Lawrence Berkeley National Laboratory
Recent Work

Title
EXTRAPOLATION OF LOW TEMPERATURE VAPOR PRESSURE DATA OF URANIUM CARBIDE TO THE LIQUID REGION

Permalink
https://escholarship.org/uc/item/04n1g1v9

Authors
Tehranian, T.
Olander, D.R.

Publication Date
1981-09-01
EXTRAPOLATION OF LOW TEMPERATURE VAPOR PRESSURE DATA OF URANIUM CARBIDE TO THE LIQUID REGION

T. Tehranian and D.R. Olander

September 1981

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
EXTRAPOLATION OF LOW TEMPERATURE VAPOR PRESSURE DATA
OF URANIUM CARBIDE TO THE LIQUID REGION

F. Tehranian and D. R. Olander

Materials and Molecular Research
Division of the Lawrence Berkeley
Laboratory and the
Department of Nuclear Engineering
University of California
Berkeley, California 94720

This work was supported by the Director, Office of Energy Research,
Office of Basic Energy Sciences, Materials Sciences Division of the
I. Introduction

Knowledge of the high temperature thermodynamic properties of refractory nuclear fuels is necessary for assessing the consequences of potential accidents involving fuel melting. Methods of extrapolating the partial vapor pressures of the gaseous uranium oxides from measurements over solid UO₂ through the melting point into the liquid region have been developed [1,2] but comparable treatments for uranium carbide have not been reported. In this work the model proposed by Nikol'skii [3,4] for solid UC is modified to estimate uranium pressures and carbon activities in the liquid region. The standard free energies of formation of the gaseous species are then used to calculate the partial pressures of different species as functions of temperature and the carbon-to-uranium ratio of the liquid.

II. Nikol'skii's Model for Solid UC₁+y

Nikol'skii's [3,4] treatment of the thermochemistry of non-stoichiometric uranium carbide considers the solid as a nonideal molecular solution of U, UC and UC₂ (these are designated by subscripts 0, 1 and 2, respectively). The three constituents are assumed to be related by the equilibrium reaction:

\[ \text{UC}_2 + 2U \rightleftharpoons 2\text{UC} \]  \hspace{1cm} (1)

It is further assumed that UC₂ is responsible for the deviation from ideality, and the chemical potentials of three components are written as:

\[ \mu = \mu_0^0 + \gamma x_2^2 + RT\ln x_0 \]  \hspace{1cm} (2)
\[ \mu_1 = \mu_0^0 + \gamma x_2^2 + RT \ln x_1 \]  
\[ \mu_2 = \mu_0^0 + \gamma (1-x_2^2) + RT \ln x_2 \]  

where \( x_0, x_1 \), and \( x_2 \) are the mole fractions of U, UC, and UC\(_2\), respectively, and \( \mu_0^0, \mu_1^0 \) and \( \mu_2^0 \) are the standard free energies of the pure substances. \( \gamma \) is a nonideality parameter which is independent of composition.

The condition for equilibrium of reaction (1) is \( \mu_2 + \mu_0 = 2\mu_1 \), which yields:

\[ \mu_0^0 + \mu_2^0 - 2\mu_1^0 + \gamma (1-2x_2^2) + RT \ln \left( \frac{x_0 x_2}{x_1^2} \right) = 0 \]  

The chemical potential of uranium is given by Equation (2) and that of carbon is obtained from the reaction:

\[ U + C \xrightarrow{\gamma} UC \]  

which yields:

\[ \mu_C = \mu_1 - \mu_0 = \mu_1^0 - \mu_0^0 + RT \ln \left( \frac{x_1}{x_0} \right) \]  

The standard state of uranium is the monoatomic ideal gas at a pressure of 1 atm, while that of carbon is graphite. The chemical potentials of these two elements in the system are:

\[ \mu_0 = RT \ln p_U \]  
\[ \mu_C = RT \ln a_C \]
Where $p_U$ is the partial pressure of uranium in equilibrium with the condensed phase and $a_C$ is the carbon activity.

Combining equations (2) and (8) yields:

$$\log p_U = A_0 + B x_2^2 + \log x_0$$  \hspace{1cm} (10)

and, from equations (7) and (9):

$$\log a_C = A_1 + \log (x_1/x_0)$$  \hspace{1cm} (11)

where:

$$A_0 = \frac{\mu_0^o}{2.3026 \cdot RT}$$  \hspace{1cm} (12)

$$A_1 = \frac{(\mu_1^o - \mu_0^o)}{2.3026 \cdot RT}$$  \hspace{1cm} (13)

$$A_2 = \frac{(\mu_0^o + \mu_2^o - 2\mu_1^o)}{2.3026 \cdot RT}$$  \hspace{1cm} (14)

$$B = \gamma/2.3026 \cdot RT$$  \hspace{1cm} (15)

The mole fractions $x_0$, $x_1$, and $x_2$ are obtained from the solution of the following system of three equations. The carbon-to-uranium ratio of the solid (C/U) is related to the mole fractions by:

$$(C/U) - x_1 - 2x_2 = 0$$  \hspace{1cm} (16)

Equation (5) is written as:

$$A_2 + B(1 - 2x_2) + \log(x_0 x_2^2/x_1) = 0$$  \hspace{1cm} (17)

and the mole fractions sum to unity.

$$x_0 + x_1 + x_2 = 1$$  \hspace{1cm} (18)

To determine the parameters $A_0$, $A_1$, $A_2$ and $B$, Nikol'skii used the uranium pressure and carbon activity measured by Storms [5]
for different compositions (i.e. C/U). By repeating the calculations for different temperatures he obtained the following temperature dependences:

\[
A_0 = 4.8283 - \frac{22243}{T} \\
A_1 = 1.3304 - \frac{9643}{T} \\
A_2 = -2.7611 + \frac{12379}{T} \\
B = 0.0041 + \frac{2089}{T}
\]  

III. Extrapolation to the Liquid Region:

To estimate the thermomechanical properties of the uranium-carbon system at temperatures above the melting point of UC, Nikol'skii's model for the solid phase is assumed to apply to the liquid phase as well. That is, liquid uranium carbide \((UC_{1+y})\) is considered as a mixture of \(U\), UC and \(UC_2\), in which the last is responsible for deviation from ideal solution behavior. Following the same steps which were taken for the solid phase, we obtain for the liquid phase equations identical in form to equations (10) - (18). The constants \(A_0\), \(A_1\), \(A_2\) and \(B\), however, are different when the condensed phase is liquid.

Since there are no uranium pressure or carbon activity data for the liquid region, we cannot determine the parameters as in the solid case. Instead, we relate liquid and solid properties through the entropy of fusion. For the solid, temperature dependence of \(\mu_i^0 (i = 0,1,2)\) is of the general form:
\[ \mu_i^0 = -a_i T + b_i \]  
(23)

If we assume that the corresponding liquid properties (denoted by primes), have similar temperature dependences,

\[ \mu_i' = -a_i' T + b_i' \]  
(24)

Then we can conclude that

\[ a_i' = a_i + \Delta S_{mi} \]  
\( (i=0,1,2) \)  
(25)

\[ b_i' = b_i + \Delta H_{mi} = b_i + T_{mi} \Delta S_{mi} \]  
\( (i=0,1,2) \)  
(26)

where \( \Delta S_{mi} \) and \( \Delta H_{mi} \) are the entropy and enthalpy of fusion of the pure components and the \( T_{mi} \) are their melting points. Estimates of these properties are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>( T_{mi}, \text{K} )</th>
<th>( \Delta S_{mi}, \text{cal/mole-K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>1408</td>
<td>1.55</td>
</tr>
<tr>
<td>UC</td>
<td>2780</td>
<td>4.0</td>
</tr>
<tr>
<td>UC_2</td>
<td>2500</td>
<td>4.0, 6.0</td>
</tr>
</tbody>
</table>

The values of \( \Delta S_m \) for U and UC are taken from the literature [6], [7]. For UC\_2 we used either the same value for UC or R per atom (6 cal/mole K) suggested by Leibowitz (8). Using the values in Table 1 in Eqs. (24) - (26) fixes the \( \mu_i'^0 \) which, when inserted into the liquid phase
analogs of Eqs. (12) - (14) yield:

\[
A_0' = 4.4883 - 2.1763 \times 10^4 / T \tag{27}
\]

\[
A_1' = 0.8018 - 7.7069 \times 10^3 / T \tag{28}
\]

\[
A_2' = -2.2325 + 1.0389 \times 10^4 / T \text{ for } \Delta S_m = 4.0 \text{ cal/mole-K} \tag{29}
\]
or

\[
A_2' = -2.6799 + 1.1607 \times 10^4 / T \text{ for } \Delta S_m = 6.0 \text{ cal/mole-K} \tag{29}
\]

To find \( B' \) we used the carbon activity at the melting point of UC [5]. This was obtained by extrapolating the data in the solid phase to the melting point and solving equations (11), (16), (17) and (18) at \( T = 2780 \text{ K} \), \( C/U = 1 \) and with the constants \( A_0, .. B \) replaced by \( A_0 \ldots \ldots B' \). Because the liquid and solid phases are equilibrium at the melting point, the carbon activity of the liquid is equal to that in the solid, obtained by extrapolation. Since this procedure gives only one value of \( B' \) in the liquid region (i.e. at melting point), we cannot find \( B' \) for different temperatures. As a result we assumed that \( \gamma' \) is constant and so \( B' = \frac{\text{constant}}{T} \), which is approximately the behavior of \( B \) for the solid (see Eq. (22)). Using the value of \( B' \) at the melting point, we find:

\[
B' = 1722.6 / T \text{ for } \Delta S_m = 4.0 \text{ cal/mole-K} \tag{30}
\]
or

\[
B' = 1753.0 / T \text{ for } \Delta S_m = 6.0 \text{ cal/mole-K} \tag{30}
\]

Even though the uranium pressure in equilibrium with UC(\&) and UC(s) at the melting point is available by extrapolation of Storms' data [5], this information is not useful in fixing \( A_2' \) or \( B' \). The reason is that the equation in which this datum appears (Eq(10)) does not contain \( A_2' \) and at the melting point of UC the term containing \( B' \) is very much smaller than the other terms. Therefore, Eq(10) serves primarily as a check on the value of \( A_0' \) and \( A_1' \) and the carbon activity at the melting point. The uranium pressure determined in this manner is \( 3.76 \times 10^{-5} \text{ atm} \) which compares well
with the extrapolated experimental value of $3.95 \times 10^{-5}$ atm.

Use of the parameters $A_0', A_1', A_2'$ and $B'$ in the calculational method previously developed for the solid gives the uranium partial pressure and the carbon activity as functions of composition and temperature in the liquid region.

IV. Partial Pressure of Other Vapor Species:

The partial pressure of C(g) is obtained by using the calculated carbon activity from Eq. (11) and the known partial pressure of C(g) over graphite. Equation (10) gives the uranium pressure. The partial pressure of other vapor species calculated by use of the gaseous equilibria:

$$\text{U(g)} + 2\text{C(g)} \rightleftharpoons \text{UC}_2(g)$$  \hspace{1cm} (31)

$$2\text{C(g)} \rightleftharpoons \text{C}_2(g)$$  \hspace{1cm} (32)

$$3\text{C}(g) \rightleftharpoons \text{C}_3(g)$$  \hspace{1cm} (33)

From which $P_{UC_2}$, $P_{C_2}$ and $P_{C_3}$ are determined by:

$$P_{UC_2} = P_{U} P_{C}^2 \exp \{[\Delta G_U^0 + 2\Delta G_C^0 - \Delta G_{UC_2}^0]/RT\}$$  \hspace{1cm} (34)

$$P_{C_2} = P_{C}^2 \exp \{[2\Delta G_C^0 - \Delta G_{C_2}^0]/RT\}$$  \hspace{1cm} (35)

$$P_{C_3} = P_{C}^3 \exp \{[3\Delta G_C^0 - \Delta G_{C_3}^0]/RT\}$$  \hspace{1cm} (36)

The free energies of formation of the gaseous molecules are given in Ref. [5].

Figures 1 and 2 show the calculated partial pressures of different species and the total vapor pressure of UC_{1+y} as a function of composition at 4000 K for the two values of $\Delta S_{m2}$ in Table 1. Figure 3
shows the temperature dependence of the total pressure calculated for $\text{UC}_{1.0}$ and compared with the result of calculations by Finn et al. [7] for stoichiometric material. The two computations differ by a factor of less than $\sim 2$. The choice of entropy of fusion of $\text{UC}_2$ affects primarily the partial pressure of this species.
References


Acknowledgement

The helpful comments of L. Leibowitz are gratefully acknowledged.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract # W-7405-ENG-48.
FIGURE CAPTIONS

1. Partial pressures of different species as a function of composition at 4000 K. $\Delta S_{m2} = 4.0$ cal/mole-K.

2. Partial pressures of different species as a function of composition at 4000 K. $\Delta S_{m2} = 6.0$ cal/mole-K.

3. Total vapor pressure over liquid UC$_{1.0}$ as a function of temperature.
Figure 2.
Present Calculations:

\[ \Delta S_m (UC_2) \]
\[ \text{cal/mole-K} \]

a \quad 4.0
b \quad 6.0

Figure 3.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.
TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720