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Abstract

The Significant Liquid Structures Theory (SST) by Eyring, which was used earlier to analyse the Equation of State of UO_2, is extended in this paper to non-stoichiometric urania. This is done by introducing an oxygen defect model in the "solidlike" partition function of the SST, and by including several gaseous species in the "gaslike" partition function. A grand partition function is used to describe the urania system, with the oxygen chemical potential as a variable. The equations are developed for hyperstoichiometric material; however, they may also be used for hypostoichiometric urania or plutonia. An extension to mixed oxide seems feasible, with some additional assumptions. Numerical results for two different data sets are presented.

Zustandsgleichung für Nichtstoichiometrisches Urandioxid unter Verwendung der Significant Liquid Structures - Theorie

Zusammenfassung

Die "Significant Liquid Structures"-Theorie von Eyring wurde bereits früher für die Zustandsgleichung von UO_2 angewandt. Hier wird über eine Erweiterung auf nicht-stoichiometrisches Material berichtet. Dafür wurde ein Sauerstoff-Defekt-Modell in die Zustandssumme für die kristalline Phase ("solidlike partition function") eingebaut, die Zustandssumme für die Gasphase ("gaslike partition function") wurde auf mehrere Komponenten erweitert. Eine großkanonische Zustandssumme wird zur Beschreibung des Systems, mit variablem chemischem Sauerstoffpotential, verwendet. Die Gleichungen sind für den Fall von überstöchiometrischem Material entwickelt, können aber ohne Schwierigkeit auch auf den unterstöchiometrischen Fall (UO_{2-x} oder PuO_{2-x}) angewandt werden. Eine Erweiterung für Mischoxid erscheint mit einigen zusätzlichen Annahmen möglich.

Numerische Ergebnisse für zwei verschiedene Datensätze werden vorgestellt.

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1. Introduction

The Significant Structures Theory (SST) of Liquids, developed by Eyring, was used successfully to describe the equation of state for a variety of materials /1/. It was noted that the method is applicable to materials with ionic binding /1,2/. It was, therefore, also employed to extrapolate the equation of state of UO_2 up to the critical temperature /2,3/. However, in earlier applications of SST, it was mostly assumed that the material evaporates congruently, i.e. the composition of the vapor phase is identical to that of the condensed phase. This assumption does not hold for urania, where the composition of both phases may be quite different.

An attempt to extend SST to the case of non-stoichiometric urania, which was published in 1979 /4/, is not satisfactory because it does not lead to equal O/M in the liquid and in the gas phase, as the critical temperature is approached.

Therefore, an alternative approach is proposed in this paper, in an attempt to remedy this shortcoming. A grand partition function is constructed for non-stoichiometric urania, which inherently fulfills the condition $(O/M)_\ell = (O/M)_g$ at the critical temperature.

The basic assumption of the SST is that the partition function (PF) of the liquid is a suitable combination of a "solidlike" and a "gaslike" PF /1/. To extend the model to the non-stoichiometric case, one has to include different gaseous species in the "gaslike" PF. This can be done in a straightforward way. However, in addition, it is necessary to introduce some sort of an oxygen potential model into the solidlike PF. In this paper, it is assumed that oxygen vacancies and interstitial atoms in the solidlike lattice are responsible for the deviation from stoichiometry. This defect model, proposed by Thorn and Winslow, was selected because of its simplicity, and because there is no general agreement as to which of the more recent oxygen potential models is the most reliable.

2. Derivation of the Equations

2.1 The Grand Partition Function for $UO_{2\pm x}$

Let the usual canonical partition function (PF) for a given number N of uranium atoms, and N_o of oxygen atoms, be $Z(T,V,N,N_o)$. The corresponding thermodynamic potential is the Helmholtz free energy, which is given by

$$F(T, V, N, N_0) = -kT \ln Z \tag{1}$$

It is well known that all the state variables (e.g. internal energy, pressure etc.) can be obtained by forming partial derivatives of (1).

In the following thermodynamic description of the system $UO_{2\pm x}$, we are mainly interested in finding the coexistence curve between the liquid and the gas. We now observe that in equilibrium, the value of the oxygen chemical potential, μ_o, is the same for the two phases, whereas the O/M ratio is usually different in the liquid and the gas. It is, therefore, obvious that a grand partition function (GPF) is a suitable tool to describe the system. For a given μ_o, the GPF is defined by

$$GPF(T, V, N, \mu_0) = \sum_{N_0} \exp\left(\frac{\mu_0 N_0}{kT}\right) Z(T, V, N, N_0) \tag{2}$$

Strictly speaking, (2) is a semi-grand PF because the sum is only over N_o, whereas the number N of uranium atoms is fixed. In the following, the GPF function (2) will be written for one mol of $UO_{2\pm x}$, and the variable N will be dropped.

The corresponding thermodynamic potential is /5/

$$J(T, V, \mu_0) = -kT \ln (GPF) \tag{3}$$

which, in thermodynamic terms, is equal to

$$J = U - TS - \mu_0 N_0 = F - \mu_0 N_0 \tag{4}$$

The differential of J is

$$dJ = -S\,dT - p\,dV - N_0\,d\mu_0$$

from which one finds the relations

$$S = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu_0} \qquad p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu_0} \qquad \bar{N}_0 = -\left(\frac{\partial J}{\partial \mu_0}\right)_{T,V} \tag{5}$$

We follow here the notation of Becker /5/; note that other authors, e.g. Fowler and Guggenheim /6/, use a different one. According to the second eq. (5), the pressure is the slope of the J versus V curve. As the coexistence curve is defined by equal pressure in both phases, the well-known double tangent method /1/ can be used to obtain the specific volume of the liquid and the vapor, for a given chemical potential μ_o. Thus, one has the condition

$$\left(\frac{\partial J}{\partial V}\right)_{V=V_\ell} = \left(\frac{\partial J}{\partial V}\right)_{V=V_g}$$

Note that $\bar{N}_o$ is different in the liquid and in the gas, as it should. However, as the critical temperature is approached, the two volumes become equal, and therefore also the $\bar{N}_o$ values.

It is known from statistical thermodynamics that the sum in eq. (2) can be replaced by the maximum term

$$\ln(GPF) \approx \ln(\text{max. term}) = \frac{\mu_0 N_0}{kT} + \ln Z(T, V, \bar{N}_0) \tag{2a}$$

Note that $\bar{N}_o$ defines the largest term, but it is equal to the average value defined by (5).

We now introduce the concept of the Significant Structures Theory (SST), which is described in detail e.g. in /3/. According to SST, the partition function is composed of a solidlike part f_s, and a gaslike part f_g

$$\ln Z(T, v, N_0) = N\frac{v_s}{v}\ln f_s + N\frac{v-v_s}{v}\ln f_g \qquad (6)$$

The logarithm of the f_s and f_g can be written as sums of the "stoichiometric" PF and a "non-stochiometric" part

$$\ln f_s = \ln f_{s(st)} + \ln Z_{def} \; ; \; \ln f_g = \ln f_{g(st)} + \ln Z_{gm}$$

so that

$$\ln(GPF) = \ln Z_{st}(T, v) + \frac{\mu_0 \bar{N}_b}{kT} + \ln Z_{ns}(T, v, \bar{N}_b) \qquad (2b)$$

Note that, by splitting the GPF like this, the non-stoichiometric part becomes a function of $N_b = N_o - N$, rather than of N_o.

The stoichiometric part is the same as in earlier work /3/ except that the "excess enthalpy" term in f_s is omitted. Thus, one has

$$\ln f_{s(st)} = \frac{E_s}{3RT}\left(\frac{v}{v_s}\right)^{\gamma} - 9\ln\left(1 - e^{-\theta_E/T}\right)$$
$$+ 3\ln\left[1 + n\left(\frac{v}{v_s} - 1\right)\exp\left(-\frac{a E_s v_s}{3RT(v - v_s)}\left(\frac{v}{v_s}\right)^{\gamma}\right)\right] \qquad (7)$$

The single-species gas PF $f_g(st)$ is composed of translational, rotational, vibrational and electronic parts. The total stoichiometric PF is then

$$\ln Z_{st} = N\frac{v_s}{v}\ln f_{s(st)} + N\frac{v-v_s}{v}\ln f_{g(st)} \qquad (8)$$

The construction of the non-stoichiometric part of the GPF, $\ln Z_{ns}$, will be described in the next section.

2.2 Construction of the Non-Stoichiometric Partition Function

2.2.1 The Defect Partition Function

The GPF (2b) can now be written

$$\ln(GPF) = \ln Z_{st} + \frac{\mu_o \bar{N}_b}{kT} + N\frac{v_s}{v}\ln Z_{def} + N\frac{v-v_s}{v}\ln Z_{gm} \qquad (2c)$$

To account for non-stoichiometry in the solidlike PF, it is necessary to introduce some sort of an oxygen potential model. In this paper, a defect model was chosen, which includes oxygen vacancies, and interstitial oxygen atoms in the solidlike lattice. This model was proposed by Thorn and Winslow /7/ in 1963. It is used in this paper, although several more recent oxygen models are known /8,9/ because a simple defect model is well compatible with the basic ideas of the SST; further, there is no general agreement which of the more recent models can be considered most reliable /9/; besides, simplicity of the equations is an important point in the formalism to be developed in this paper.

The PF for non-stoichiometry through oxygen defects is given by

$$Z_{s(ns)} = \sum_{N_v N_i} \frac{(2N)!}{N_v!(2N-N_v)!}\,\frac{N!}{N_i!(N-N_i)!}\, q_i(T)^{N_i}\, q_v(T)^{N_v}$$

$$\exp\left(\frac{N_i(\varepsilon_i+\mu_o) - N_v(\varepsilon_v+\mu_o)}{kT}\right) \qquad (9)$$

where N_i, N_v are the numbers of interstitials and vacancies per mol; ε_i, ε_v are the energies to remove an interstitial, or a lattice atom to infinity. The functions q_i and q_v account for the vibrational modes associated with the defects. According to Thorn and Winslow we have /8/

$$\ln q_i(T) = -3\left[\frac{\vartheta_i}{2T} + \ln\left(1 - e^{-\vartheta_i/T}\right)\right]$$

$$\ln q_v(T) = -3\left[\frac{\vartheta_v}{2T} + \ln\left(1 - e^{-\vartheta_v/T}\right)\right] - 1.725 \tag{10}$$

We now observe that $N_b = N_i - N_v$, and each term in (9) contains the factor $\exp(N_b\mu_o/kT)$. We want to write (9) as a sum over N_b and either N_i or N_v. For hyperstoichiometric material, N_v is smaller than N_i, and it is preferable for numerical calculations to sum over N_v, rather than over N_i. The following equations will be written in this way, and they can be applied for numerical calculations only for hyperstoichiometric material. However, the equations for hypostoichiometric material can be developed in the very same way.

Eq. (7) can be written

$$Z_{s(ns)} = \sum_{N_b} \exp\left(\frac{N_b\mu_o}{kT}\right) \sum_{N_v} \varphi(N_b+N_v, N_v, T) \tag{11}$$

where φ is obtained by comparison with (9). For any term of the sum over N_b

$$\ln Z_{s(ns)} = \frac{N_b\mu_o}{kT} + \ln \underbrace{\sum_{N_v} \varphi(N_b+N_v, N_v, T)}_{Z_{def}(N_b,T)} \tag{12}$$

Later on, N_b will be fixed to give the maximum of the total GPF, defined by (2c); so far we leave it as a variable. The function Z_{def} can be approximated for a given N_b by the maximum term of the sum over N_v. The procedure is standard in statistical mechanics, and will not be spelled out here. We introduce the variables

$$\theta_v = N_v/2N \quad \text{and} \quad \theta_i = N_i/N, \quad x = \theta_i - 2\theta_v$$

and obtain

$$\ln Z_{def}(T,x) = 2\left[-\theta_v \ln \theta_v - (1-\theta_v)\ln(1-\theta_v) - \theta_v\left(\ln q_v + \frac{\varepsilon_v}{kT}\right)\right] - (x+2\theta_v)\ln(x+2\theta_v) - (1-x-2\theta_v)\ln(1-x-2\theta_v) + (x+2\theta_v)\left(\ln q_i + \frac{\varepsilon_i}{kT}\right) \tag{13}$$

The value of θ_v to be used in this equation is determined by the condition

$$\frac{\partial}{\partial \theta_v} \ln Z_{def}(T,x,\theta_v) = 0 \tag{14}$$

where $Z_{def}(T,x,\theta_v)$ is one term in the sum over N_v, eq. (10). This condition is

$$\frac{\theta_v(x+2\theta_v)}{(1-\theta_v)(1-x-2\theta_v)} = A = \frac{q_i}{q_v}\exp\left(\frac{\varepsilon_i-\varepsilon_v}{kT}\right)$$

The explicit solution is

$$\theta_v = \frac{1}{4(1-A)}\left[-(x+(3-x)A) + \sqrt{(x+(3-x)A)^2 + 8A(1-A)(1-x)}\right] \tag{15}$$

2.2.2 The Non-Stoichiometric Part of the Gas Partition Function

The vapor phase in equilibrium with liquid $UO_{2\pm x}$ consists of several species. The more important uranium bearing species, which are included in the present model, are UO, UO_2, and UO_3. Gaseous U has such a low concentration that it can be neglected. After deciding to include three species, it is a straightforward matter to develop the GPF for one mol of vapor, assuming again that the oxygen chemical potential μ_o is given.

Let f_i be the PF for N_i particles of UO_i. It is given by

$$f_i = \frac{(Z_i V)^{N_i}}{N_i!}$$

where Z_i is of the form

$$\ln Z_i = \frac{n}{2} \ln T - \sum \ln (1 - e^{-\theta v/T}) + \ln fel + K_i - 1 + \ln N_i \tag{16}$$

The canonical PF of a mixture containing N_1, N_2, N_3 particles is then

$$Z_{gas} = \frac{(Z_1 V)^{N_1}}{N_1!} \frac{(Z_2 V)^{N_2}}{N_2!} \frac{(Z_3 V)^{N_3}}{N_3!} \tag{17}$$

If instead the chemical potentials of the species, μ_1, μ_2, μ_3, are given, one obtains the GPF as a sum over the particle numbers

$$GPF_{gas} = \sum_{N_1 N_2 N_3} \exp\left(\frac{N_1\mu_1 + N_2\mu_2 + N_3\mu_3}{kT}\right) Z_{gas}(T, V, N_1, N_2, N_3) \tag{18}$$

The following relations hold in equilibrium

$$\mu_1 + \mu_0 = \mu_2 \quad ; \quad \mu_2 + \mu_0 = \mu_3 \tag{19}$$

where μ_i is the chemical potential of UO_i.

Using these relations, one can write the GPF

$$GPF_{gas} = \sum \exp\left(\frac{N\mu_2 + (N_3 - N_1)\mu_0}{kT}\right) Z_{gas}(T, V, N_1, N - N_1 - N_3, N_3) \tag{18a}$$

The equilibrium ratios of the N_i follow from the relations (19)

$$\frac{N_1}{N_2} = \frac{Z_1}{Z_2}\, e^{-\mu_0/kT} \quad ; \quad \frac{N_3}{N_2} = \frac{Z_3}{Z_2}\, e^{\mu_0/kT}$$

However, this implies that the partition functions Z_i are normalized to the same energy level at T = 0, i.e.

$$Z_i \longrightarrow Z_i + \frac{\Delta H_i}{RT} \tag{20}$$

where ΔH_i is the enthalpy of formation from UO_2 and O at T = 0.

We now assume that we have one mol of vapor, so that N is fixed, rather than μ_2. The factor $\exp(N\mu_2/kT)$ and the sum over N must then be dropped. Observing that $N_b = N_3 - N_1$, we obtain the final form of the gas GPF

$$GPF_{gas} = \left(\frac{Z_2 e V}{N}\right)^N \sum_{N_b} \exp\left(\frac{N_b \mu_0}{kT}\right) \cdot \sum_{N_1} \left(\frac{N}{N-2N_1-N_b}\right)^{N-2N_1-N_b} \left(\frac{N}{N_1}\right)^{N_1} \left(\frac{N}{N_b+N_1}\right)^{N_b+N_1} \left(\frac{Z_1}{Z_2}\right)^{N_1} \left(\frac{Z_3}{Z_2}\right)^{N_b+N_1} \tag{21}$$

As was done with the GPF for the defects, the sum over N_b can be replaced by the maximum term. Taking the logarithm of eq. (21) gives

$$\ln GPF_{gas} = N \ln \frac{Z_2 e V}{N} + \frac{\mu_0 N_b}{kT} + N \ln Z_{gm}(T, N_b) \tag{22}$$

A comparison of this equation with (2c) shows that the first term is just the stoichiometric part of the GPF for the gas. The non-stoichiometric part, Z_{gm}, is just the sum over N_1 in eq. (21), taken to the power 1/N.

Again, the function Z_{gm} can be replaced by the largest term of the sum over N_1. Introducing the variable $y_1 = N_1/N$, one has

$$\ln Z_{gm}(T,x) = y_1\left(\ln\frac{Z_1}{Z_2} - \ln y_1\right) + (x+y_1)\left(\ln\frac{Z_3}{Z_2} - \ln(x+y_1)\right) - (1-x-2y_1)\ln(1-x-2y_1) \tag{23}$$

The value of y_1 is determined by the "maximum" condition

$$\frac{\partial}{\partial y_1} \ln Z_{gm}(T,x,y_1) = 0 \tag{24}$$

This condition is a quadratic equation for y_1

$$\frac{y_1(x+2y_1)}{(1-x-2y_1)^2} = \frac{Z_1 Z_3}{Z_2^2}$$

with the explicit solution ($a = \ln Z_1 + \ln Z_3 - 2\ln Z_2$)

$$y_1 = \frac{1}{2(1-4a)}\left[-x-4a(1-x)+\sqrt{x^2(1-4a)+4a}\right] \tag{25}$$

2.2.3 The Non-Stoichiometric Partition Function

We can now proceed to write down the expression for the non-stoichiometric GPF. According to (2c)

$$\ln GPF_{(ns)} = N\frac{v_s}{v}\ln Z_{def} + N\frac{v-v_s}{v}\ln Z_{gm} + \frac{\mu_0 \overline{N_b}}{kT} \tag{26}$$

It remains to determine x, or $N_b = 2Nx$ as a function of V and μ_o such that (26) is a maximum; i.e. the derivative with respect to x is zero. For this purpose, we need the derivative of ln Z_{def}, and of ln Z_{gm}

$$\frac{d}{dx}\ln Z_{def}(T, x, \theta_v(x)) = \frac{\partial}{\partial x}\ln Z_{def} + \frac{d\theta_v}{dx}\frac{\partial}{\partial \theta_v}\ln Z_{def}$$

The second term on the right hand side is zero because of eq. (14), so that

$$\frac{d}{dx}\ln Z_{def} = -\ln\frac{x+2\theta_v}{1-x-2\theta_v} + \ln q_i + \frac{\varepsilon_i}{kT}$$

The derivative of ln Z_{gm} can be found in a similar way; the maximum condition for x is then

$$\frac{v_s}{v}\left[-\ln\frac{x+2\theta_v}{1-x-2\theta_v} + \ln q_i + \frac{\varepsilon_i}{kT}\right] + \frac{v-v_s}{v}\left[-\ln\frac{x+y_1}{1-x-2y_1} + \ln\frac{Z_3}{Z_2}\right] + \frac{\mu_0}{RT} = 0 \tag{27}$$

This equation determines x as a function of V. However, it cannot be solved explicitly for x. Therefore, a suitable numerical method must be used. It is known that for hyperstoichiometric material, x is always larger in the gas phase than in the condensed phase. In a first approximation, assuming that y_1 and $2\theta_v$ are not too much different, this means that the condition

$$\ln\frac{Z_3}{Z_2} > \ln q_i + \frac{\varepsilon_i}{kT} \tag{28}$$

must hold. With any set of accepted data, this condition is well fulfilled at the melting temperature. However, when choosing data suitable for extrapolation, one has to make sure that eq. (28) is fulfilled up to the critical temperature.

2.3 Comment on Thermodynamic State Variables

2.3.1 The Internal Energy and the Gas Composition

Apart from the pressure, and the specific volume of both the liquid and the gas phase, which come out of the present model directly, another important state variable is the internal energy. Although the expression for this quantity can be developed in a straightforward manner, it will be quoted here explicitly because it is helpful to make the interpretation of the present model clear.

From eq. (4) and (5), one obtains for the non-stoichiometric part of the internal energy, U_{ns}

$$\frac{U_{ns}}{RT^2} = \frac{V_s}{V}\left[2\theta_v\left(\frac{\varepsilon_v}{RT^2} - \frac{q_v'}{q_v}\right) + (x+2\theta_v)\left(\frac{q_i'}{q_i} - \frac{\varepsilon_i}{RT^2}\right)\right]$$

$$+ \frac{V-V_s}{V}\left[y_1\left(\frac{z_1'}{z_1} - \frac{z_2'}{z_2}\right) + (x+y_1)\left(\frac{z_3'}{z_3} - \frac{z_2'}{z_2}\right)\right] \qquad (29)$$

The primes in this equation denote temperature derivatives. Each term in (29) has a simple meaning: In the solidlike lattice, there is the energy of $2\theta_v$ oxygen vacancies, and of $(x+2\theta_v)$ interstitial atoms per mol. Similarly, the energy of the gas phase deviates from the stoichiometric value because the phase contains y_1 moles of UO, and $(x+y_1)$ moles of UO_3.

As far as the gas phase is concerned, the present model gives the specific volume, and the O/M ratio; however, it does not give directly the composition in terms of the fractions of UO, UO_2, and UO_3. However, eq. (29) suggests the following interpretation: There are two kinds of oxygen vacancies in the liquid, with different energies of formation; one is included in the solidlike PF, the other one in the gas PF. In the gas phase, i.e. for $V = V_{gas}$, they manifest themselves through the presence of UO(g), instead of UO_2(g). Thus, the fraction of UO(g) in the vapor phase is given by

$$2\theta_v\frac{V_s}{V} + y_1\frac{V-V_s}{V}$$

Similarly, the fraction of $UO_3(g)$ is

$$(x+2\theta_v)\frac{v_s}{v} + (x+y_1)\frac{v-v_s}{v}$$

These expressions hold in the "real gas" case, where the first terms are not negligible. Far away from the critical temperature (in practice up to ∿5000 K), where V_g is much larger than V_s, and the gas behaves ideally, the fractions are those given by the gaslike partition function.

It must be pointed out that eq. (29), and the interpretation concerning the gas composition, results quite naturally from the way Eyring's model is built. According to the idea that the PF is composed of a "solidlike" and a "gaslike" component, it is obvious that there is a contribution from each component, to an extensive thermodynamic quantity, like the internal energy.

2.3.2 The Dependence of the Pressure on Temperature and Chemical Potential

Assume that the thermodynamic potential $J(T,V,\mu_o)$ is given, and the attention is focussed on the liquid-gas coexistence region. Then, the independent variables are T, and the oxygen chemical potential μ_o. It is instructive to write down the p-T relation (the appropriate form of the Clausius-Clapeyron equation), and the dependence of p on μ_o. Note that the following equations are thermodynamic relations, which are independent of Eyring's model.

Assuming constant μ_o, one finds easily the following modified Clausius-Clapeyron equation

$$\left(\frac{dp_{sat}}{dT}\right)_{\mu_o} = \frac{Q-\mu_o(x_g-x_\ell)}{T(v_g-v_\ell)} \qquad (30)$$

Also, from straight-forward thermodynamics

$$\left(\frac{dp_{sat}}{d\mu_o}\right)_T = \frac{x_g - x_l}{v_g - v_l} \quad (31)$$

In the hyperstoichiometric case, there is always $x_g > x_l$. Thus, an increase in the oxygen chemical potential leads always to an increase in pressure (via increasing UO_3 density).

The oxygen chemical potential μ_o determines the pressure of atomic oxygen, p_o, through the equation

$$RT \ln p_o = \mu_o + T(fef) - (H^0_{298} - H^0_0)$$

where fef is the free energy function. It is tabulated e.g. by Stull and Sinke /10/, up to 3000 K. For a monatomic gas, the data can be safely extrapolated to higher temperatures, assuming $C_p = 5/2$ R. At the temperatures of interest, the pressure p_{O_2} of molecular oxygen is always a lot lower than p_o, and can be neglected in first approximation. Therefore, no values for the oxygen potential will be quoted in this paper. If desired, it can be estimated from the relation

$$\ln p_{O_2} = 2 \ln p_o + \frac{2\Delta G_f(0)}{RT}$$

where $\Delta G_f(0) = 256.803 - 67.562 \times 10^{-3} T$ (kJ/mol), from the JANAF Table /11/. However, one should be aware that an extrapolation of a linear fit is valid only over a limited temperature range.

3. Method of Solution

3.1 Comments on the Selection of the Model Parameters

The SST model involves several parameters, which were determined by Eyring, for simple liquids, from basic physics considerations /1/. For the UO_2 molecule, these parameters must be adjusted to reproduce certain thermodynamic quantities. The following conditions were used to determine the parameters for the calculations in this paper:

First, the triple point (assumed to be at 3120 K), is defined by the condition that the three values of J(V), corresponding to the solid, liquid, and gas volume, are all on the same straight line. Second, the liquid specific volume at the triple point is given by the experiment, as $V_l = 30.87$ cm^3/mol. These two conditions can be fulfilled by adjusting the parameters a and γ in eq. (7). Third, an effective Einstein temperature is used in eq. (7), to reproduce the partial pressure of UO_2 at 3120 K. The value of the partial pressure is obtained by extrapolating the Ackermann-Rand vapor pressure (see Section 4.1) at 2150 K to the triple point. The extrapolated value depends, of course, on the gas partition function used. Fourth, the binding energy E_s of the model is adjusted to obtain a consistent vapor pressure slope at the triple point. In other words, the heat of evaporation, H_g-H_l, at $T = 3120$ K must be consistent with the data used for vapor pressure over the solid material, and the heat of fusion.

3.2 Numerical Methods

The double tangent on the curve J(V), which defines the liquid and the vapor volumes, V_l and V_g, is obtained by an iterative procedure. Clearly, for any given temperature T_n below the critical temperature T_c, the curve J(V) has two inflection points. These points are obtained first, from the condition $\partial^2 J/\partial V^2 = 0$. The liquid volume then lies between V_l at the previous temperature, T_{n-1}, and the lower inflection point. Similarly, the vapor volume is between the upper inflection point, and V_g at T_{n-1}. The true values are then found by a successive interval bisection procedure.

To obtain J(V), observe that the non-stoichiometric part is a function of x (24), which in turn is an implicit function of V through the relation (27). To solve for x, a table V(x) is first prepared, for each temperature. This is straightforward because eq. (27) can be solved explicitly for V, if x is given. For the above mentioned iterative procedure, x is then found, for a given V, by interpolating between tabulated values.

4. Calculations and Results with Two Different Data Sets

4.1 Selection of the Input Data

In this section, results obtained with two different data sets will be presented. Both cases are consistent with the "international average" vapor pressure at 2150 K, as proposed by Ackermann, Rand et al. in 1979 /12/; the value is 1.29×10^{-6} at. In the first data set, electronic excitation of the gas species is described by a constant level density, of a magnitude which is compatible with observed level densities. As is well known /13,14/ this leads to a rather low vapor pressure, in the order of 1.5 - 2.0 Mpa, at 5000 K. In the second data set, a strongly increasing density of electronic excitation levels for the gaseous species was assumed, as originally suggested by Rand /12/, and worked out by the Los Alamos group /15/. These data lead to a vapor pressure curve which is compatible with most earlier evaluations, e.g. the classical vapor pressure curve by Menzies /16/, and the curve proposed by the International Working Group on Fast Reactors (IWGFR) at Harwell in 1978 /17/. The purpose of the present paper is to propose a theoretical framework which can, within certain limits, be used with any reasonable material data. Moreover, it can be modified easily for other non-congruently evaporating materials, besides urania. An extension to $(U,Pu)O_2$ is planned.

It is known that there is a disparity between different vapor pressure data over liquid UO_2 /13,14/. However, considering that the purpose of this paper is to present the extended model, it is not intended to discuss uncertainties in vapor pressure data. Besides, a new series of vapor pressure measurements was carried out by the in-pile technique in the ACRR reactor at Sandia National Laboratories. However, at this time, the data evaluation is still in progress, and only the results of the first experiment in the whole series are available /18/. As soon as the complete data become available, a re-consideration of UO_2 thermodynamic data will be necessary.

It will turn out that the first of the above mentioned data sets is about compatible with the recent evaluation by Long /13/, whereas the second one is consistent with the IWGFR recommendation /17/, and earlier SST evaluation /3/.

The input data for the two cases are gathered in Tables I - III. The model parameters in Table I were discussed in Section 3.1, and no further comments are necessary. The energies for formation of an oxygen vacancy, ε_v, and interstitial, ε_i, are essentially those of Thorn and Winslow /7/, except that ε_v was slightly reduced, to produce an oxygen potential at the melting point which is compatible with other evaluations / 8,13 /. The molecular parameters in Table II are those suggested by the Argonne group /19/, with the following exceptions:

Unlike the measured stretching frequencies ν_1 and ν_3 of the UO_2 molecule, the bending frequency ν_2 was estimated from theoretical considerations, and is, therefore, uncertain. In our evaluation, this quantity was considered as a free parameter /14/, to adjust the entropy of $UO_2(g)$ at 2150 K to obtain agreement with the vapor pressure suggested in /12/. In addition, the enthalpy of formation of UO_3, eq. (20), was adjusted so that the gas composition, for a given oxygen potential, agrees with Blackburn's data /8/ and with the data used by Long /13/, at the melting point. The values used are somewhat lower than the one suggested in /19/, which is 594 kJ/mol.

The electronic PF's for the two cases are rather different. In Case 1, electronic excitation is treated approximately by assuming a constant level density, as suggested in /3/. The chosen density, 0.303×10^{-3} mol/J above the energy 33.49 kJ/mol, and the ground state multiplicity 3 can be considered as "normal" data. Contrary to this, a high and strongly increasing density of (unobserved) electronic levels, of the type suggested by the Los Alamos Group /15/, was assumed in Case 2. It is felt that the data can be better characterized by tabulating enthalpy and entropy of gaseous UO_2 (Table III), rather than by quoting a distribution of the electronic levels. The same electronic PF was used for all three gaseous species. In view of the existing uncertainties, and of the relative importance of the species UO and UO_3, this is probably an acceptable assumption.

4.2 Results and Discussion

In this section, the results for both cases will be presented. Table IV shows the important thermodynamic data at the melting point, and the predicted critical data for stoichiometric material, for both cases. Note that the model parameters were adjusted to reproduce the experimental value of the molar volume, V_1, and the vapor pressure p_{UO_2}, as obtained by extrapolating the Ackermann-Rand data /12/ to the melting point. The values predicted by the model for C_p and the heat of fusion are well compatible with the available experimental data, C_p = 136 J/mol-K /20/, and ΔH_f = 74.1 kJ/mol /20/. The agreement in C_p may be fortuitous because SST predicts a rather low value for the isothermal compressibility, $\beta = 1.46\times10^{-12}$ cm^2/dyn, which leads to a large C_p through the equation /3/

$$C_p = C_v + \frac{\alpha^2 T v}{\beta}$$

The oxygen pressure, P_{O_2}, is compatible with the evaluations by Long et al. /13/, and by Bober et al. /21/; however, it is lower than the one used by Green and Leibowitz /9/.

Table V shows the partial vapor pressures as a function of x_1, for three different temperatures, as calculated for Case 1. Note that at 5000 K, the pressure of the U-bearing species is 2.19 Mpa (for stoichiometric material), which is a lot lower than the IWGFR curve, but somewhat higher than Long et al. /13/. On the other hand, the pressure at 7500 K (35.7 Mpa) is well compatible with Long. Note that a critical temperature, T_c, of 12900 K is calculated in this case. This is far above most earlier predictions, which are generally in the range 7000 - 9000 K /3/. Of course, there is a large uncertainty in such a prediction and the present model, which neglects phenomena like ionization and dissociation in the gaseous PF, is certainly not adequate. However, the rather low vapor pressure at 7500 K, and the associated low vapor density of only 0.18 g/cm^3 (about one tenth of the critical density) indicate that the critical temperature must be substantially higher than 7500 K. Therefore, if a low vapor pressure curve is realistic, a major revision of the critical data accepted so far is necessary.

For variable O/M, one obtains a critical line, rather than a critical point, because T_c becomes a function of O/M, or of μ_o. As is obvious from eq. (29), the vapor pressure, and thus the vapor density increases with increasing μ_o; therefore, the critical temperature decreases. This is indeed predicted by the model, as shown in Fig. 1.

The partial vapor pressures calculated for Case 2 are shown in Table VI, again for three different temperatures. They are compatible with the IWGFR curve. The critical temperature, 7900 K (Table IV), is in the range of earlier predictions /3/. The critical line is shown in Fig. 2. It is obvious from the model that $x_g = x_l$ at the critical line. To demonstrate how x_g and x_l converge, O/M is shown as a function of μ_o in the vicinity of the critical line in Fig. 3.

List of Symbols

a	parameter of the SST model, eq.(7) also, Z_1Z_3/Z_2^2 , eq.(25)
F	Helmholtz free energy (J/mol)
f_g	partition function (PF) for gaslike molecules
$f_g(st)$	gaslike PF for stoichiometric UO_2
f_s	solidlike PF
$f_{s(st)}$	solidlike PF for stoichiometric UO_2
f_{el}	electronic PF
GPF	grand PF
J	thermodynamic potential, eq.(3) (J/mol)
k	Boltzmann's constant (J/K)
$K_{1,2,3}$	lumped constant for gas PF, eq.(16)
n	parameter of the SST model, eq.(7)
N	number of U atoms/mol (= Avogadro's number)
N_o	number of O atoms/mol
$N_{1,2,3}$	i=1,2,3 number of UO_i gas atoms/mol
$N_p=N_o - N = x\cdot N$	number of excess oxygen atoms
N_i	number of oxygen interstitials/mol

N_v	number of oxygen vacancies/mol
$q_{i,v}$	PF for extra vibrational modes associated with oxygen intenstitials/ vacancies
Q	enthalpy of vaporisation (J/mol)
S	molar entropy (J/mol-K)
T	absolute temperature (K)
U	molar internal energy (J/mol)
V	molar volume (cm^3/mol)
$V_{s,l,g}$	molar volume of solid/liquid/gaseous $UO_{2\pm x}$ (cm^3/mol)
$x = O/M-2$	
$x_{l,g}$	O/M-2 for liquid/gaseous $UO_{2\pm x}$
$y_{1,2,3}$	mol fractions of gaseous $UO/UO_2/UO_3$
$Z_{1,2,3}$	PF for gaseous $UO/UO_2/UO_3$
Z_{gas}	PF for gaseous mixture
$Z_{s(ns)}$	non-stoichiometric part of the solidlike PF, eq.(12)
Zst	PF for stoichiometric UO_2
Z_{def}	PF for oxygen defects
Zgm	PF the gas mixture $UO+UO_2+UO_3$
$\Delta H_{1,3}$	enthalpy of formation of UO/UO_3 from $UO_2 \pm O$ at OK (J/mol)
ΔH_g	enthalpy of fusion (J/mol)

γ	parameter of the SST model, eq.(7)
ε_i	energy to remove an oxygen interstitial atom to infinity (J/mol)
ε_v	energy to remove an oxygen lattice atom to infinity (J/mol)
μ_o	chemical potential of monatomic oxygen (J/mol)
$\mu_{1,2,3}$	chemical potential of gaseous $UO/UO_2/UO_3$
$\theta_i = N_i/N$	fraction of oxygen interstitials
$\theta_v = N_v/2N$	fraction of oxygen vacancies
θ_E	effective Einstein temperature of solid UO_2
$\vartheta_{i,v}$	oscillator temperature for extra vibrational modes associated with interstitials/vacancies

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Table I : Input Parameters for SST: Data for the Solidlike Partition Function

	Case 1	Case 2
E_s (kJ/mol)	530.4	548.4
V_s (cm^3)	27.9	27.9
n	10.5	10.5
a	0.00472	0.00475
γ	-0.294	-0.294
ε_v (kJ/mol)	732.5	816.3
ε_i (kJ/mol)	393.3	393.3
θ_E (K)	170.27	173.04

Table II : Input Parameters for SST: Data for the Gaslike Partition Function

	UO	UO_2	UO_3
Bond length (nm)	0.1764	0.179	
Moment of inertia	7.74×10^{-39} gcm^2	1.702×10^{-37} gcm^2	1.806×10^{-57} g$^{3/2}$cm^3
Vibrational frequencies (cm^{-1}) (degeneracy)	825(1)	765(1) 91(2) (Case 1) 190(2) (Case 2) 776.1	843.5(1) 745.6(1) 852.6(1) 180 (1) 150 (1) 130 (1)
Rotational degeneracy, σ	1	2	1
ΔH_i (kJ/mol) (eq. 20)	725.0	0	514.9 (Case 1) 552.5 (Case 2)
Lumped constant K_i	1.889	2.071	3.252

Table III : Enthalpy and Entropy Incrementa for UO_2 Gas

T (K)	no electronic contribution	Case 1		Case 2	
	$H-H_{298}$	$H-H_{298}$	S	$H-H_{298}$	S
2150	126.6	134.66	401.88	126.58	402.07
3120	171.5	212.20	431.74	243.28	446.06
4000	226.3	278.86	450.54	379.77	484.66
5000	288.6	352.41	466.99	502.86	512.3
7500	444.5	532.42	496.17	702.18	548.16
10000		710.53	516.68		

$H-H_{298}$ is in kJ/mol, S is in J/molK

Table IV : Results: Thermodynamics Data at the Melting Point ($T = 3120$ K), and Critical Data

		Case 1	Case 2
Melting Point:			
molar Volume, V_ℓ (cm^3/mol)		30.875	30.875
Cp (J/mol K)		127.7	139.6
Heat of Fusion (kJ/mol)		74.4	77.2
For x_ℓ=0:			
P_{UO}	(Mpa)	3.1×10^{-5}	9.0×10^{-6}
P_{UO_2}	(Mpa)	2.75×10^{-3}	3.35×10^{-3}
P_{UO_3}	(Mpa)	1.52×10^{-3}	1.77×10^{-3}
P_O	(Mpa)	8.5×10^{-5}	8.5×10^{-5}
P_{O_2}	(Mpa)	2.53×10^{-6}	2.53×10^{-6}
μ_O	(kJ/mol)	774.4	774.4
Critical Data (x=0):			
T_c	(K)	12900	7900
p_c	(Mpa)	212	178
V_c	(cm^3/mol)	158	127
μ_{Oc}	(kJ/mol)	1899	1287

Table V: Partial Pressures (MPa) over UO_{2+x} (Case 1)

x_ℓ	x_g	P_{UO}	P_{UO_2}	P_{UO_3}	$P_{U_{tot}}$	P_O	μ_o (J/mol)
TEMP= 5000.0 K							
0.002	0.341	1.5141E-01	1.1448E+00	8.9933E-01	2.1955E+00	2.3290E-01	-9.6170E+05
0.005	0.351	1.4722E-01	1.1449E+00	9.2498E-01	2.2171E+00	2.3953E-01	-9.6053E+05
0.010	0.368	1.4051E-01	1.1449E+00	9.6917E-01	2.2546E+00	2.5100E-01	-9.5858E+05
0.015	0.384	1.3411E-01	1.1447E+00	1.0151E+00	2.2939E+00	2.6297E-01	-9.5664E+05
0.020	0.400	1.2802E-01	1.1442E+00	1.0626E+00	2.3348E+00	2.7544E-01	-9.5472E+05
0.030	0.432	1.1674E-01	1.1425E+00	1.1622E+00	2.4214E+00	3.0178E-01	-9.5093E+05
0.040	0.462	1.0659E-01	1.1399E+00	1.2672E+00	2.5137E+00	3.2987E-01	-9.4723E+05
0.060	0.517	8.9432E-02	1.1324E+00	1.4905E+00	2.7123E+00	3.9074E-01	-9.4017E+05
0.080	0.564	7.5985E-02	1.1224E+00	1.7264E+00	2.9248E+00	4.5692E-01	-9.3371E+05
0.100	0.602	6.5705E-02	1.1106E+00	1.9690E+00	3.1453E+00	5.2726E-01	-9.2802E+05
TEMP= 7500.0 K							
0.002	0.179	7.2735E+00	1.4701E+01	1.3662E+01	3.5636E+01	1.8286E+01	-1.2342E+06
0.005	0.184	7.2170E+00	1.4706E+01	1.3777E+01	3.5700E+01	1.8438E+01	-1.2337E+06
0.010	0.191	7.1235E+00	1.4713E+01	1.3971E+01	3.5807E+01	1.8695E+01	-1.2329E+06
0.015	0.199	7.0307E+00	1.4719E+01	1.4167E+01	3.5916E+01	1.8955E+01	-1.2320E+06
0.020	0.206	6.9386E+00	1.4724E+01	1.4365E+01	3.6028E+01	1.9219E+01	-1.2311E+06
0.030	0.221	6.7569E+00	1.4731E+01	1.4768E+01	3.6256E+01	1.9758E+01	-1.2294E+06
0.040	0.236	6.5783E+00	1.4736E+01	1.5179E+01	3.6493E+01	2.0314E+01	-1.2277E+06
0.060	0.265	6.2305E+00	1.4734E+01	1.6025E+01	3.6990E+01	2.1473E+01	-1.2242E+06
0.080	0.293	5.8954E+00	1.4718E+01	1.6904E+01	3.7517E+01	2.2699E+01	-1.2208E+06
0.100	0.321	5.5730E+00	1.4688E+01	1.7813E+01	3.8074E+01	2.3996E+01	-1.2173E+06
TEMP=10000.0 K							
0.002	0.065	3.2914E+01	3.7765E+01	4.0153E+01	1.1083E+02	1.7015E+02	-1.5205E+06
0.005	0.069	3.2751E+01	3.7776E+01	4.0374E+01	1.1090E+02	1.7108E+02	-1.5201E+06
0.010	0.074	3.2481E+01	3.7792E+01	4.0745E+01	1.1102E+02	1.7262E+02	-1.5193E+06
0.015	0.080	3.2211E+01	3.7806E+01	4.1118E+01	1.1114E+02	1.7419E+02	-1.5186E+06
0.020	0.086	3.1942E+01	3.7819E+01	4.1493E+01	1.1125E+02	1.7577E+02	-1.5178E+06
0.030	0.097	3.1407E+01	3.7841E+01	4.2249E+01	1.1150E+02	1.7897E+02	-1.5163E+06
0.040	0.109	3.0875E+01	3.7857E+01	4.3014E+01	1.1175E+02	1.8225E+02	-1.5148E+06
0.060	0.131	2.9821E+01	3.7872E+01	4.4570E+01	1.1226E+02	1.8900E+02	-1.5118E+06
0.080	0.154	2.8782E+01	3.7864E+01	4.6160E+01	1.1281E+02	1.9603E+02	-1.5087E+06
0.100	0.177	2.7758E+01	3.7832E+01	4.7784E+01	1.1338E+02	2.0336E+02	-1.5057E+06

Table VI : Partial Pressures (MPa) over UO_{2+x} (Case 2)

x_ℓ	x_g	P_{UO}	P_{UO2}	P_{UO3}	P_{Utot}	P_O	μ_o (J/mol)
TEMP= 4000.0 K							
0.002	0.376	1.8312E-03	2.1031E-01	1.3068E-01	3.4282E-01	1.1432E-02	-8.5087E+05
0.005	0.389	1.7332E-03	2.1029E-01	1.3804E-01	3.5006E-01	1.2077E-02	-8.4904E+05
0.010	0.412	1.5818E-03	2.1018E-01	1.5109E-01	3.6285E-01	1.3227E-02	-8.4601E+05
0.015	0.435	1.4451E-03	2.0998E-01	1.6507E-01	3.7649E-01	1.4466E-02	-8.4303E+05
0.020	0.457	1.3224E-03	2.0969E-01	1.7991E-01	3.9093E-01	1.5788E-02	-8.4012E+05
0.030	0.499	1.1146E-03	2.0890E-01	2.1178E-01	4.2180E-01	1.8658E-02	-8.3457E+05
0.040	0.539	9.5129E-04	2.0786E-01	2.4592E-01	4.5473E-01	2.1776E-02	-8.2942E+05
0.060	0.604	7.3344E-04	2.0536E-01	3.1796E-01	5.2405E-01	2.8512E-02	-8.2054E+05
0.080	0.648	6.1899E-04	2.0281E-01	3.8997E-01	5.9340E-01	3.5509E-02	-8.1381E+05
0.100	0.662	5.5808E-04	2.0086E-01	4.5586E-01	6.5729E-01	4.2281E-02	-8.0961E+05
TEMP= 5000.0 K							
0.002	0.358	8.7691E-02	3.8825E+00	2.3508E+00	6.3210E+00	3.2338E-01	-9.4805E+05
0.005	0.363	8.6184E-02	3.8834E+00	2.3929E+00	6.3625E+00	3.2912E-01	-9.4732E+05
0.010	0.370	8.3720E-02	3.8845E+00	2.4647E+00	6.4330E+00	3.3894E-01	-9.4610E+05
0.015	0.378	8.1316E-02	3.8851E+00	2.5384E+00	6.5048E+00	3.4907E-01	-9.4487E+05
0.020	0.385	7.8972E-02	3.8852E+00	2.6140E+00	6.5781E+00	3.5951E-01	-9.4364E+05
0.030	0.401	7.4464E-02	3.8837E+00	2.7705E+00	6.7287E+00	3.8130E-01	-9.4120E+05
0.040	0.416	7.0194E-02	3.8801E+00	2.9341E+00	6.8845E+00	4.0431E-01	-9.3876E+05
0.060	0.446	6.2365E-02	3.8669E+00	3.2810E+00	7.2103E+00	4.5395E-01	-9.3394E+05
0.080	0.476	5.5435E-02	3.8459E+00	3.6527E+00	7.5540E+00	5.0848E-01	-9.2923E+05
0.100	0.505	4.9328E-02	3.8179E+00	4.0470E+00	7.9142E+00	5.6791E-01	-9.2463E+05
TEMP= 6000.0 K							
0.002	0.306	1.0784E+00	2.2851E+01	1.2094E+01	3.6023E+01	2.7404E+00	-1.0540E+06
0.005	0.308	1.0686E+00	2.2866E+01	1.2221E+01	3.6156E+01	2.7683E+00	-1.0535E+06
0.010	0.313	1.0524E+00	2.2891E+01	1.2436E+01	3.6380E+01	2.8154E+00	-1.0526E+06
0.015	0.317	1.0364E+00	2.2913E+01	1.2655E+01	3.6604E+01	2.8633E+00	-1.0518E+06
0.020	0.322	1.0205E+00	2.2934E+01	1.2876E+01	3.6830E+01	2.9119E+00	-1.0510E+06
0.030	0.331	9.8921E-01	2.2971E+01	1.3328E+01	3.7287E+01	3.0115E+00	-1.0493E+06
0.040	0.340	9.5861E-01	2.3000E+01	1.3791E+01	3.7750E+01	3.1144E+00	-1.0476E+06
0.060	0.358	8.9946E-01	2.3038E+01	1.4755E+01	3.8693E+01	3.3303E+00	-1.0443E+06
0.080	0.376	8.4309E-01	2.3049E+01	1.5764E+01	3.9656E+01	3.5608E+00	-1.0409E+06
0.100	0.394	7.8959E-01	2.3032E+01	1.6817E+01	4.0639E+01	3.8064E+00	-1.0376E+06

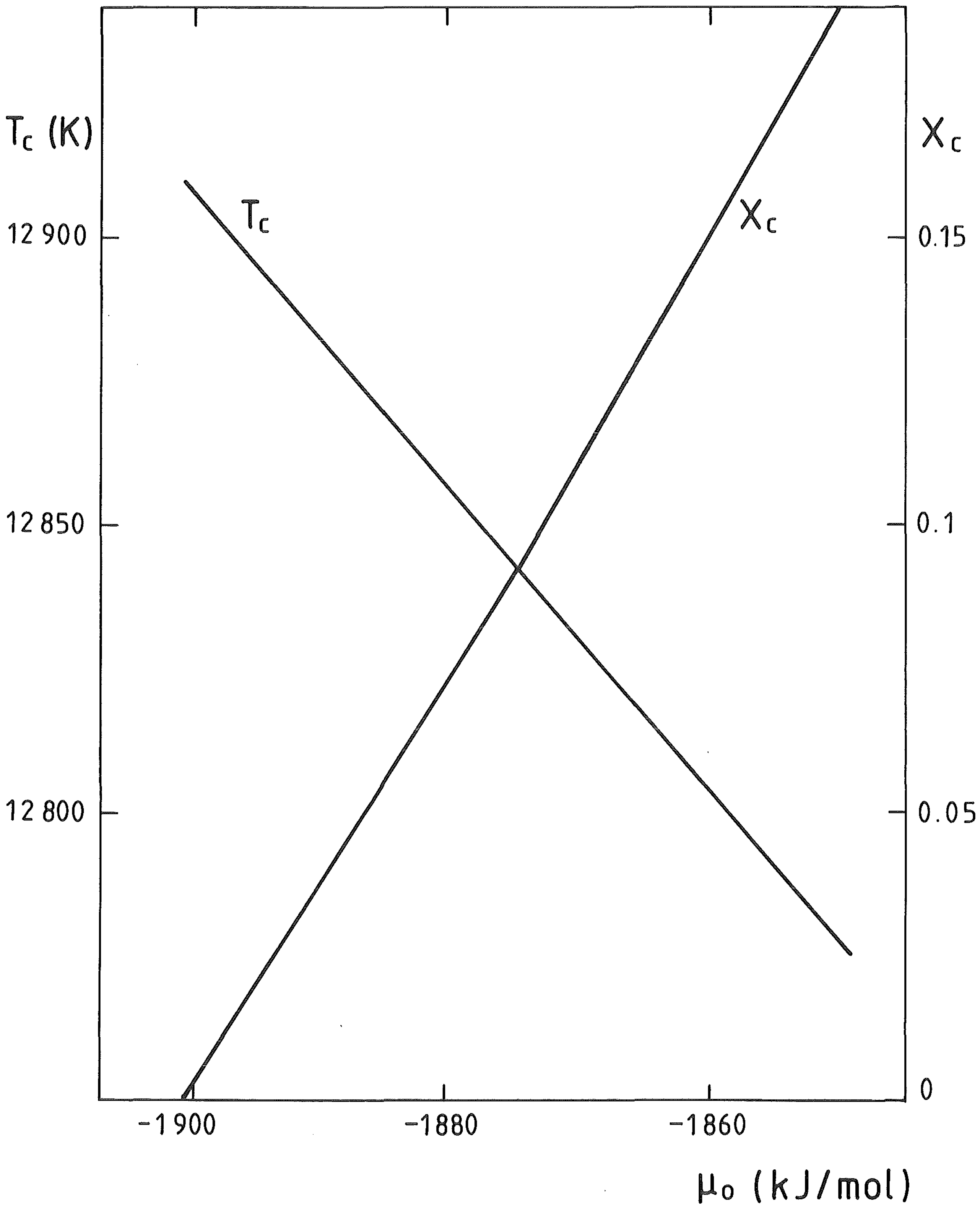

Fig. 1 Critical Line, Case 1

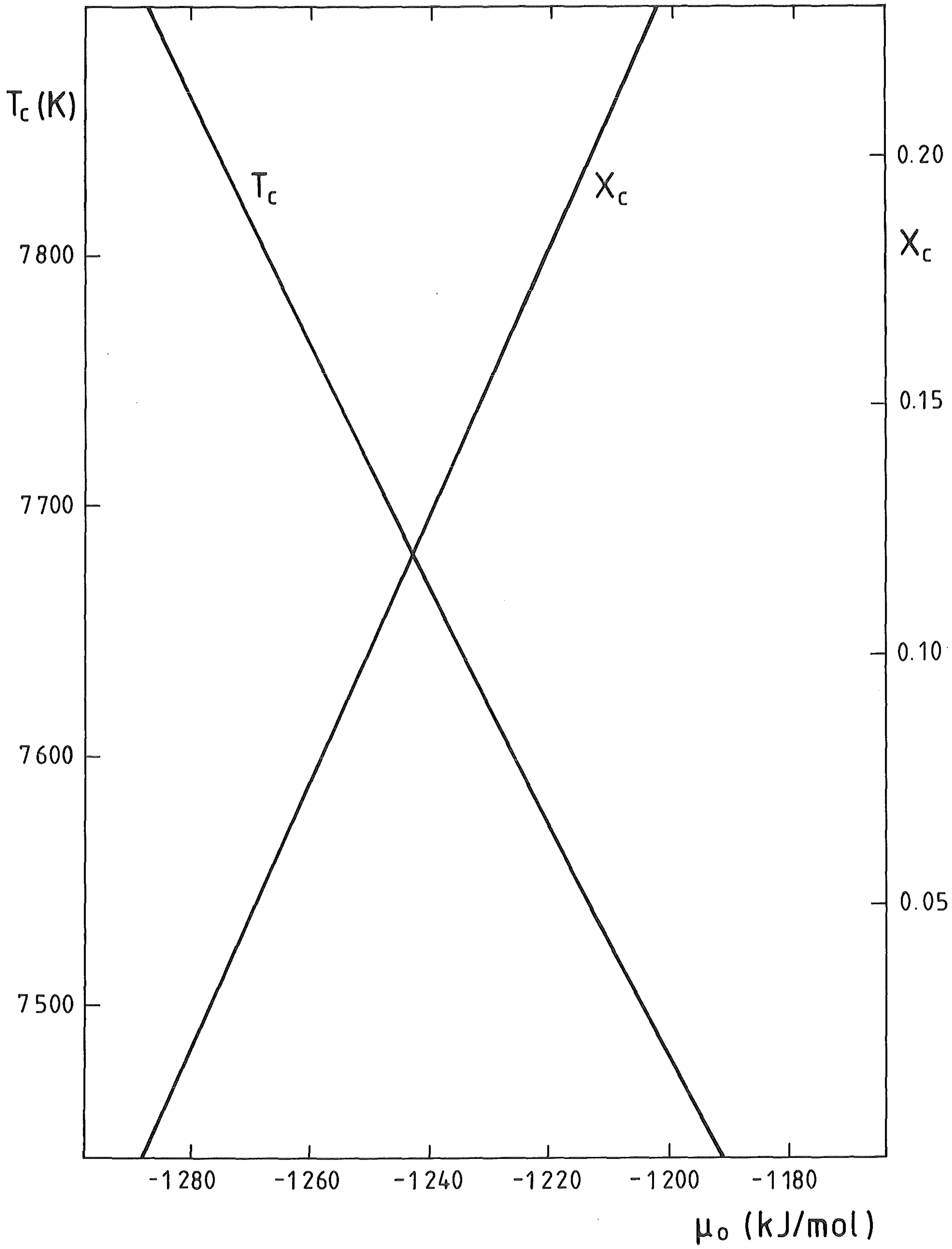

Fig. 2 Critical Line, Case 2

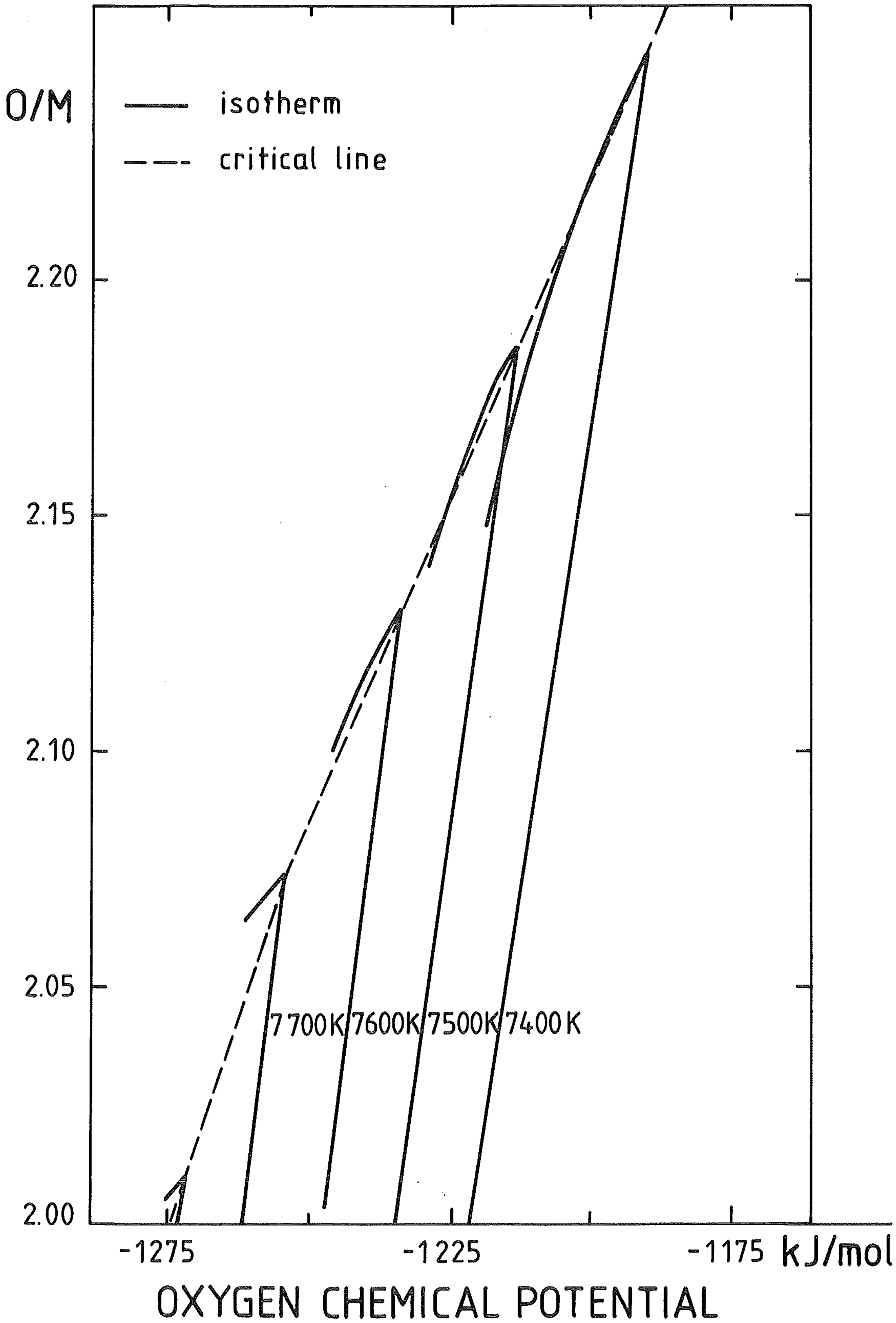

Fig. 3 O/M in the Vicinity of the Critical Line, Case 2