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A MASS SPECTROMETRIC STUDY OF THE VAPOR PRESSURE OF $U_{(g)}$ AND $UC_{2(g)}$ OVER
VARIOUS COMPOSITIONS IN THE URANIUM-CARBON SYSTEM

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ABSTRACT

The pressure of $U_{(g)}$ and $UC_{2(g)}$, and the resulting partial heats of vaporization of $U_{(g)}$ and $C_{(g)}$ have been measured as a function of composition from $UC + U_{(l)}$ to $UC_2 + C$. An abrupt pressure change with composition was found near $UC_{1.0}$ and a much lesser change within the UC_2 region. The partial heat of vaporization of $U_{(g)}$ at $\sim 2200^\circ K$ shows a similar rapid change in value through $UC_{1.0}$ with a maximum near $UC_{1.2}$ at 167 ± 2 kcal/mole. Another maximum occurs in the UC_2 region at 147 ± 2 kcal/mole and $UC_{1.85}$. The heat of vaporization based on the $UC_2 + C$ region is too low since the UC_2 phase changes composition with temperature.

The measured pressures are consistent with congruent vaporization near $UC_{1.1}$.

Evidence is presented supporting a value for the heat of vaporization of uranium near 126 kcal/mole. Using this value, the measured pressures in the U-C system show excellent agreement with the other thermodynamic measurements.

A re-evaluation has been made of the high temperature thermal functions of U, UC and UC_2 with the result that significant changes must be made in the currently used values.

Several areas of the phase diagram have been determined both directly and from the pressure measurements and are compiled into a phase diagram of the system.

1. INTRODUCTION

There have been numerous vapor pressure measurements of the uranium-carbon system, all in sufficiently poor agreement that the actual vaporization behavior is in some dispute. In the two phase region consisting of $UC_2 + C$, six Knudsen effusion studies using target collection [1-6]; a measurement by weight loss from a cell [7]; and one mass spectrometric study [8] have been reported. In addition, two laboratories have reported studies at a composition near UC, one using Langmuir evaporation [9,10] and the other using target collection techniques [2]. The results of measurements using $UC_2 + C$ are shown in Figure 1 as equilibrium evaporation rates. By comparing these to the equilibrium evaporation rate of carbon, as presented by Stull and Sinke[11], one can see that all except two investigations predict a preferential loss of carbon from $UC_2 + C$. This is consistent with observations of a congruently vaporizing composition near $UC_{1.1}$ [5,10,12]. However, the thermodynamic values adopted by the Vienna Panel [13] predict that uranium will be lost faster than carbon from all compositions in this system. Support for this view has been presented in papers by Alcock, Eick, Rauh and Thorn [14] in which they suggest that the measured uranium pressure over UC_2 is too low because of its slow diffusion through a graphite layer which forms on the surface, and that the congruent composition was obtained because of an excessive loss of carbon as CO. On the other hand, Alexander and co-workers [2] have argued that the congruent composition is dictated by the kinetics of vaporization and

Figure 1. A comparison between the "equilibrium" evaporation rates of U_(g) from UC₂ and of carbon from graphite.

not by the equilibrium pressures. Therefore, the pressure of $U_{(g)}$ and $UC_2(g)$ were re-measured over $UC_2 + C$ as well as over eighteen other compositions within the system.

Recently, Drowart, Pattoret and Smoes [15] have re-determined the heat of vaporization of pure uranium using a mass spectrometer. From this work, and previous mass spectrometer studies [16,17], with supporting arguments based on thermodynamic cycles within several uranium systems, they conclude that the value reported by Rauh and Thorn [18] is too low. Because of this conflict, measurements were made which set limits to the heat of vaporization and pressure of uranium. This included a determination of the solubility of carbon in liquid uranium.

An additional problem, not specific to this system, is that in a two phase region the composition of the phases will change with temperature. Unless the magnitude of this change is known to be small, the thermodynamic values have no simple significance. All of the vapor pressure measurements using $UC_2 + C$ suffer from this uncertainty. Consequently, the composition of the β - $UC_2 + C$ phase boundary was determined.

2. EXPERIMENTAL

2.1 Sample Preparation and Analysis

Samples of various compositions were prepared by arc-melting uranium and graphite rods together using a graphite electrode and a copper hearth. All of the samples were analyzed for uranium by ignition at 800°C and some were analyzed for C, N, O and various other elements. The results are listed in Table I. As a check, some samples were analyzed repeatedly

for uranium by a gravimetric technique [19]. The agreement between the methods was excellent and gave an uncertainty in the C/U atomic ratio of ± 0.005 .

X-ray diffraction examination of the important samples was made using a 114.6 mm Debye-Scherrer camera with copper radiation and a nickel filter. Metallographic examination of certain samples was also undertaken.

2.2 Vapor Pressure Determination

A 60° sector, 12 inch radius, differentially pumped mass spectrometer was used for these studies. Electron bombardment heating was used but several important improvements were made in the conventional oven design. In order to control or eliminate the axial temperature gradient within the crucible, three independently controlled tungsten filaments were used as the electron source. This arrangement is shown in Figure 2. The top and center filaments surrounded the top and bottom of the crucible, respectively, while the bottom filament heated mainly the base. By changing the filament temperature, the amount of bombardment current to these regions could be changed with a resulting change in the temperature gradient. The radiation shield was allowed to float electrically. Elimination of the gradient was found to be no easy task, especially when uranium compounds were used. At low temperatures ($< 1500^{\circ}\text{C}$) equal power to each filament produced a slight gradient, but as the temperature was increased the gradient between the ends became increasingly worse. Adjustment of the relative filament power could keep this gradient

Figure 2. Electromagnet over assembly.

small until the top filament was essentially off and control was lost. The temperature at which this occurred depended on the amount of uranium activation the top filament had experienced and was the upper limit to the measurements. If the radiation shield was grounded, this limit was much lower. In addition to the problem of keeping the ends of the crucible at the same temperature, it was found that above 1500°C the temperature at the position of the evaporating surface increased over the end temperature. The magnitude of this effect was determined by measuring the temperature in holes drilled at various levels in an empty crucible. This gave a correction factor which was subsequently applied to the measured top and bottom temperature. A complete study of the gradient effect was made and reported previously [20]. The results of this study indicate that if the temperature at the evaporating surface is known, temperature and pressure are uniquely related regardless of the temperature in the remainder of the cell. This generalization is complicated somewhat if condensation is occurring within the cell.

As a further check on the temperature, pieces of metal-carbide eutectic compositions were placed in the cell and, after cooling from various temperatures, an indication of melting was determined by visual inspection. This temperature was compared to measurements made in a special black-body crucible using induction heating and the "Rupert" thermal analysis apparatus [21]. The Rh-RhC eutectic melting point, at $1650 \pm 2^{\circ}\text{C}$, showed no more than a 5° difference between that observed in the spectrometer and the thermal arrest method. A similar comparison

with the Mo-Mo₂C eutectic temperature at $2208 \pm 5^\circ\text{C}$ also gave agreement within 5° . The Pyro Micro Optical pyrometers used in both studies were compared to a NBS-calibrated pyrometer and band lamp. As a result of this effort, a measurement of Au_(l) over three pressure decades (1474° - 1838°K) gave $\Delta H_{\text{Au}}^\circ(298^\circ, \text{2nd Law}) = 87.0 \pm 0.9 \text{ kcal/mole}$ compared to a 3rd Law value of $88.3 \pm 0.9 \text{ kcal/mole}$ obtained by Hildenbrand and Hall [23]. In addition, a determination of Mo_(g) pressure over Mo between 1830° and 2080°C gave a slope which differed from measurements of Vozzella and co-workers [22] by 2.2% (see Table II). In all of the pressure measurements most of the points differed from the least squares line by no more than 5° . Everything considered, the temperature error is probably no more than 7° throughout the measurement range.

The crucible consisted of a tantalum shell and an inner graphite cell having a conical shaped interior. Black-body holes were located at the top and bottom. A cross-section drawing is shown in Figure 3. Most studies were made using a 1.0 mm orifice diameter. When compositions below UC_{1.9} were examined, a Ta or TaC cup was placed in the crucible well to prevent the diffusion of carbon into the material. Over the temperature range of these measurements, this was the only significant source of carbon to the sample. A comparison of the composition before and after a run (Table I) shows that, if anything, the material lost carbon due to the loss of surface oxide as CO. This occurred as the material was heated through 1600°C with a characteristic evolution of gas.

Figure 3. Cross section of the Knudsen cell.

Knudsen conditions might not have existed within the cell when low carbon samples were used. Although this problem was minimized by the $UC_2 + UC$ diffusion barrier which formed on the graphite surface, the measured pressures could be too low if the evaporation coefficient is much less than unity.

The crucible assembly was designed to allow the crucible to be moved in any direction externally. Thus, compensation could be made for any sagging of the supports and the crucible position could be re-established after disassembly.

Each crucible was calibrated initially using molten gold. The spectrometer was then vented with He, and the Au was replaced by the carbide sample. This consisted of several grams of coarse fragments, broken from an arc-melted button. The presence of powder or fine pieces caused an exceptionally large evolution of CO as the temperature was raised and a pronounced decrease in the stoichiometry. Frequently, a series of compositions were run in the same crucible after the initial calibration. Appropriate, previously measured samples ($UC_2 + C$ or $UC + UC_2$) were then interspersed to check the calibration consistency. In general, the machine calibration did not change significantly during this procedure. Data were taken over several temperature cycles following an anneal at the highest temperature. The final values were based on at least two temperature cycles which showed agreement within the temperature error.

The calculation of pressure was based on the following constants.

The pressure of gold at 1667°K was assumed to be 1.04×10^{-5} ^{atm} ~~torr~~ [23], and its relative ionization cross-section was taken as 35 from the measurement by Ackerman, Stafford and Drowart [24]. A cross-section of 50 for uranium was based on a measurement by DeMaria, Burns, Drowart and Inghram [16], and the value for carbon was taken from the paper by Ötös and Stevenson [25]. The cross-section of UC₂ was assumed equal to the sum of uranium and twice the carbon values. Measurements of the multiplier gain showed that the U/Au current ratio is inversely equal to the square root of the atomic weight ratio. UC₂ was assumed also to follow this relationship. Since an ionization energy of 100 v was used, 11% of the Au ions, 23% of the U ions and < 3% of the UC₂ ions were multicharged. All of the ions were included when calculating the beam intensity. The small amount of Au₂⁺ was neglected. No U₂⁺ was observed, but it is interesting that when U and Au were mixed, small amounts of UAu⁺ appeared.

A least-squares fit of the final pressure data was made using an IBM 7094 and was based on a weighting scheme which depended on the meter range used to measure the current. The uncertainty in the current precision varied from 1% to 10%.

3. EXPERIMENTAL RESULTS

The various compositions and the range over which they were studied are shown on the phase diagram in Figure 4. Beginning with UC₂ + C, the uranium pressure measurement of each region will be discussed separately.

Figure 4. Phase diagram of the U-UC₂ system.

3.1 UC₂ + C

The two determinations made in this study were based on separate gold calibrations using different crucibles. The consistency is within the temperature error. Samples of UC₂ + C showed no detectable UO⁺ and, except for a peak at UC⁺ and UC₄⁺ at very high temperatures, nothing unexpected was seen in the spectrum.¹ No reluctance to reach pressure equilibrium was observed. Data taken during heating and cooling showed excellent agreement, and an anneal at 2170°C for 3 hr produced only a small increase in pressure. No change in pressure was observed when the orifice area was changed from 0.011 cm² to 0.021 cm².

Besides comparing this study, in Figure 5, to the previous measurements, it is instructive to examine these measurements in light of what is now known about the reactive properties of the system.

The data reported by Leitnaker and Witterman [5] was obtained by total collection using < 325 mesh UC₂ + C powder in a graphite cell. Within a given series the material was not exposed to air. The first series (E) was started after considerable time at temperature and shows good agreement with this study except for a point taken just before the window was cleaned. Therefore, this point (42E) was omitted from the recalculation. During the early part of the second series (EE), in spite of a pre-treatment at 1900°C for 6 hr, the pressure started high and dropped with

¹As explained later, the UC⁺ is probably a decomposition fragment of UC₂⁺, but the UC₄⁺ appears to be real. At 2450°K the UC₂⁺/UC₄⁺ ratio was ~10. One would expect UC₄⁺ to become a more important species at higher temperatures.

Figure 5. A comparison between this study and other measurements of the $U_{(g)}$ pressure over $UC_2 + C$. Corrections applied for $UC_2(g)$ where appropriate.

time. This suggests that all of the oxide had not been eliminated and UO was evaporating. Therefore, the points (47EE, 48EE, 49EE) which showed this trend were omitted. With these changes, a correction for the collected $\text{UC}_{2(g)}$, and the omission of all points below the α - β transition temperature, the 2nd Law apparent heat of vaporization increased by 4.7 kcal/mole over the value originally reported. (These changes were made with the concurrence of W. Witterman.)

Lonsdale and Graves [6] used partial collection from a graphite cell containing powdered carbide. Their procedure consisted of grinding the charge after each measurement, then pretreating the cell at 200° below the collection temperature for 20 to 60 min. As a result, their sample would have been re-contaminated with oxide after each run, and this would not have been removed by such a short pre-treatment unless the temperature was above ~2000°C. Thus, one would expect the measured pressures below ~2500°K to have become progressively higher than the correct values as the collection temperature was reduced.

The mass spectrometric measurements by Norman and Winchell [8] give pressures which deviate slightly toward higher temperatures as the temperature is raised. Considering the arrangement of their electron bombardment furnace and that the temperature was measured only at the midplane of a bare graphite crucible, there is little doubt that a temperature gradient existed which would have become worse as the temperature increased. However, at low temperatures the agreement is excellent.

The results of Eick, Rauh and Thorn [3] are in disagreement, but the reasons are harder to understand. They observed that the data appeared to fall into two groups, depending on the temperature and sample size. Also there appeared to be a slowness to reach equilibrium. If the composition of their sample is correct ($UC_{1.78} \pm 0.05$), it was either not in equilibrium with graphite, which is unlikely at the measurement temperature, or more likely the sample contained some undetected impurity which, in addition to the 0.1% Ta, lowered the activity of uranium.

The very limited measurements by Alcock and Grieveson [7] gave pressures which are higher than most of the other studies and which would predict preferential loss of U from $UC_2 + C$. However, since the pressures were obtained from total weight-loss measurements, the effusion of both CO and UO would add to the apparent U pressure. Without some knowledge of the sample purity, these values are best ignored.

The work of Alexander, Ward and Ogden [2], in addition to giving high uranium pressures also showed a rather pronounced orifice effect. This is in contrast to the absence of such an effect in the work of Lonsdale and Graves [6] and in this study. In the absence of experimental details, the reasons for this are hard to determine.

After correcting for the UC_2 collected, the effusion measurements of Fujishiro [4] give a slope which agrees well with this study, but the pressures are about 10 times higher. The carbide was prepared by heating metallic uranium in graphite at $2400^\circ C$ for 10 hr and it would have been oxide free if it were not subsequently powdered. In any case, since the

carbide would have equilibrated with graphite at 2400°, it would have contained very little free carbon at the collection temperatures. In the absence of a final analysis, there is no assurance that the evaporating material was in equilibrium with carbon.

By considering these possible sources of error, good agreement can be obtained between the various measurements. In other words, most of the differences are not due to errors in basic technique but are due to an unfortunate combination of chemical properties.

3.2 Single Phase UC₂

Single phase compositions near the UC₂ + C phase boundary were obtained by equilibrating a solid piece of carbon-deficient UC₂ with carbon above the α - β transition temperature. Because the boundary moves to higher carbon contents as the temperature is raised, samples prepared in this way were single phase throughout the range of measurement. The other compositions were obtained from fragments of an arc-melted button. A TaC cup was used to contain the material. The resulting pressures, compared in Figure 6, show clearly the effect of the composition change when graphite was present.

3.3 UC₂ + UC

Measurements in this two-phase region are shown in Figure 7. Three different compositions and five samples were used and each run was based on a separate gold calibration. A check on the machine calibration was made by Krupka [26] using a total-collection effusion apparatus with a TaC cell containing UC_{1.49} (same material used for V-10, Table I). A

Figure 6. $\log P_U$ vs $1/T$ for compositions between $\text{UC}_2 + \text{C}$ and $\text{UC} + \text{UC}_2$.

Figure 7. A comparison between measurements made in the high carbon region of UC.

vacuum of 10^{-8} to 10^{-9} torr was maintained. This result and others which will be discussed later, give excellent support to the pressures measured by the spectrometer.

The Langmuir measurements of Vozzella and co-workers [10] using $UC_{1.1}$ are also shown in Figure 7. Since this composition is in the single phase UC region, the pressures should actually be higher than those measured for $UC_2 + UC$. The fact that the values are lower suggests either that a temperature error existed in the inductively heated plugs used in their study or the accommodation coefficient for uranium evaporation is not unity at this composition. In addition, the slope has no significance unless the congruent composition is independent of temperature, i.e., unless the partial heats of vaporization of U and C are equal. More will be said of these possibilities later.

3.4 UC Single Phase

The data obtained in this region are shown in Figures 7 and 8. Because of the rapid change in pressure with composition, some difficulty was experienced in obtaining constant pressure when a TaC cup was used to contain the sample. This problem was solved by using a Ta cup which had been previously equilibrated with the UC composition. Most samples showed a high uranium pressure during the initial heating which rapidly approached an equilibrium value as the temperature was increased. Additional temperature cycles produced no further changes in the pressure. Apparently the removal of the oxide film during the early stages of heating produced a deficiency of carbon at the evaporating surface. Gradually, as the

Figure 8. $\log P_U$ vs $1/T$ for compositions in the low carbon region of UC.

temperature was raised, the loss of uranium and the diffusion of carbon returned the surface to the interior composition. Although some $\text{UO}_{(g)}$ was observed initially, its final pressure dropped to near the limit of detection.

Krupka [26], using the same effusion apparatus described previously, measured the uranium pressure over $\text{UC}_{1.03}$ as part of an earlier study. His values, as will be seen, again show excellent agreement.

Measurements of UC by Alexander and co-workers [2] gave pressures which would agree with this work if their material had a composition of about $\text{UC}_{0.96}$. Unfortunately, they did not report the final composition.

Pressures in this region, shown in Figure 8, were obtained by placing a solid piece of clean uranium rod in the crucible well and heating it to the desired temperature. Subsequent examination showed that the molten uranium was contained in a shell consisting of solid UC_2 and UC. Although the molten uranium saturated rapidly, the growth of solid UC_2 and UC was slow. As a result, samples could be examined for several hours without losing the liquid phase. The presence of UO^+ was always observed initially but after a heating cycle, it dropped to a small fraction (0.01) of the uranium peak without affecting the uranium pressure.

Since gas phase equilibrium is impossible to achieve under these conditions, it is possible that the measured uranium pressure is too low. As a check, the graphite crucible top was replaced by one made from TaC. Although equilibrium still might not be realized, one would expect the

conditions to be improved. However, no significant difference in pressure was noticed. If, on the other hand, evaporation coefficient of uranium from the liquid is unity, the absence of vapor phase equilibrium should not affect the measured pressure. When the UC_2 -UC surface layer on a well covered graphite top was removed, the apparent pressure was reduced initially by one half. Thus, the coefficient is apparently slightly less than one and, to the extent that equilibrium between the vapor and the walls was not achieved, the measured pressures in this region might be slightly low.

As part of the following study, the effect of tungsten saturation in this region was measured and found to be negligible.

3.6 Single Phase Uranium Liquid

Some preliminary measurements were made using a W cup to contain the molten uranium. Various amounts of carbon were added (as $UC_{1.0}$) and the pressure was studied as a function of carbon content. Although these studies are inconclusive, the following observations can be made:

1. During a run, a change in UO pressure from twice to one tenth the uranium pressure made no significant change ($< 5\%$) in the uranium pressure.

2. The pressure of uranium did not change rapidly with carbon content.

3.7 Measurement of the $UC_{2(g)}$ Pressure

The $UC_{2(g)}$ pressure was obtained from the beam current ratio, I_{UC_2}/I_u , by applying the cross-section ratio (0.858) and multiplying by the uranium

pressure. The results from the various compositions are shown in Figure 9. Essentially no change in pressure occurs between $UC_2 + C$ and $UC_{1.087}$, but it drops rapidly with composition below $UC_{1.078}$.

The possible errors in measuring the UC_2 pressure are more difficult to evaluate than those affecting the U pressure. Aside from the uncertainty in the cross-section, there is the possibility that a significant amount might decompose after being ionized. The presence of some UC^+ in the spectrum added support to this suspicion. Because of its small intensity, neither the heat of vaporization nor the appearance potential could be measured accurately, however, the UC_2^+/UC^+ ratio was essentially the same over $UC_{1.1}$ and $UC_2 + C$. Therefore UC^+ is probably a fragment of UC_2^+ . Nevertheless, the possible error in the UC_2 pressure from this source is negligible. The appearance potential curves for U^+ and UC_2^+ were examined carefully to determine if any breaks could be associated with the decomposition reaction $UC_2^+ \rightarrow U^+ + C_2$. A hump in the U^+ curve was observed both in the presence and absence of UC_2^+ and, therefore, cannot be due to this reaction.² It was found that the I_{UC_2}/I_U ratio changes appreciably with ionization voltage. Thus, measurements of this ratio by Eick, Rauh and Thorn [3] at 25 v and by Norman and Winchell [8] at 8 v would give values which are lower than those found at 100 v.

²It is interesting that a similar hump was observed by Mann [27] in the presence of UO^+ and was blamed on the dissociation of the UO^+ ion. The complete absence of UO^+ in this study eliminates this explanation.

Figure 9. Log P_{UC_2} vs $1/T$ for compositions throughout the system.

The pressures reported by Norman and Winchell [8] are compared to this work in Figure 9. Their pressures are much lower, probably due to the difference in ionization voltage used, and show an 8% greater slope.

3.8 Phase Boundary Studies

In order to better understand the pressure measurements, several features of the phase diagram were determined.

The composition of the UC_2 -C phase boundary was measured as a function of temperature by equilibrating a solid piece of carbon deficient UC_2 with carbon at a fixed temperature, cooling and analyzing for uranium by ignition. Equilibrium was assumed when samples heated for much different times (Table III) gave the same composition. The surface carbon was removed previous to analysis by an S. S. White abrasive unit using Al_2O_3 . All of the remaining carbon, regardless of its form at room temperature, would have been dissolved in the cubic UC_2 phase at temperature and, therefore, represents the phase composition at this temperature. An upper limit of $UC_{1.89}$ to the composition of UC_2 at the α - β transition, and a lower limit of $UC_{1.94}$ to the composition at the eutectic temperature reported by Wittman and Bowman [29] are in good agreement.

The saturation limit of carbon in liquid uranium was determined by heating a clean uranium rod in a graphite crucible to the desired temperature. Studies with the spectrometer showed that equilibrium was rapidly attained. The graphite was broken from the metal plug, and any UC_2 or UC on its surface was removed by a combination of dilute HNO_3 and an S. S. White abrasive unit. Since UC turns dark brown in nitric acid,

it was easy to tell when the surface had been cleaned. An analysis for total carbon and uranium was made, and the material was examined metallographically. The results, in Figure 4 and Table III, show excellent agreement with similar measurements by Mallett, Gerds and Nelson [28].

4. DISCUSSION

An internal comparison of the data will be made first at the measurement temperature starting with a plot of log uranium pressure vs composition in Figure 10. As was expected, the large change in uranium pressure was found in the UC region. Here the values can be fit best if slope of the curve is allowed to maximize at $UC_{1.0}$. This behavior is consistent with the idea that two competing reactions are operating, i.e., that substoichiometric UC is produced by vacancies in the carbon lattice while higher compositions result when the carbon atoms are replaced by C_2 groups. Also shown are the results of the collection study by Krupka [26]. Between UC and UC_2 a miscibility gap exists below $\sim 2100^\circ C$. The boundaries of this region were determined from the vapor pressure and are indicated in Figure 4. Values for the upper temperature limit of this gap have ranged up to $2100^\circ C$ [29,30]. This value is not inconsistent with the pressure measurements. In the UC_2 region the pressure changes rather slowly with composition. However, as the temperature is raised, the change becomes especially rapid at the high carbon phase boundary. The implication of this behavior is best seen in Figure 11 where the partial heat of vaporization of uranium ($\Delta \bar{H}_u$),

Figure 10. Pressure of $U_{(g)}$ as a function of composition at various temperatures.

Figure 11. Average $\Delta \bar{H}_u$ (2nd Law), over the measured temperature range, shown as a function of composition.

obtained from the slope of the pressure data, is plotted as a function of composition. Apparently $\Delta\bar{H}_u$ maximizes at about UC_{1.84} and 147 kcal/mole, then drops to 142 kcal/mole at UC_{1.90}. Because the composition of UC₂ changes with temperature when excess carbon is present, the two-phase material shows a significantly lower value. Near the boundaries of the miscibility gap, the values are somewhat erratic due probably to a difficulty in reaching equilibrium. In the UC region another maximum near 167 kcal/mole is indicated, but the upper temperature limit prevented an examination of the single phase region above the gap to define its position. Presumably, a behavior indicated by the dashed line would be found if this region could be studied. As the composition is reduced through UC_{1.0} there is a drastic drop in $\Delta\bar{H}_u$ followed by a much smaller change throughout the defect region. This behavior should be reflected in the other thermodynamic quantities such as heat capacity and heat of formation. Unfortunately these measurements have not, as yet, been made as a function of composition.

4.1 Carbon Activity

If U_(g), C_(g) and UC_{2(g)} are in equilibrium, the UC₂/U pressure ratio is proportional to the carbon activity squared. Since the activity is unity at the UC₂ + C phase boundary, α_c^2 can be obtained at any composition simply by dividing its UC₂/U pressure ratio by that measured over UC₂ + C at the same temperature. The results of this calculation are shown in Figure 12 at 2100° and 2300°K, and the values and equations are given in Table IV.

Figure 12. Activity of carbon as a function of composition.

An extrapolation to the UC phase boundary allows the carbon activity in the carbon saturated liquid uranium phase to be determined. Although the values have a large uncertainty because of the uncertain shape of the curve in this region, they give a carbon activity coefficient (γ_c) of 0.43 at both temperatures. The effect of this negative deviation from ideal on the uranium activity will be discussed later. In any case, at lower temperatures, where the carbon content is smaller, the solution should approach an ideal behavior.

At the other end of the phase diagram, the carbon activity at the $UC_2 + C$ eutectic temperature (2700°K) extrapolates to unity at $UC_{1.96}$. This is, therefore, the maximum solubility of carbon in UC_2 .

The manner in which the activity of carbon changes with temperature shows that $\Delta\bar{H}_c$ is ~5.5 kcal/mole less than the heat of vaporization of graphite throughout the range of UC_2 . Within the UC region, $\Delta\bar{H}_c$ reaches a minimum near $UC_{1.087}$ and becomes equal to $\Delta H_{\text{graphite}}^O$ at $UC_{1.083}$. Near $UC_{1.1}$ the values for $\Delta\bar{H}_c$ and $\Delta\bar{H}_u$ become equal. This means that the congruent composition will change little with temperature and accounts for the agreement between this work and the measurements of Vozzella and co-workers [10] (see Figure 11).

It is important to realize that the activity of carbon obtained from the UC_2/U ratio is independent not only of the spectrometer calibration, but also of the ionization cross-section, the possible loss of UC_2 ions due to decomposition, and it is very insensitive to temperature errors.

4.2 Congruent Vaporization

Assuming that the only evaporating species, U, UC_2 , C_1 and C_3 , are in equilibrium and have equal evaporation coefficients, the total molar evaporation rates for U and C were calculated. These are plotted in Figure 13 as log evaporation rate ratio against C/U in the solid. The vapor pressure of graphite was based on the compilation by Stull and Sinke [11]. The figure shows that below $\sim 2200^\circ K$ the congruent composition lies in the UC_2 region and that it moves toward the $UC_2 + C$ boundary as the temperature is lowered. If the evaporation coefficient for carbon should be less than that for uranium at this composition, below $\sim 2200^\circ K$ a plug of UC_2 could lose uranium preferentially and acquire a layer of carbon as was observed by Alcock and co-workers [14]. However, above $2200^\circ K$ the congruent composition moves to $UC_{1.11}$ and thereafter is fairly independent of temperature. This agrees with numerous [5,10,12] observations of a congruent composition near $UC_{1.10}$ and with the observation by Witteman and Krupka [32] that a plug of $UC_{2.2}$ loses carbon preferentially when heated at $2300^\circ K$. At still higher temperatures, the composition apparently moves to $UC_{1.3}$ [31] at the melting point.

On the other hand, a comparison between the Langmuir measurements of Vozzella and co-workers [10] and this work suggests that the evaporation coefficient for U could be about 0.44 at $UC_{1.1}$. If this assumption is made, the calculated congruent composition remains at $UC_{1.08}$ between at least 2100° and $2300^\circ K$. Unfortunately, this composition is sufficiently close to the direct measurements that no conclusions can be made from it concerning the evaporation coefficient.

Figure 13. Comparison of the vapor and solid compositions of UC during free evaporation.

4.3 Heat of Vaporization of Uranium Metal

Before a further analysis of the data is made it is necessary to choose a value for the heat of vaporization of uranium. The value reported by Rauh and Thorn [18], which has been used extensively in the past, has been recently disputed by Drowart and co-workers [15, 17]. For this reason, an effort was made to add more evidence to the argument.

The pressure of $U_{(g)}$ over $U_{(l)} + UC$ and its change with temperature give a means to obtain limits for the heat of vaporization. Since this measurement does not suffer from the presence of oxygen nor does the liquid creep out of the crucible, as is the case with Ta and W crucibles, it is probably less prone to error than the direct measurements. The major uncertainty, however, is the effect of the dissolved carbon. One would expect that this carbon would lower the pressure of uranium and that there would be a negative deviation from ideal behavior. As the temperature is lowered and the solubility of carbon drops, the pressure should approach that over an ideal solution. Thus, by calculating the pressure over the ideal solution (Figure 8) a minimum uranium pressure or, in other words, a maximum value for ΔH_u^O can be obtained. In addition, the second law treatment would give a minimum value for ΔH_u^O . This reasoning leads to $\Delta H_u^O(298^\circ, \text{3rd Law}) = 130.7 \text{ kcal/mole}$ as the maximum and $\Delta H_u^O(298^\circ, \text{2nd Law}) = 127.9 \text{ kcal/mole}$ as the minimum value.

Using the same thermal data as above, the measurements of Rauh and Thorn [18] give $\Delta H_u^O(298^\circ, \text{3rd Law}) = 117.6 \text{ kcal/mole}$ and $\Delta H_u^O(298^\circ, \text{2nd Law}) = 116.3 \text{ kcal/mole}$, and the measurements of Drowart and co-workers [17]

give 125.8 ± 0.2 kcal/mole and 122.4 ± 3.6 kcal/mole, respectively. As can be seen, the values of Rauh and Thorn do not fall near these limits. Furthermore, if their value is used the activity of uranium in the carbon-saturated solution would be much less than the activity of carbon (see Table IV), and it would increase as the temperature is raised and more carbon is dissolved. If their value is indeed correct, the behavior of this solution is certainly very unusual. In addition, as pointed out by Drowart and co-workers [15], this value is inconsistent with thermodynamic cycles in the U-C and U-O systems, but is consistent with the behavior of $U_{(l)} + UO_2$.

For these reasons $\Delta H_u^O(298^\circ) = 126.0 \pm 1$ kcal/mole will be used in subsequent calculations. This gives the following equation for the pressure of uranium:

$$\log P_u(\text{atm}) = -2.554 \times 10^4/T + 5.890.$$

This results in an activity coefficient of 0.33 for uranium in the saturated liquid between 2100° and 2300°K . Thus, the uranium in the solution deviates more from an ideal behavior than does the carbon.

4.4 Free Energy of Formation Between 2100° and 2400°K

The free energy of formation was calculated from the relation $\Delta F_f^O = RT(\ln \alpha_u + C/U \ln \alpha_c)$ and is plotted in Figure 14 at 2300°K as a function of composition. At this temperature the formation of the liquid solution and the filling of the vacancies in the UC lattice absorb the bulk of the energy. A decrease in temperature causes ΔF_f^O in the UC region to become more negative while just the opposite effect occurs in

Figure 14. Free energy of formation at 2300°K as a function of composition.

Figure 16. Heat capacity of $UC_{1.02}$ to 2500°K.

Figure 17. Heat content of UC_2 from 298.15° to 2500°K .

Figure 18. Heat capacity of UC_2 to 2500°K.

Figure 19. Heat content of U from 298.15 to 1600°K.

ments have been made as a function of composition, it was assumed that S° , ΔH and Δf_{ef} divided by $(1 + C/U)$ are a linear function of mole fraction. On such a basis, these values change by only ~5% between $UC_{1.02}$ and $UC_{1.90}$.

4.6 Heat of Formation at 298.15°K

$\Delta H_f^\circ(298^\circ, \text{3rd Law})$ was obtained from ΔF_f° at 2100° and 2400°K using the equations for ΔF_f° listed in Table V and Δf_{ef} values obtained as described above. The 2nd Law heat of formation was calculated from the relationship

$$\Delta H_f^\circ = -\Delta \bar{H}_u + C/U(\Delta H_c^\circ - \Delta \bar{H}_c) + \Delta H_u^\circ$$

where $\Delta \bar{H}_u$ was obtained from the slope of $\log P_u$ vs $1/T$, $(\Delta H_c^\circ - \Delta \bar{H}_c)$ was calculated from the slope of $\log \alpha_c$ vs $1/T$, and the heat of vaporization of uranium (ΔH_u°) was obtained as described previously. Since ΔC_p (vaporization) has not been measured as a function of composition, it was assumed that the partial heats of vaporization were typical of a temperature at the center of the measured range. The results are listed in Table V.

Within the UC_2 region, there is very little temperature trend of $\Delta H_f^\circ(3\text{rd Law})$ and the difference between the 2nd and 3rd Law values could be caused by only a 7° temperature error between 2100° and 2400°K. An average of the 3rd Law values gives -22.2 kcal/mole as the probable value for $\Delta H_f^\circ(298^\circ)$ of UC_2 . Heat of combustion measurements of Huber and co-workers [46] give -21.1 ± 1.4 kcal/mole for $UC_{1.9}$. If $\Delta H_u^\circ = 127$ kcal/mole had been used in the calculations, the agreement would have been almost exact.

The UC region is not so clear cut. A trend of ΔH_f° (3rd Law) with temperature exists which becomes worse as the composition is reduced. In addition, the agreement between the 2nd and 3rd Law values also becomes worse. There are several errors which could lead to this result, such as an error in the U-or UC₂-pressure slopes, but this would also result in inconsistencies elsewhere in the data. Therefore, the error is probably mainly in the 2nd Law values. Such a discrepancy would result if the heat content had a minimum in the region near UC_{1.08}. The 3rd Law values are independent of composition at -23.8 kcal/mole down to a composition near UC_{1.0}, but within the defect region they drop rapidly with composition. Attempts to compare this value to the results of combustion measurements are difficult because both Farr and co-workers [47], and Droege and co-workers [48] used UC which was in equilibrium with uranium. The former study was based on UC_{0.98} and gave a value of -21.7 ± 1.0 kcal/mole. Since ΔH_f° is changing rapidly with composition in this region, one can only conclude that their value is in the proper relationship to the results of this study.

5.0 Comments

There is now considerable reason to believe that the measured pressures over the U-C system are essentially correct. Within a reasonable evaluation of the possible errors, there is good consistency between the various studies, and, if a value of 126 ± 1 kcal/mole is adopted for the heat of vaporization of uranium metal, there is excellent agreement with the heat of combustion measurements. It is believed that

the apparent inconsistencies were due primarily to the use of impure materials in the pressure measurements, the reliance on a heat of vaporization for uranium which was too low, and the use of inaccurate high temperature thermal functions. In addition, too little attention has been given to using materials of fixed and characterized composition. It is this final point which needs emphasis. Measurements made using two-phase samples can be severely compromised by a change in phase composition as the temperature is changed, even if this change is known to be small. The effect of a small change in composition can be unexpectedly magnified by a steep change in properties near the phase boundary, as was found at the $UC_2 + C$ boundary. Furthermore, the use of congruently vaporizing material does not guarantee a fixed composition at all temperatures either unless the partial heats of vaporization of the evaporating species are equal. One would expect this to be a rare coincidence. In the U-C system the problem is further complicated by the unavoidable presence of combined oxygen. Its loss as $CO_{(g)}$ and $UO_{(g)}$ can change the composition, but, far worse, it can add to the apparent uranium pressure if collection or weight-loss techniques are used. Agreement between measurements will not be obtained until this problem is taken into account.

Between UC and UC_2 there is a common crystal structure and, at a sufficiently high temperature, there is a continuous change from the one compound to the other. This results from the replacement of C by C = C groups in the regular cubic lattice sites. The substitution does not go

to completion, however, since $UC_{1.96}$ is the upper limit to the UC_2 phase. No gross changes in the chemical or physical properties occur in this region although the lattice is weakened slightly in going from UC to UC_2 . There is, however, a reversal in the temperature coefficient of ΔF_f^O which correctly predicts that UC_2 becomes less stable with respect to UC as the temperature is lowered. On the other hand, near $UC_{1.0}$ an entirely different phenomenon occurs which has a profound effect on all of the measured properties. In this region vacancies are formed in the normal carbon lattice with the result that as the stoichiometry is reduced the melting point, the lattice parameter and all of the thermodynamic measurements show a pronounced decrease in value. It is to be expected that the other properties would show a similar drastic change in this region and, therefore, great care must be taken when measurements are made. This behavior pattern is shared with the other defect compounds of which the carbides are extreme examples.

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TABLE I

Composition of Samples Before and After Vapor Pressure Measurements

	Comp. c/u	O ^a ppm	N ^b ppm	Si ^c ppm	Cu ^c ppm	Comp. c/u	O ^a ppm	Phases present at room temp.	Lattice Parameter Å
V-0	Uranium	saturated with carbon					575	U + UC	
V-1	0.933	30	<200	200	6	0.930	75	UC	4.9564 ± 0.0001
V-2	0.968	30	<200	80	200	0.946	100		4.9555 ± 0.0003
V-3	0.968					0.973	<225		4.9565 ± 0.0003
V-4	1.004			50	< 5	0.995	<225	UC	4.9609 ± 0.0002
V-5	1.060		<200	50	< 5	1.078			4.9610 ± 0.0002
V-6	1.121	25	<200	200	5	1.087			
V-7	1.121					1.114	70	UC > UC ₂	4.9608 ± 0.0001
V-8	1.286					1.276	65		
V-9	1.286					1.286		UC > UC ₂	4.9616 ± 0.0003
V-10	1.492	115	<200	150	15	1.487		UC ₂ = UC	
V-11	1.665	50	< 50			1.599	25		
V-12	1.665					1.646	80	UC ₂ > UC	
V-13	1.776					1.713		UC ₂ > UC	
V-14	1.776					1.781	25		
V-15	1.848	45	<200	70	10	1.846	50		
V-16	1.890	210		70	10	1.877	130	Equilibrated with C at 1795°C	
V-17	1.890					1.884	140	Equilibrated with C at 1903°C	
V-18	2.08	40	<200	15	15	2.080		UC + C	

^aOne determination^bAlthough no N₂ was detected, the reported value is an upper limit because of the small sample available^cSpectroscopic analysis (V, Nb, Ta, W, Mo - not detected)

TABLE II
SUMMARY OF LEAST SQUARES EQUATIONS

	$\log P_u(\text{atm}) = A - B/T$		Slope $\Delta \bar{H}_u (\text{kcal/mole})$	Comp., c/U
	A	$-B \times 10^{-4}$		
V-0	5.039 ± 0.051	2.499 ± 0.011	114.4 ± 0.5	$U(l) + UC$
V-1	4.527 ± 0.054	2.410 ± 0.011	110.3 ± 0.5	0.930
V-2	4.662 ± 0.136	2.476 ± 0.029	113.3 ± 1.3	0.946
V-3	4.170 ± 0.089	2.404 ± 0.018	110.0 ± 0.8	0.973
V-4	6.769 ± 0.215	3.121 ± 0.049	142.8 ± 2.2	0.995
V-5	8.040 ± 0.204	3.501 ± 0.046	160.0 ± 2.1	1.078
V-6	8.378 ± 0.132	3.608 ± 0.031	165.1 ± 1.4	1.087
V-7	7.238 ± 0.081	3.374 ± 0.019	154.4 ± 0.9	1.114
V-8	-	- ^a	151.1 ± 2.6	1.276
V-9	6.758 ± 0.368	3.267 ± 0.085	149.5 ± 3.0	1.286
V-10	6.671 ± 0.098	3.256 ± 0.023	149.0 ± 1.1^b	1.407
V-11	-	- ^a	146.2 ± 0.8	1.599
V-12	5.911 ± 0.070	3.101 ± 0.017	141.9 ± 0.8	1.646
V-13	5.806 ± 0.077	3.077 ± 0.018	140.8 ± 0.8	1.713
V-14	6.271 ± 0.087	3.193 ± 0.020	146.1 ± 0.9	1.781
V-15	6.253 ± 0.126	3.228 ± 0.029	147.7 ± 1.3	1.846
V-16	5.789 ± 0.070	3.139 ± 0.016	143.6 ± 0.7	1.877
V-17	5.881 ± 0.143	3.165 ± 0.033	144.8 ± 1.5	1.884
V-18	4.808 ± 0.094	2.939 ± 0.022	134.5 ± 1.0	$\beta \cdot UC + C$
Ideal Solution				
	5.529	2.583	118.2	$U(l)$
Krupka ^c [26]				
	7.219 ± 0.773	3.291 ± 0.171	150.6 ± 7.8	$UC_{1.03}$
Vozzella and co-workers ^c [10]				
	8.358 ± 0.722	3.676 ± 0.173	168.2 ± 7.9	(Congruent)
Leitnaker and Wittenman ^d [5]				
	5.227 ± 0.652	3.018 ± 0.143	138.1 ± 6.5	$\beta \cdot UC_2 + C$
UC_2 pressure				
V-6 to 18	7.399 ± 0.188	3.725 ± 0.045	170.5 ± 2.1	$UC_2 + C$ to $UC_{1.087}$
V-5	8.381 ± 0.812	3.993 ± 0.189	182.7 ± 8.6	$UC_{1.078}$
V-4	10.89 ± 2.77	4.628 ± 0.644	211.8 ± 29.5	$UC_{0.995}$
$Mo(s) \rightarrow Mo(g)$				
	7.235 ± 0.016	3.394 ± 0.037	155.3 ± 1.7	

^a Absolute calibration not obtained.

^b Average of 3 independent runs.

^c Corrected for $UC_2(g)$ evaporation.

^d Points eliminated as described in the text. Corrected for UC_2 collected.

TABLE III
PHASE BOUNDARY STUDIES
UC₂ + C phase boundary

<u>Composition, C/U</u>	<u>Temperature, °C</u>	<u>Time at Temperature, hr.</u>	<u>Oxygen, ppm</u>
1.927	2384	0.5	
1.921	2364	0.4	
1.909	2301	3.0	
1.909	2281	1.0	
1.923	2250	1.3	
1.915	2146	1.5	
1.908	2138	5.0	
1.905	2044	5.0	
1.901	2028	15.5	
1.903	1992	15.0	
1.900	1971	17.0	
1.890 (V-17)	1903	20.0	
1.896	1837	18.5	
1.883	1815	87.0	65
1.890 (V-16)	1795	69.0	210
1.891	1794	62.5	
1.864	1743	45.0	
1.865	1733	16.0	
1.868	1696	87.0	25
1.870	1670	48.0	
1.866	1587	148.0	75

U_(l) + UC phase boundary

<u>Composition, C/U</u>	<u>Temperature, °C</u>	<u>Oxygen, ppm^a</u>	<u>Nitrogen, ppm^b</u>
0.041	1420		
0.096	1561		
0.146	1784		
0.281	1868		
0.297	1898	850	<500
0.347	2001		
0.314	2007	1100	<500
0.423	2106	790	<500
0.560	2250		

^aOne determination

^bNo N₂ detected

TABLE IV
ACTIVITY OF CARBON AND URANIUM

Composition, C/U	Carbon Activity				$\Delta H_C^O - \Delta \bar{H}_C$ kcal/mole	Uranium Activity ^a			
	$\log \alpha_c = A + B/T$		Activity			$\log \alpha_u = A + B/T$		Activity	
	A	B x 10 ⁻³	2100°K	2300°K		A	B x 10 ⁻³	2100°K	2300°K
U _(l) + UC			0.08	0.12 ^b		-0.851	+0.55	0.26	0.24
0.930						-1.363	1.44	0.21	0.18
0.946						-1.228	0.78	0.14	0.13
0.973						-1.720	1.50	0.10	0.086
0.995	0.765	-3.605	0.11	0.16	-16.5	0.879	-5.67	0.015	0.026
1.078	-1.124	1.470	0.38	0.33	6.7	2.150	-9.47	0.0044	0.011
1.087	-1.785	3.345	0.64	0.47	15.3	2.438	-10.54	0.0029	0.0080
1.114	-1.215	2.175	0.66	0.54	9.9	1.348	-8.20	0.0028	0.0061
UC ₂ + UC	-0.932	1.587	0.67	0.57	--	0.781	-7.02	0.0028	0.0054
1.713	-0.499	0.690	0.68	0.63	3.2	-0.084	-5.23	0.0027	0.0044
1.781	-0.732	1.270	0.75	0.66	5.8	0.381	-6.39	0.0022	0.0040
1.846	-0.722	1.445	0.93	0.81	6.6	0.363	-6.74	0.0014	0.0027
1.877	-0.491	1.000	0.97	0.88	4.6	-0.101	-5.85	0.0013	0.0023
1.884	-0.536	1.130	1.00	0.90	5.2	-0.009	-6.11	0.0012	0.0022
UC ₂ + C	--	--	1.00	1.00		-1.082	-3.85	0.0012	0.0018
U _(l) + UC								0.0297	0.0342

^a based on $\Delta H_u^0 = 126$ kcal/mole

^b extrapolated value

^c based on $\Delta H_u^0 = 117$ kcal/mole

TABLE V

FREE ENERGY AND HEATS OF FORMATION

Composition, C/U	ΔF_f^0 (kcal/mole) = AT-B		$-\Delta H_f^0$ (298°, 3rd Law) kcal/mole			$-\Delta H_f^0$ (298°, 2nd Law) kcal/mole
	A x 10 ⁻³	B	2100°K	2400°K	Ave.	
0.90	-	-	13.7 ^a			
0.995	+7.50	42.33	24.66	22.46	23.6	27.3
1.078	+4.29	36.08	24.79	23.39	24.1	34.4
1.087	+2.51	31.76	24.18	23.29	23.7	30.6
1.114	-0.03	26.44	24.06	23.88	24.0	25.6
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1.713	-4.30	18.53	22.44	22.37	22.4	23.2
1.781	-4.22	18.90	22.33	22.13	22.2	24.2
1.846	-4.44	18.64	22.24	21.96	22.1	24.6
1.877	-4.68	18.17	22.14	21.86	22.0	24.3
1.884	-4.67	18.21	22.12	21.84	22.0	24.4

^aBased on an extrapolated carbon activity

TABLE VI
THERMAL VALUES OF U, UC_{1.02} AND UC_{1.90}

Temperature, °K	Uranium			
	H _T - H ₂₉₈ kcal/mole	S _T ^o e.u.	fef ₂₉₈ cal/mole·deg	C _p cal/mole·deg
1500	14.86	29.27	19.36	11.45
1600	16.01	30.01	20.01	11.45
1700	17.15	30.71	20.62	11.45
1800	18.30	31.36	21.19	11.45
1900	19.44	31.98	21.75	11.45
2000	20.59	32.57	22.28	11.45
2100	21.73	33.13	22.78	11.45
2200	22.88	33.65	23.25	11.45
2300	24.02	34.14	23.69	11.45

$$(H_T - H_{298})_{\alpha} = 2.43 - 8.00 \times 10^{-3}T + 1.872 \times 10^{-5}T^2 - 6.56 \times 10^{-11}T^3 - 4.582 \times 10^{-2}T^{-1}$$

(kcal/mole, 298° - 939.1°K)

$$(H_T - H_{298})_{\beta} = 1.268 \times 10^{-2}T - 5.83$$

(kcal/mole, 939.1° - 1044.9°K)

$$(H_T - H_{298})_{\gamma} = 1.038 \times 10^{-2}T - 2.46$$

(kcal/mole, 1044.9° - 1390°K)

$$(H_T - H_{298})_{\text{liq}} = 1.145 \times 10^{-2}T - 2.32$$

(kcal/mole, above m.p.)

UC _{1.02}				
1700	20.78	39.12	26.90	16.78
1800	22.47	40.09	27.61	17.12
1900	24.21	41.03	28.29	17.48
2000	25.97	41.93	28.94	17.86
2100	27.78	42.82	29.59	18.26
2200	29.63	43.67	30.20	18.68
2300	31.52	44.51	30.81	19.12
2400	33.45	45.34	31.40	19.58
2500	35.43	46.15	31.98	20.06

$$H_T - H_{298}^{\circ} = -4.825 + 1.410 \times 10^{-2}T - 2.56 \times 10^{-6}T^2 + 3.261 \times 10^{-10}T^3$$

+1.832 $\times 10^2 T^{-1}$ (kcal/mole, 298° - 2500°K)

TABLE VI (continued)

 β -UC_{1.90}

2100	43.09	57.03	36.51	29.44
2200	46.04	58.40	37.47	29.44
2300	48.98	59.71	38.41	29.44
2400	51.93	60.96	39.32	29.44
2500	54.87	62.16	40.21	29.44
2600	57.81	63.32	41.09	29.44

$$\alpha\text{-UC}_2 \quad H_T - H_{298} = -8.091 + 2.240 \times 10^{-2}T - 4.50 \times 10^{-6}T^2 + 2.31 \times 10^{-9}T^3 + 5.225 \times 10^2 T^{-1}$$

(kcal/mole, 298° - 2038°K)

$$\beta\text{-UC}_2 \quad H_T - H_{298} = -18.73 + 2.944 \times 10^{-2}T$$

(kcal/mole, 2038°-2600°K)