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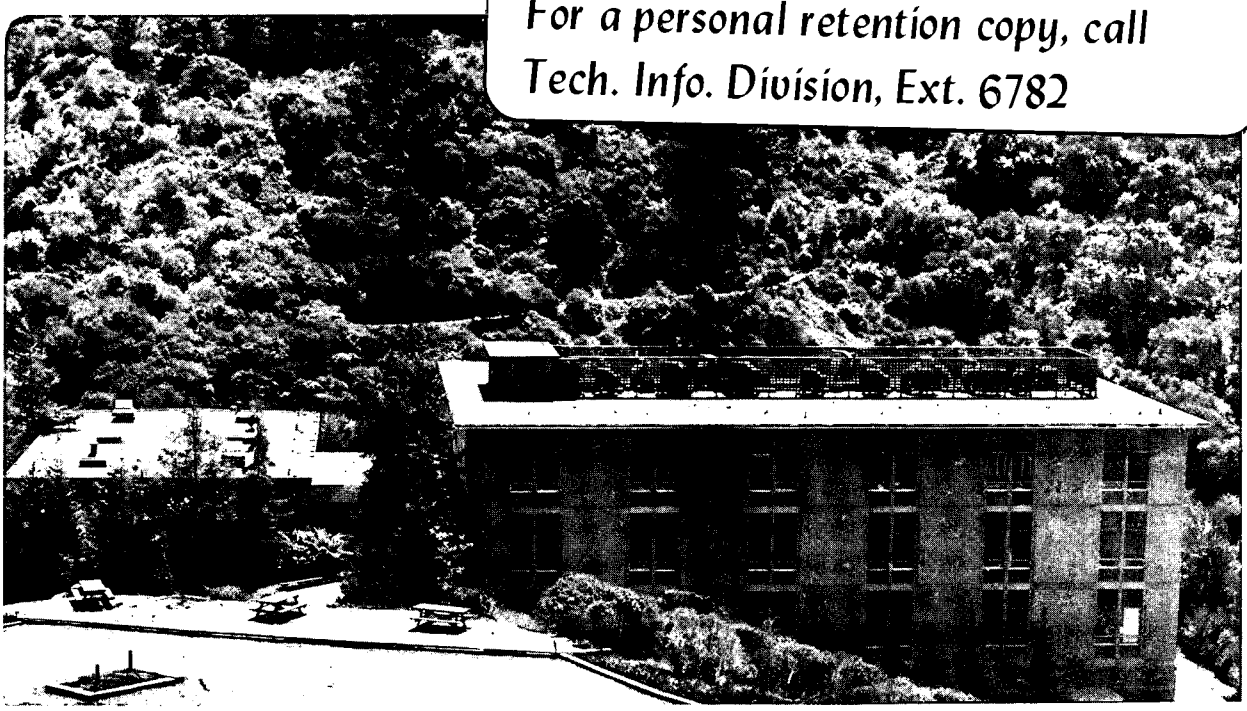

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EXTRAPOLATION OF LOW TEMPERATURE VAPOR PRESSURE DATA OF URANIUM CARBIDE TO THE LIQUID REGION

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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 UO_2 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 $UC_{1\pm y}$

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 UC_2 (these are designated by subscripts 0, 1 and 2, respectively). The three constituents are assumed to be related by the equilibrium reaction:

$$UC_2 + U \rightleftarrows 2\ UC \qquad (1)$$

It is further assumed that UC_2 is responsible for the deviation from ideality, and the chemical potentials of three components are written as:

$$\mu_0 = \mu_0^o + \gamma\ x_2^2 + RT\ell n x_0 \qquad (2)$$

$$\mu_1 = \mu_1^o + \gamma x_2^2 + RT\ell n x_1 \quad (3)$$

$$\mu_2 = \mu_2^o + \gamma (1-x_2)^2 + RT\ell n x_2 \quad (4)$$

where x_0, x_1 and x_2 are the mole fractions of U, UC and UC_2, respectively and μ_0^o, μ_1^o and μ_2^o are the standard free energies of the pure substances. γ 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:

$$\mu_0^o + \mu_2^o - 2\mu_1^o + \gamma(1-2x_2) + RT\ell n \left(\frac{x_0 x_2}{x_1^2}\right) = 0 \quad (5)$$

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

$$U + C \rightleftarrows UC \quad (6)$$

which yields:

$$\mu_C = \mu_1 - \mu_0 = \mu_1^o - \mu_0^o + RT\ell n \left(\frac{x_1}{x_0}\right) \quad (7)$$

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:

$$\mu_0 = RT\ell n\, p_U \quad (8)$$

$$\mu_C = RT\ell n\, a_C \quad (9)$$

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:

$$\log p_U = A_0 + Bx_2^2 + \log x_0 \tag{10}$$

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

$$\log a_C = A_1 + \log (x_1/x_0) \tag{11}$$

where:

$$A_0 = \mu_0^o/2.3026\ RT \tag{12}$$

$$A_1 = (\mu_1^o - \mu_0^o)/2.3026\ RT \tag{13}$$

$$A_2 = (\mu_0^o + \mu_2^o - 2\mu_1^o)/2.3026\ RT \tag{14}$$

$$B = \gamma/2.3026\ RT \tag{15}$$

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:

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

Equation (5) is written as:

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

and the mole fractions sum to unity.

$$x_0 + x_1 + x_2 = 1 \tag{18}$$

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:

$$A_0 = 4.8283 - (22243/T) \tag{19}$$

$$A_1 = 1.3304 - (9643/T) \tag{20}$$

$$A_2 = -2.7611 + (12379/T) \tag{21}$$

$$B = 0.0041 + (2089/T) \tag{22}$$

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 ($UC_{1\pm y}$) 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 μ_i^o (i = 0,1,2) is of the general form:

$$\mu_i^o = -a_i T + b_i \tag{23}$$

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

$$\mu_i'^o = -a_i' T + b_i' \tag{24}$$

Then we can conclude that

$$a_i' = a_i + \Delta S_{mi} \qquad (i=0,1,2) \tag{25}$$

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

where ΔS_{mi} and ΔH_{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 1: Entropies of fusion

	T_{mi}, K	ΔS_{mi} cal/mole-K
U	1408	1.55
UC	2780	4.0
UC_2	2500	4.0, 6.0

The values of ΔS_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 $\mu_i'^o$ which, when inserted into the liquid phase

analogs of Eqs. (12) - (14) yield:

$$A_0' = 4.4883 - 2.1763 \times 10^4/T \quad (27)$$

$$A_1' = 0.8018 - 7.7069 \times 10^3/T \quad (28)$$

$$A_2' = -2.2325 + 1.0389 \times 10^4/T \text{ for } \Delta S_{m2} = 4.0 \text{ cal/mole-K}$$

or $$A_2' = -2.6799 + 1.1607 \times 10^4/T \text{ for } \Delta S_{m2} = 6.0 \text{ cal/mole-K} \quad (29)$$

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 K, C/U = 1 and with the constants A_0, ..B replaced by A_0' .... 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 γ' 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:

$$B' = 1722.6/T \text{ for } \Delta S_{m2} = 4.0 \text{ cal/mole-K}$$

or (30)

$$B' = 1753.0/T \text{ for } \Delta S_{m2} = 6.0 \text{ cal/mole-K}$$

Even though the uranium pressure in equilibrium with UC(ℓ) 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 3.76×10^{-5} atm which compares well

with the extrapolated experimental value of 3.95×10^{-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:

$$U(g) + 2C(g) \rightleftarrows UC_2(g) \tag{31}$$

$$2C(g) \rightleftarrows C_2(g) \tag{32}$$

$$3C(g) \rightleftarrows C_3(g) \tag{33}$$

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

$$p_{UC_2} = p_U \, p_C^2 \exp\{[\Delta G_U^o + 2\Delta G_C^o - \Delta G_{UC_2}^o]/RT\} \tag{34}$$

$$p_{C_2} = p_C^2 \exp\{[2\Delta G_C^o - \Delta G_{C_2}^o]/RT\} \tag{35}$$

$$p_{C_3} = p_C^3 \exp\{[3\Delta G_C^o - \Delta G_{C_3}^o/RT\} \tag{36}$$

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 $UC_{1\pm y}$ as a function of composition at 4000 K for the two values of ΔS_{m2} in Table 1. Figure 3

shows the temperature dependence of the total pressure calculated for $UC_{1.0}$ 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 ~ 2. The choice of entropy of fusion of UC_2 affects primarily the partial pressure of this species.

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FIGURE CAPTIONS

1. Partial pressures of different species as a function of composition at 4000 K. ΔS_{m2} = 4.0 cal/mole-K.
2. Partial pressures of different species as a function of composition at 4000 K. ΔS_{m2} = 6.0 cal/mole-K.
3. Total vapor pressure over liquid $UC_{1.0}$ as a function of temperature.

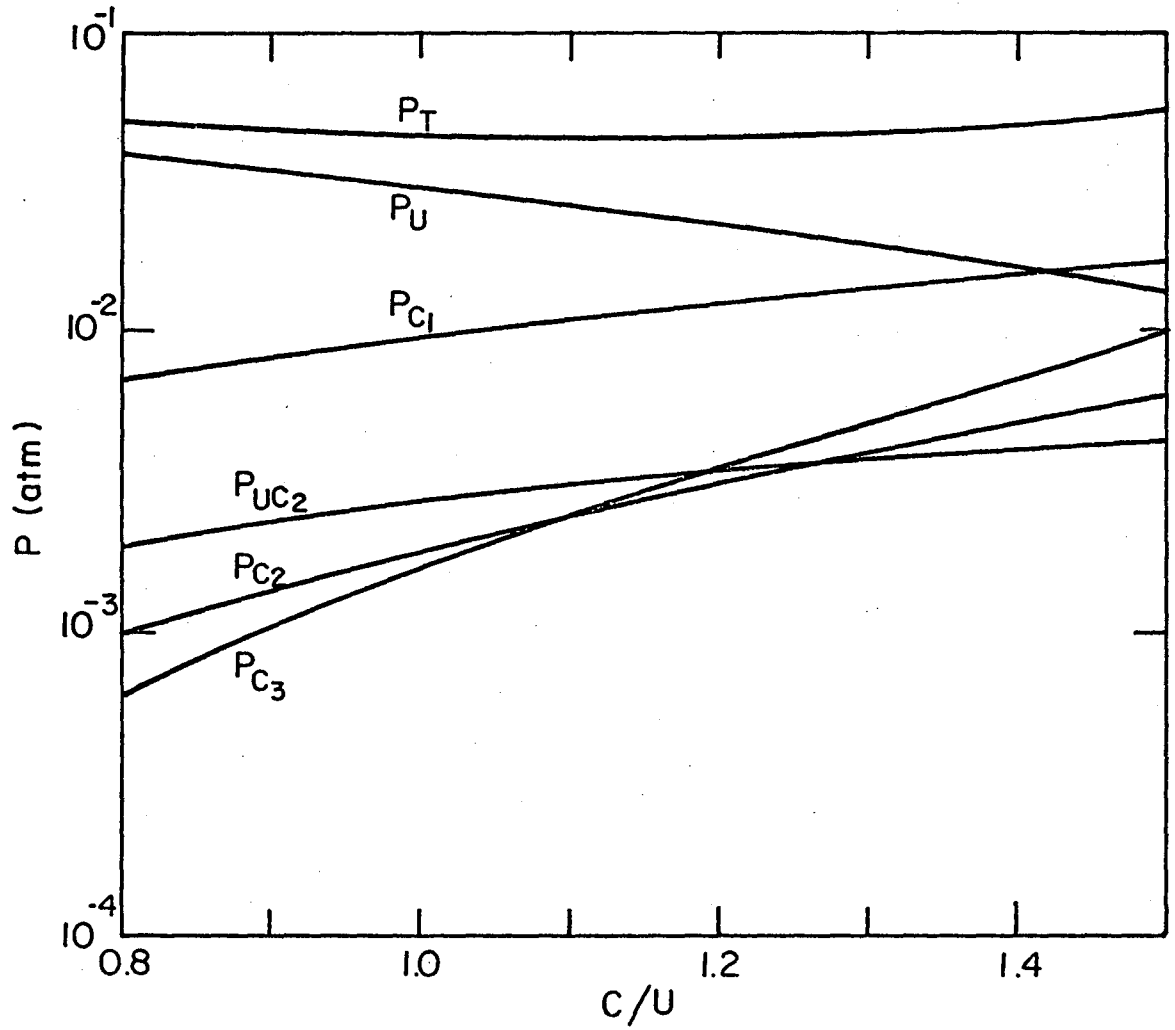

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Figure 1

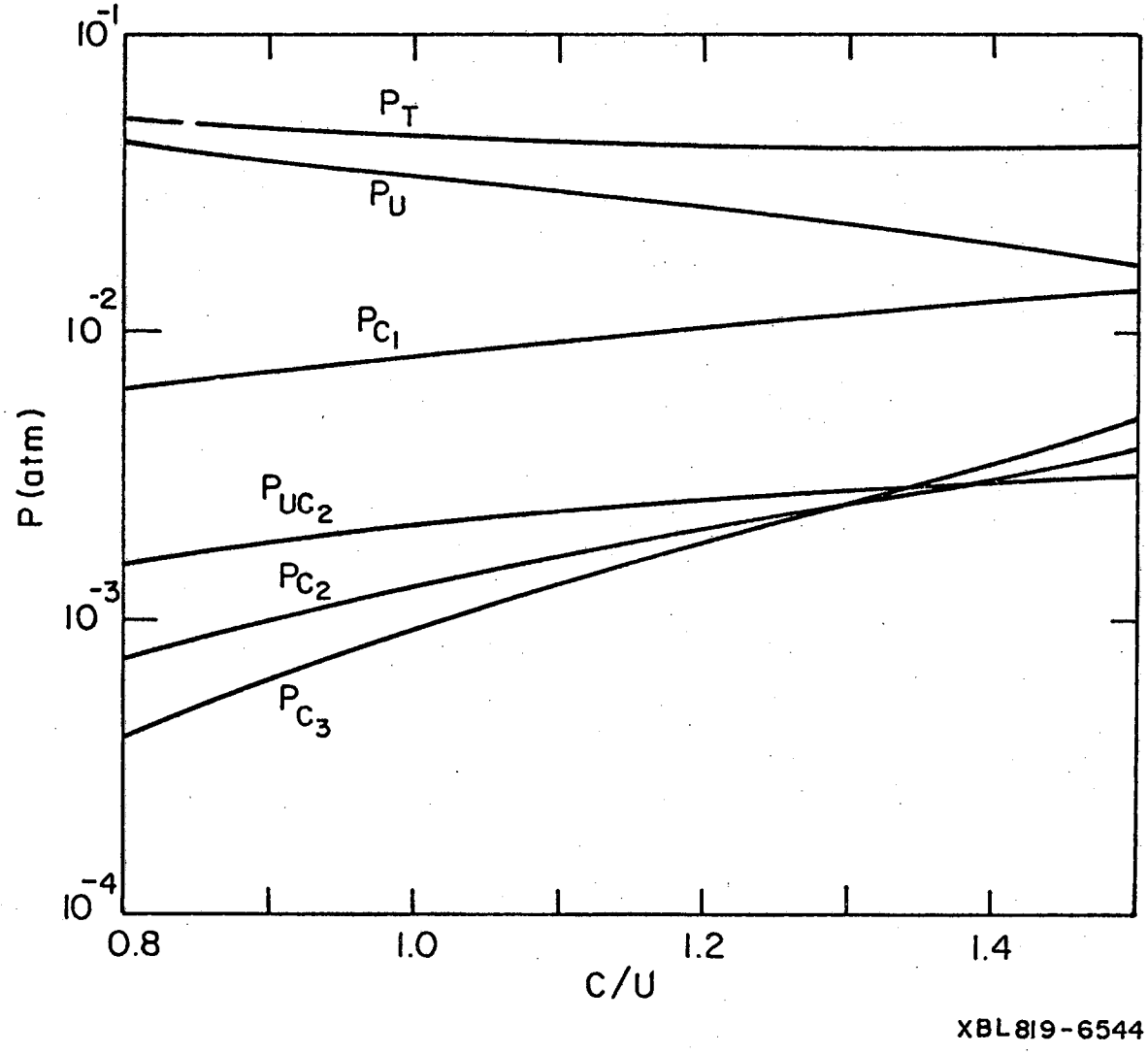
10^{-1}
10^{-2}
10^{-3}
10^{-4}
P (atm)
P_T
P_U
P_{C_1}
P_{UC_2}
P_{C_2}
P_{C_3}
0.8
1.0
1.2
1.4
C/U
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Figure 2.

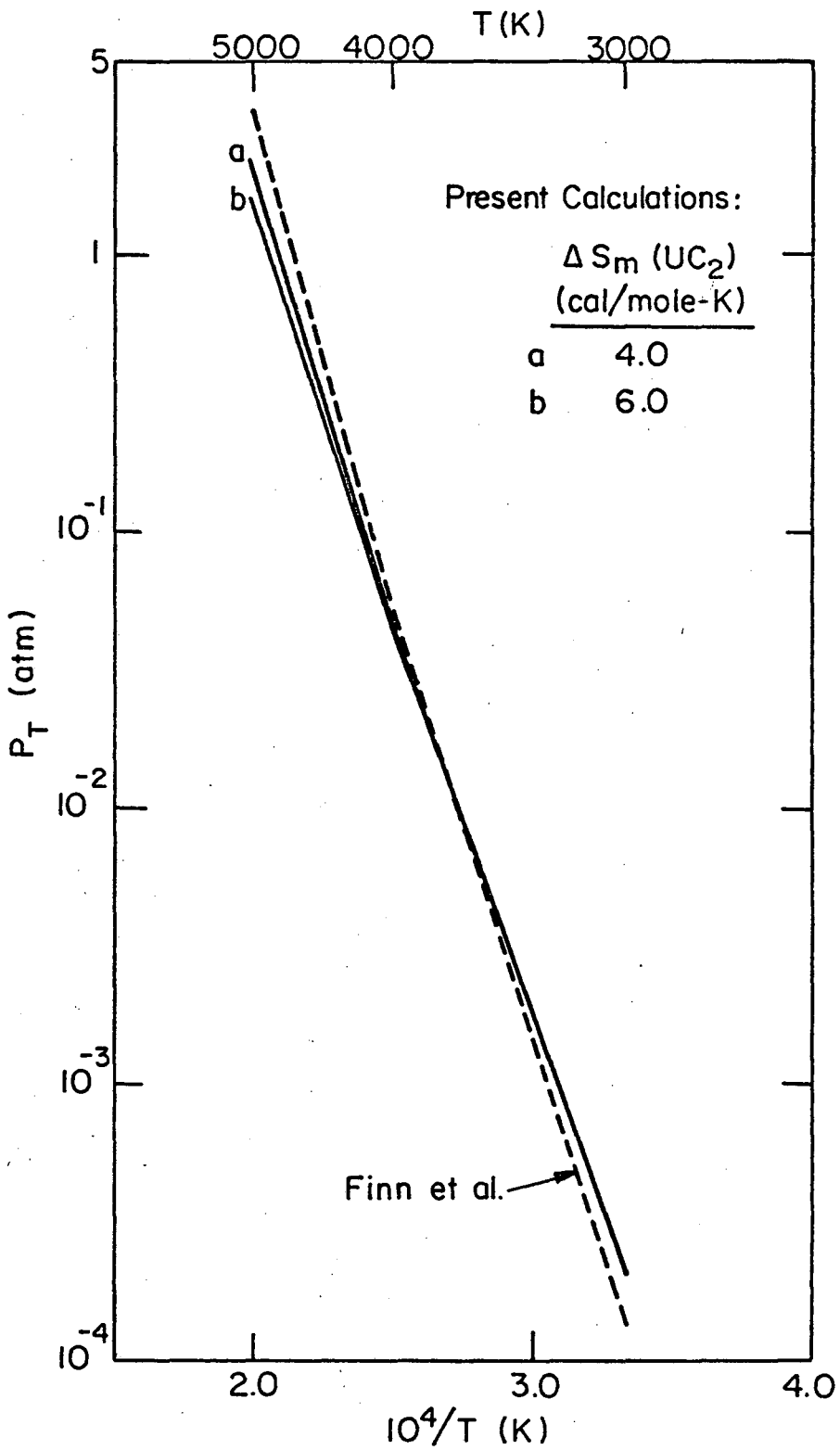

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Figure 3.

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