.86×10^{-2}	22.92
				0.91	3.50×10^{-1}	1.69×10^{-2}	22.72
				0.90	3.85×10^{-1}	1.52×10^{-2}	22.52

*Heat of vaporization of uranium =
128.0 kcal/mole

uranium. A further refinement results if the solution is assumed to be ideal. This provides another lower limit to the pressure, but one which would be closer to the truth. With this assumption, a third law treatment gives 130.2 kcal/mole as the upper limit to the heat of vaporization at 298.15°K. Since the solubility of carbon becomes quite small as the eutectic temperature is approached, the measured pressure should approach that for the pure liquid as the temperature is dropped. As a result, the slope of the log P vs 1/T curve should be less than that of the pure liquid, and give a lower limit to the heat of vaporization. A value of 123.2 ± 0.5 kcal/mole is obtained from a second law treatment. The error is due solely to the statistical uncertainty in fitting the pressures with a straight line. This limit would apply to pure uranium only if the dissolution of carbon had no effect on its vapor pressure, a rather unlikely possibility. If an ideal solution is assumed, this limit becomes 126.4 kcal/mole. These limits encompass the spectrum of values which are currently being reported as the heat of vaporization, but the value which was adopted by the last Vienna Panel (1963) is completely excluded.

The calculation of ΔF_f for UC from the vaporization behavior presents some problems. Since the activities change very rapidly in this region, it is difficult to draw a proper curve through the data and pick a value from it. Nevertheless, the free energy, shown in Table 2.4, will be used. For this calculation, 128.0 kcal/mole will be used as the heat of vaporization of uranium [ΔH_v^0 (298.15°)]. On this basis, the free energy of formation for UC_{1.0} is shown in Figure 2.4. It is apparent from this figure that if the heat of combustion value is correct, then the vapor pressures are

too low by 1.5 kcal/mole. In short, there is a discrepancy of 1.5 kcal/mole which could be eliminated by choosing 126.5 kcal as the heat of vaporization of uranium. The rather scattered values which were obtained from other techniques give no help in resolving this problem.

A composition near $UC_{1.1}$ is congruently vaporizing above $\sim 2300^\circ K$. This fact has been amply demonstrated by direct evaporation (Vozzella, 1965; Bowman and Krupka, 1963; Leitnaker and Wittman, 1962) and it is consistent with the vapor pressures shown in Figure 2.6. This is apparent in Figure 2.9 where the molar evaporation rate ratio, C/U is plotted against the solid composition, C/U atom ratio. The congruent composition occurs where these two quantities are equal. Vozzella (1965) has used the Langmuir technique to measure the uranium pressure over the congruent composition. However, the resulting uranium pressures are a factor of 0.3 below those obtained from Knudsen measurements (Figure 2.6). This would suggest a low evaporation coefficient for uranium. On the other hand, Pattoret et al. (1967), using a mass spectrometer, conclude that the evaporation coefficient for $U_{(g)}$ is unity. These inconsistencies subject the Langmuir measurements to a very large uncertainty. The apparent agreement with other data occurs because the measurements also lead to a very high carbon activity (Figure 2.8) which compensates for the low uranium pressure when the total free energy is calculated.

Figure 2.9. A comparison between the solid and gas composition as a function of composition at 2100° and 2300°K.

II. U_2C_3 :

A. Low Temperature Heat Capacity

Low temperature data for this compound has been provided by Farr et al. (1965) and by Andon et al. (1964a).^{*} As is generally the case with this compound, the data, shown in Table 2.1, are in excellent agreement.

B. High Temperature Heat Content

No studies have been reported. The unusual behavior of UC_2 and UC would make any attempt to estimate values very uncertain.

C. Thermochemical Measurements

A heat of formation of -49 ± 4 kcal/mole of U_2C_3 was obtained by Huber and Holley (1962) from the heat of combustion. A repeat of this measurement by the same workers (1968) gave -43.3 ± 0.9 kcal/mole when purer materials were used. Galvanic measurements between 700° and 900°C by Behl and Egan (1966) gave the equation $F_f^0 = -43,860 - 7T^\circ K$ (cal/mole).

^{*}The reported values were subsequently amended slightly (Andon et al., 1964b).

Unit carbon activity was assumed although there was no experimental justification for this reported. The free energy can also be calculated from the equilibrium $U_2C_3 = 0.72UC_{1.67} + 1.242UC_{1.75}$ which occurs near 2000°K and the reaction $U_2C_3 + 0.76C = 2UC_{1.67}$ which is found near 1790°K. If the free energy values obtained from the vapor pressure measurements are used (Table 2.4) for the first reaction and Figure 2.12 for the second, the respective reactions result in -49.96 kcal/mole and -52.0 kcal/mole. These measurements are compared in Figure 2.10. Because of the absence of thermal data, it is impossible to know if these measurements are internally consistent. However, the value based on the vapor pressures is clearly much too low if 128.0 kcal/mole is used as the heat of vaporization of uranium. Again, the use of 126.5 kcal/mole produces better consistency, as can be seen in the Figure.

III. UC_2 :

A. Low Temperature Heat Capacity

UC_2 has been studied at two different compositions. For $UC_{1.90}$, Andon et al. (1964a) as well as Westrum et al. (1965) obtained essentially identical results. A study of single-phase $UC_{1.94}$ reported by Farr et al. (1965), also shows no significant difference from the lower composition. These values are compared in Table 2.1.

B. High Temperature Heat Content

Two measurements of this property have been reported, Macleod and Hopkins (1967) and Levinson (1963). These are compared in Figure 2.11. When these two studies are combined and fit by equation (1), Section I-B, two points of interest emerge.

Figure 2.10 Free Energy of Formation of U_2C_3 .

Figure 2.11 Heat Content and Heat Capacity of $UC_{1.9}$.

$$U + 1.9C = UC_{1.9}$$

Randomization Entropy Included

The two highest data points of Macleod and Hopkins (1967) suggest a somewhat lower heat content curve at higher temperatures and, as a result, a lower heat capacity. This trend is attractive in view of the sharply rising heat capacity reported by Levinson (1963). On the other hand, this small difference could result because different compositions were used. The heat content of $UC_{1.34}$ should be higher than that of $UC_{1.89}$ and the difference should increase as the temperature is increased. In the absence of more data, there is little reason to question the values given by Levinson (1963) below $\sim 1650^\circ K$.

Above 1650° , however, some caution must be used. When $UC_2 + C$ is cooled from above $2028^\circ K$, the presence of precipitated UC is often observed. Presumably this occurs between 2038° and approximately 1650° , as the metastable phase diagram indicates (Figure 1.1). Such a precipitation would probably occur during Levinson's measurements. Leitnaker and Godfrey (1967) chose to correct for this by calculating the thermal functions for the mixture $0.055UC + 0.945 UC_{1.91} + 0.07C$. In principle this is perfectly correct, but there is no way of knowing how much UC actually precipitated during cooling in Levinson's calorimeter. Besides, the correction to the free energy function is very small, although the heat capacity would be reduced somewhat. Consequently, this refinement will be ignored in subsequent calculations in this paper.

One factor which cannot be ignored is the randomization entropy in substoichiometric UC_2 . As discussed by Leitnaker and Godfrey (1967), 0.65 e.u. must be added to the measured entropy of $UC_{1.90}$ if the structure does not order within the range of the low temperature heat capacity measurements. Since there is no evidence that such ordering occurs, this value should be added to the thermal functions listed in Table 2.5.

Within these limitations, the thermal functions of UC_2 appear to be essentially correct.

C. Thermochemical Measurements

A number of free energy of formation values are compared in Figure 2.12. The curve is based on the thermal functions listed in Table 2.5 and its position was adjusted to average the measurements (2), (3), and (5). These will be discussed according to the numbering system on the Figure.

(1) A redetermination of the heat of combustion of $UC_{1.90}$ (Huber et al., 1963) has yielded -21.1 ± 1.4 kcal/mole at 298.15° . The Vienna Panel (1963) adopted -23 ± 2 kcal/mole. This has been converted to the free energy of formation through the thermal functions in Table 2.5 and Section 2.I.D.

(2) McIver (1966) measured the emf produced by the cell described in the UC section, but with electrodes of U and UC_2 containing oxygen, in one case, and with electrodes of UC and UC_2 of various purities in the other case. An effect of oxygen on the stability of UC_2 was claimed. In each case, the arc-melted material was annealed at $1500^\circ C$ for 24, 26 and 72 hr., and the respective samples were each compared to UC in the cell. A decrease in potential was found when the annealing time was lengthened. This was attributed to an increased purity. On this basis, the data were adjusted to minimum oxygen content.

(3) Craig (1966) equilibrated $UC_2 + C$ with liquid Bi and, from the uranium concentration in the melt, obtained the uranium activity.

(4) Rice et al. (1958) used the same technique as described above.

(5) By measuring the emf developed by a cell involving C, UC_2 , UF_2 , and U, Behl and Egan (1966) obtained the equations $\Delta F_f^0 = -15,820 - 8.2T$ (cal/mole, 973° - 1145°) and $\Delta F_f^0 = -18,980 - 5.2T$ (cal/mole, 1045° - 1193°) for the free energy of UC_2 .

(6) The CO pressure over an initial mixture of UC_2 and graphite has been measured and attributed to the equilibrium $UO_2 + 4C = UC_2 + 2CO$ (Piazza and Sinnott, 1962). The values shown in the figure are based on a re-evaluation of this measurement by Leitnaker and Godfrey (1967). If oxygen stabilization of UC_2 , as claimed by McIver (1966), is a real phenomenon, then the good agreement between this measurement and those where oxygen was absent must be pure coincidence. On the other hand, it suggests the unattractive possibility that oxygen stabilization of the UC_2 phase is actually small.

(7) The various vapor pressure measurements were treated as described in Section 2.I.D and were converted to the free energy of formation using 128.0 kcal/mole as the heat of vaporization of uranium. Once again, agreement between the vapor pressures and other free energy data can be obtained if a value of 126.5 kcal/mole is adopted for the heat of vaporization of uranium.

IV. Some General Comments

During the past 10 years there has been a controversy between 117 kcal/mole and a value near 126 kcal/mole for the heat of vaporization of pure uranium. Two direct measurements, one by mass spectrometry

(Pattoret et al., 1967) and one by direct collection (Olson, 1968) both support the higher value as do the thermodynamic cycles in various uranium binary systems. It is inconceivable that this large and thoroughly studied body of data could be wrong by almost 10 kcal/mole. However, even if this problem is laid to rest and the larger value is accepted, there still remain several discrepancies. Olson (1968) and Pattoret et al. (1967) observed uranium pressures which lead to 130.4 and 128.5 kcal/mole, respectively, for the heat of vaporization at 298.15°. Olson (1968) observes that carbon has little effect on the vapor pressure. Consequently, the pressures over $U_{(s)} + UC$, as measured by Storms (1966), add support. However, the second law heats obtained from these studies are consistently lower than the third law. This is one discrepancy. Another one occurs when the measured uranium pressures are combined with the pressures over the U-C system. The resulting free energy values are much too low as can be seen in Figure 2.4 and 2.12. Is there perhaps a single factor which will eliminate each of these differences as Olson has suggested? One possibility is that the thermal functions for uranium (condensed state) are wrong. In fact, an increase of 2 entropy units in the free energy function of uranium would lead to total agreement. This calculation is summarized in Appendix I. Furthermore, if this change is made and the values are used to compare the various free energy measurements, as is done in Figure 2.13, the effect of oxygen stabilization on the UC_2 phase now becomes more obvious. However the study involving $UC_2 + CO$ (6), which should show the largest effect, still is apparently unaffected by oxygen.

A considerable improvement in the consistency between various measurements

can be obtained if the entropy of U at 298.15° is 14 e.u. instead of 12 e.u. With this change, the heat of vaporization of uranium would become 126.5 kcal/mole.

One naturally asks how such a large amount of entropy could have been missed by the various low temperature heat capacity studies? Alpha uranium shows an anomaly in several elastic properties (Flotow and Osborne, 1966; Fisher, 1964) near 41°K. While neutron diffraction studies fail to reveal a structure change, there is evidence for a magnetic transition (Mueller, et al., 1964). Whether this could contribute 2 entropy units is uncertain, but it does suggest the possibility and the need for a closer examination in this temperature range.

14. Six J

2000°K

1. Assume thermal functions in Table 2.4 are correct
2. Assume $\Delta H_f^0(298) = -21.1 \text{ kcal/mole}$
3. Assume pressures in Figure 2.6 are correct.
4. Assume pressures measured over pure uranium by Olson (1968) are correct.

$$\Delta F_{\text{vap}} = -23.01 \text{ kcal}$$

$$\Delta H = -21.1$$

$$\text{fef}_U = \frac{H_{-1} / 10^0}{T} + \text{fef}_{UC_2} - 1.9 \text{fef}_C$$

$$\text{fef}_{\text{UC}_2} = -36.11$$

$$1.9 \text{ fef}_c = -10.43$$

$$f_{cf_{II}} = -24.73$$

measured $f_{cf} = -22.23$

$$\Delta = 2.50 \text{ e.u.}$$

2000°K

1. Assume pressures measured by Olson (1968) are correct, i.e. $\Delta H_V^0(298) = 130.4$ kcal/mole
2. Assume pressures in Figure 2.6 are correct.
3. Assume the heat of formation of $UCl_{1.0} = -23.3$ kcal/mole at 298.15°
4. Calculate f_{ef_H} to give agreement.

$$\Delta H^{\circ} = \Delta F^{\circ} - T \Delta \text{ref}$$

$$\Delta f_{ef} = f_{ef_{UC}} - f_{ef_U} - f_{ef_C}$$

$$\text{fef}_U = \frac{\Lambda_{U-1} P^0}{q} + \text{fef}_{UC} - \text{fef}_C$$

$$\text{fef}_{\text{UC}} = -23.81 \text{ e.u.}$$

$$f_{CF} = -5.49$$

$$f_{cf,II} = -24.14$$

measured $f_{ef} = -22.23$

$$\Lambda = 1.91 \text{ e.u.}$$

2000°K

$$U_{(l)} = U_{(g)}$$

1. Assume pressures and slope measured by Olson (1968) are correct
 $\Delta H(2nd) = 126.5$ kcal/mole.
2. Calculate $fe_{U(l)}$ to give second and third law agreement.

$$\log P = -2.941 \times 10^4/T + 5.39$$

$$\Delta F_T = +66.947 \text{ kcal}$$

$$\Delta H^0 = 126.5$$

$$\Delta fe_f = fe_{U(g)} - fe_{U(l)}$$

$$fe_{U(l)} = \frac{\Delta H - \Delta F_T}{T} + fe_{(g)}$$

$$fe_{(g)} = -53.83$$

$$fe_{U(l)} = -24.05$$

$$\text{measured} = -22.23$$

$$\Delta = 1.82 \text{ e.u.}$$

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PLUTONIUM-CARBON SYSTEM

1. Phase Relationship

It is not surprising that data on the properties of the plutonium carbides are few and a knowledge of this system is growing rather slowly. Consequently the review by Storms (1967) is still topical and will not be repeated here. A phase diagram based on this evaluation is shown in Figure 1.1. There have been, however, several recent studies which lead to free energy information at high temperatures. These will be discussed in the following sections.

Figure 1.1. Phase diagram of the Pu-C system.

2. Thermochemical Properties

I. Pu₂C₃ + C and PuC₂ + C

A. Vaporization Behavior

Mulford and co-workers, in a continuing study of the vaporization behavior, have determined the following least squares equations for the

indicated temperature and composition ranges.

$$\log P = -17920/T + 2.779 \quad (2000-2500^\circ\text{K}) \quad \text{PuC}_2 + \text{C} \quad \text{Mulford et al. (1962)}$$

$$\log P = -(20330 \pm 140)/T + (4.39 \pm 0.08) \quad (1514-1989^\circ\text{K}) \quad \text{Pu}_2\text{C}_3 + \text{C} \\ \text{Olson and Mulford (1968)}$$

$\text{PuC}_2(\text{g})$ was found to be a minor species over $\text{Pu}_2\text{C}_3 + \text{C}$ and undetectable over $\text{PuC} + \text{Pu}_2\text{C}_3$. The first two equations were used to obtain the free energy of formation shown in Figure 2.1. The lines marked (2) and (3) should have a common value at 2000°K if this is indeed the decomposition temperature of PuC_2 . The fact that they do not indicates an inconsistency between the two studies which could be due to an error in the pressures reported by Mulford et al. (1962). Ward, (see Olson and Mulford, 1968) found that when Pu evaporates from a graphite cell, the vapor does not leave the orifice with a cosine distribution. As a result, the measured pressures tend to be too low. Since Mulford et al. (1962) used a graphite cell and the measured pressures are indeed low compared to a tungsten cell which does not show this effect (Olson and Mulford, 1968), the former measurement should be considered a lower limit to the Pu pressure.

A transpiration study by Harris et al. (1967) which cannot be quoted, is in much better agreement with (2) than with (3).

Ainsley et al. (1964) measured the Pu pressure over oxide-carbon mixtures and obtained values which were about 0.1 of those over $\text{Pu}_2\text{C}_3 + \text{C}$. Apparently, the presence of oxygen has a stabilizing effect on this system.

B. EMF Measurements

Campbell (1968) has studied cells of the type $\text{M}/\text{Pu}^{+3}, \text{LiCl-KCl}/\text{PuRu}_2 + \text{Ru}$ where M is $\text{Pu}_{(l)}$, $\text{PuC} + \text{Pu}_2\text{C}_3$ or $\text{Pu}_2\text{C}_3 + \text{C}$. The resulting free energy of formation of Pu_2C_3 is shown in Figure 2.1. A comparison to the vapor pressure studies is limited by the absence of thermal values for this compound. Nevertheless, the slope given by the EMF measurement would appear

to be in error. In addition, since the EMF and vapor pressure studies were made in a two phase region, a change in the Pu_2C_3 composition as the temperature is changed could also introduce a large uncertainty in the slopes.

While the free energy of this compound is still uncertain, it is clearly more stable than indicated by the combustion measurements of Huber and Holley (1962).

II. $\text{PuC} + \text{Pu}_2\text{C}_3$

A. Vaporization Behavior

Olson and Mulford (1968) obtained

$$\log P = -(19160 \pm 260)/T + (5.30 \pm 0.17) \quad (1366^\circ\text{--}1835^\circ\text{K})$$

for the pressure of Pu over $\text{PuC} + \text{Pu}_2\text{C}_3$. The resulting partial molar free energy of formation is shown in Figure 2.2. If a value for the free energy of formation for Pu_2C_3 is taken from Olson and Mulford (1968) and if this value is assumed not to change with the composition of the Pu_2C_3 phase, then the free energy of formation of PuC varies according to the equation $\Delta G = -11053 - 0.64T$ (cal/mole of $\text{PuC}_{0.87}$).

The transpiration study by Harris et al. (1967) gives pressures which are basically consistent but the slope is much different from that found in the above study.

The Langmuir measurements of Potter (1964) cannot be used to generate thermochemical data because of composition gradients which were demonstrated to be present in their sample.

B. EMF

Campbell (1968), using the cell $\text{Pu}_2\text{C}_3 + \text{PuC}/\text{Pu}^{+3}$, $\text{LiCl-KCl}/\text{PuRu}_2 + \text{Ru}$, obtained a partial molar free energy of formation as indicated in Figure 2.2. Again the slope is inconsistent with that obtained from the vapor pressure measurements.

It is generally accepted that the high carbon phase boundary of PuC moves to a lower stoichiometry as the temperature is increased. This will lead to an increasing Pu pressure compared to the behavior if the composition remained fixed. Therefore the slope of lines shown in Figure 2.2 may be too steep and not directly related to the entropy of $\text{PuC}_{0.87}$. The change in Pu pressure at 1800°K between the various 2 phase regions is diagrammed in Figure 2.3. Carbon activities, obtained from a Gibbs-Duhem integration of the curve, are also shown.

Figure 2.3. Pressure of $\text{Pu}_{(g)}$ over various compositions in the Pu-C system.

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