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**CALCULATION OF THE THERMODYNAMIC PROPERTIES
OF FUEL-VAPOR SPECIES
FROM SPECTROSCOPIC DATA**

MASTER

by

David W. Green

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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David W. Green

Chemical Engineering Division

September 1980

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ABSTRACT

Measured spectroscopic data, estimated molecular parameters, and a density-of-states model for electronic structure have been used to calculate thermodynamic functions for gaseous ThO , ThO_2 , UO , UO_2 , UO_3 , PuO , and PuO_2 . Various methods for estimating parameters have been considered and numerically evaluated. The sensitivity of the calculated thermodynamic functions to molecular parameters has been examined quantitatively. New values of the standard enthalpies of formation at 298.15 K have been derived from the best available ΔG_f° equations and the calculated thermodynamic functions. Estimates of the uncertainties have been made for measured and estimated data as well as for various mathematical and physical approximations. Tables of the thermodynamic functions to 6000 K are recommended for gaseous thorium, uranium, and plutonium oxides.

I. INTRODUCTION

Thermodynamic functions of fuel-vapor species may be calculated from spectroscopic data on internal molecular energy levels. The thermodynamic functions obtained by this method are generally more reliable for vapor-pressure calculations at high temperatures than functions obtained either by extrapolation of lower-temperature data or by experimental methods that have not been calibrated (*i.e.*, when the accuracy of the method has not been demonstrated). Thus, these calculated functions are useful for the analysis of hypothetical reactor accidents. Experimental spectroscopic data are available for uranium, plutonium, and thorium oxides and nitrides. However, because the data are incomplete in every case, estimates are required for missing spectroscopic data and molecular parameters.

Figure 1 outlines the steps necessary for the calculation of vapor pressures. The steps leading to gas-phase thermodynamic functions must be

Fig. 1

A Scheme to Calculate
Vapor Pressures from
Spectroscopic Data

followed for each important vapor species. The condensed-phase data must be known as a function of composition, and both the condensed-phase and gas-phase data must be known as functions of temperature.

The internal molecular partition function Q_{int} (separating out the translational contribution) may be factored into vibrational, rotational, and electronic parts, provided the internal molecular energy levels may be considered separately; i.e.,

$$Q_{int} = Q_{vib} \cdot Q_{rot} \cdot Q_{el} \quad (1)$$

The validity of the approximation in Eq. (1) will be considered further; however, let us take this to be a sufficient first approximation at this point.

It is convenient for the calculation of thermodynamic functions to define the following:¹

$$Q = \sum_i g_i \cdot \exp(-\epsilon_i/kT) \quad (2)$$

$$Q' = \sum_i g_i \cdot \left(\frac{\epsilon_i}{kT}\right) \cdot \exp(-\epsilon_i/kT) = T \frac{dQ}{dT} \quad (3)$$

$$Q'' = \sum_i g_i \cdot \left(\frac{\epsilon_i}{kT}\right)^2 \cdot \exp(-\epsilon_i/kT) = T^2 \frac{d^2Q}{dT^2} + 2T \frac{dQ}{dT} \quad (4)$$

Here Q represents the total internal partition function or any one of the contributions to it that are given in Eq. (1); ϵ_i represents the corresponding set of internal molecular energy levels; and g_i is the degeneracy of the state with energy ϵ_i . With these definitions, we can calculate the contribution of vibrational states, rotational states, or electronic states to each of the following thermodynamic functions:

$$C^o = R \left[\frac{Q''}{Q} - \left(\frac{Q'}{Q} \right)^2 \right] \quad (5)$$

$$[E^o - E^o(0 K)] = RT(Q'/Q) = [H - H(0 K)] \quad (6)$$

$$S^o = R[\ln Q + (Q'/Q)] \quad (7)$$

$$-[G^o - H^o(0 K)]/T = R \ln Q \quad (8)$$

(In these equations, the symbols have their usual thermodynamic meaning.)

The free-energy function, $f_{ef} \equiv -[G^0 - H^0(0\text{ K})]/T$ has been chosen as a representative thermodynamic function to evaluate the effects of assumptions, approximations, and estimates in the molecular energy-level expressions (the set of ϵ_i). This choice is made because the free-energy function is most directly related to the vapor pressure. It is the absolute error in the free-energy function of the gaseous species [$f_{ef}(g)$] that determines the uncertainty in vapor pressure [$\delta \ln p \propto \delta f_{ef}(g)$].

The various contributions to the total free-energy function are additive, provided that Eqs. (1) and (8) are valid; thus, we may speak of a "vibrational contribution," for example. Therefore, it follows that a large percentage uncertainty in the vibrational contributions to the calculated f_{ef} , for example, may be less important than a smaller percentage uncertainty in the rotational contribution. These questions will be examined quantitatively for the vapor species of uranium, plutonium, and thorium oxide.

The development of the recommended thermodynamic functions is done in a manner that will accommodate future revision. Thus, revision of one part of the calculation should be easily accomplished when new data become available. Furthermore, different judgments, estimates, or models for one molecular parameter can be incorporated into the calculations without destroying the usefulness of the remainder of the calculations.

It is useful to point out at the beginning several characteristics of the molecules of interest as well as the requirements and goals of the calculations. The combination of these characteristics and requirements has provided the basis for many of the choices that were made about different methods.

1. The dissociation energies are relatively high for the oxides of thorium, uranium, and plutonium.
2. The electronic contribution to the calculated thermodynamic functions can be relatively large.
3. The maximum temperature to be considered is 6000 K because this is often the highest temperature of interest in reactor safety analysis.
4. The primary goal of these calculations is accuracy in vapor pressures at high temperatures.
5. Upper and lower limits on the calculated vapor pressures are useful to define the uncertainties introduced by vapor pressure in the analysis of hypothetical reactor accidents.
6. The combination of the temperature range of interest and the molecular energy levels of the molecules of interest make some of the models used of limited general applicability.

The goals of this report are: (1) to provide a consistent "best estimate" of the thermodynamic functions of gaseous thorium, uranium, and plutonium oxides; (2) to provide sufficient discussion of the methods used so that future improvements in data can be conveniently incorporated; and (3) to estimate the uncertainties in various contributions to the total calculated thermodynamic functions.

II. TRANSLATIONAL CONTRIBUTION

The translational contribution to each calculated thermodynamic function depends upon the molecular weight of the species and the temperature. The formulas are available in many places¹ and are given below:

$$S_{\text{trans}}^{\circ} = R[1.5 \ln(M) + 2.5 \ln(T)] - 9.686 \quad (9)$$

$$\begin{aligned} f_{\text{trans}} &= R[1.5 \ln(M) + 2.5 \ln(T)] - 30.472 \\ &= S^{\circ} - C_p^{\circ} \end{aligned} \quad (10)$$

$$[H^{\circ} - H^{\circ}(0 \text{ K})]_{\text{trans}} = 2.5RT \quad (11)$$

$$C_p^{\circ} = 2.5R \quad (12)$$

In these equations, S° , f_{trans} , C_p° , and R are given in units of $\text{J mol}^{-1} \text{K}^{-1}$; $[H^{\circ} - H^{\circ}(0 \text{ K})]$ is in J mol^{-1} , molecular weight M is in amu; and T is in K. The value of R is $8.3144 \text{ J mol}^{-1} \text{K}^{-1}$.

If we use calories instead of joules, $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ and the constants in Eqs. (9) and (10) are -2.315 and -7.283 , respectively.

For all practical considerations, there is no uncertainty in the translational contribution to the calculated thermodynamic functions for $T > 298.15 \text{ K}$.

III. VIBRATIONAL CONTRIBUTION

A. General

Every molecule has $3n - 6$ (or $3n - 5$ if the molecule is linear) vibrational degrees of freedom, where n is the number of atoms in the molecule. For each vibrational degree of freedom there is a vibrational motion (or vibrational mode) with a corresponding frequency of vibration, ν . Generally the wavenumber, ω (or sometimes $\bar{\nu}$), will be used both for a vibrational "frequency" and a vibrational "energy" although it is neither. The energy (E in erg), wavelength (λ in cm), wavenumber (ω in cm^{-1}), frequency (ν in Hz), Planck's constant (h in $\text{erg}\cdot\text{s}$), and the speed of light (c in $\text{cm}\cdot\text{s}^{-1}$) are related as follows:

$$\omega = \nu/c \quad (13)$$

$$E = h\nu \quad (14)$$

$$c = \lambda\nu \quad (15)$$

For each vibrational mode, an energy-level expression or function, $G(\nu)$, is generally written as a power series in the vibrational quantum number, ν , or more precisely in $(\nu + 1/2)$. The total vibrational energy of a molecule is characterized by the set of quantum numbers, ν_i , one per mode.

The case of a diatomic molecule is considered in Section III-B. Anharmonic effects are evaluated in Section III-C and polyatomic molecules are considered in Section III-D. For both diatomic and polyatomic molecules, approximations and estimates are involved so that uncertainties in the calculated thermodynamic functions arise because of uncertainties in both the formulas and the data. These uncertainties are numerically evaluated in Section III-E.

B. Diatomic Molecules--Harmonic Oscillator

The vibrational energy levels in units of cm^{-1} , $G(\nu)$, may be represented by a power series in the quantum number ν of the following form:

$$G(\nu) = \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2 + \dots \quad (16)$$

where ω_e and $\omega_e x_e$ are constants (in cm^{-1}) that are characteristic of the molecule in a particular electronic state. The first term in Eq. (16) is the "harmonic-oscillator" term and the neglect of all other terms is called the "harmonic-oscillator approximation." The sign for the second term is chosen so that $\omega_e x_e$ almost always has a positive value. The inclusion of the $\omega_e x_e$ term is a first-order correction for anharmonicity. Although $\omega_e x_e$ is a single spectroscopic constant, it will be treated, for convenience, as the product of the spectroscopic constant ω_e and a "correction term," x_e , where $x_e \ll 1.0$.

The zero-point energy, $G(0)$, must be subtracted from all vibrational energy levels given by Eq. (16) to obtain the physically accessible states of the molecule. If we let the "frequency" of the vibrational transition (in cm^{-1}) from $v = 0$ to $v = 1$ be called ω_0 , then excluding anharmonicity:

$$\begin{aligned} G_0(v) &= G(v) - G(0) \\ &= \omega_0(v + 1/2) - \omega_0/2 \\ &= \omega_0 v. \end{aligned} \tag{17}$$

The vibrational contribution to the free-energy function, for example, may be calculated from a knowledge of the vibrational partition function,

$$f_{\text{vib}} = R \ln Q_{\text{vib}} \tag{18}$$

where

$$Q_{\text{vib}} = \sum_i \exp(-\epsilon_i/kT) \tag{19}$$

This sum extends over all of the discrete vibrational energy levels, ϵ_i .

For the case of the "harmonic oscillator," Eq. (17), we have the approximation $\epsilon_i = hc G(v)$, and we obtain:

$$Q_{\text{vib}} = \sum_{v=0}^{v_{\text{max}}} \exp(-hc\omega_0 v/kT). \tag{20}$$

where v_{max} is the largest value of v for which the energy is less than dissociation.

We define $u = hc\omega_0/kT = 1.4387\omega_0/T$, for ω_0 in cm^{-1} and T in K. Because the harmonic-oscillator approximation is valid only if the value of u is relatively large (low T or large ω_0), then for all practical cases,

$$\begin{aligned} Q_{\text{vib}} &= \sum_{v=0}^{v_{\text{max}}} \exp(-uv) \\ &= \sum_{v=0}^{\infty} \exp(-uv) \\ &= [1 - \exp(-u)]^{-1} \end{aligned} \tag{21}$$

Thus, from Eq. (18),

$$f_{\text{efvib}} = -R \ln[1 - \exp(-u)]. \quad (22)$$

For very large values of u , e^{-u} is very much less than 1.0; thus, according to Eq. (22), there is no vibrational contribution to the calculated thermodynamic functions. For example, $\omega_0 = 1556 \text{ cm}^{-1}$ for O_2 so that at room temperature (298 K), $u = 7.51$; thus, $\exp(-u) = 5.5 \times 10^{-4}$ and $f_{\text{efvib}} = 0.005 \text{ J K}^{-1} \text{ mol}^{-1}$. This contribution is negligible compared to the translational contribution for O_2 of $131 \text{ J K}^{-1} \text{ mol}^{-1}$. The first range of values in Fig. 2 is that for which the harmonic-oscillator approximation and, thus, Eq. (21) are valid approximations. In another range of values for u --at somewhat higher temperatures or lower frequencies--the first two terms in Eq. (16) give a valid approximation to the energy levels. Finally, at even higher temperatures, Eq. (16) is insufficient, and anharmonic corrections become more complicated. We shall next attempt to better define the range of u values for the molecules of interest for which the harmonic-oscillator approximation is valid and for which the first anharmonic correction is sufficient.

POTENTIAL CURVE	MINIMUM	DEVIATIONS	EXACT
VIBRATIONAL POPULATION	A FEW LEVELS	SEVERAL LEVELS	ALL LEVELS
HARMONIC OSCILLATION APPROX.	GOOD	FAILING	NOT USEFUL
ANHARMONICITY	NOT IMPORTANT	APPROXIMATED	COMPLICATED

Fig. 2

Representation of the Knowledge Required of the Potential Energy Curve, the Vibration Energy Level Population, the Harmonic-oscillator Approximation, and the Vibrational Anharmonicity as a Function of $u = hc\omega_0/kT$

C. Anharmonicity

We shall examine the usefulness and limitations of the first-order correction to the harmonic-oscillator approximation. Let us assume that the first two terms in Eq. (16) give a sufficiently accurate representation of the vibrational energy levels. Then the zero-point energy including anharmonicity is given by:

$$G(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4}. \quad (23)$$

Thus, the vibrational energy levels relative to the $v = 0$ level, $G_0(v)$, are given by:

$$\begin{aligned} G_0(v) &= G(v) - G(0) \\ &= \omega_e v - \omega_e x_e v(v+1) \\ &= \omega_0 v - \omega_0 x v(v-1) \end{aligned} \quad (24)$$

where $\omega_0 = G(1) - G(0)$ as before, $x_0 = \omega_0 x_e / \omega_e \approx \omega_e x_e / \omega_e$, and $x_0 = x_e / (1 - 2x_e) \approx x_e$. Here we treat the $\omega_e x_e$ spectroscopic constant as the product of the harmonic frequency, ω_e , and a correction term, x ($= x_e = x_0$).

This expression for $G_0(v)$ can be used for ϵ_i , in Eq. (19) in a manner similar to that used previously to derive Eq. (20).

$$\begin{aligned}
 Q_{\text{vib}} &= \sum_{v=0}^{v_{\text{max}}} \exp[-hcG_0(v)/kT] \\
 &= \sum_{v=0}^{v_{\text{max}}} \exp\left\{-\frac{hc}{kT} [\omega_0 \cdot v - \omega_0 x v(v-1)]\right\} \\
 &= \sum_{v=0}^{v_{\text{max}}} \exp[-uv + uxv(v-1)] \quad (25)
 \end{aligned}$$

Here, as in the case of the harmonic oscillator, $u = hc\omega_0/kT$.

Now a mathematical difficulty arises that was not present in the case of the harmonic oscillator. Clearly, changing the summation limit from v_{max} (the largest value of v before dissociation) to infinity, analogous to Eq. (21), is not possible because the exponent increases without limit. The following approximation to Eq. (25) is found in several standard texts (although it is generally not derived or proved valid):

$$Q_{\text{vib}} = \sum_{v=0}^{\infty} \exp(-uv) \cdot [1 + uxv(v-1)]. \quad (26)$$

This approximation is useful, as will be shown, because it leads to a separation of the contributions to the free-energy function. One contribution is identical to that obtained from the harmonic-oscillator approximation and the other is a "correction term" attributable to anharmonicity. The approximation given in Eq. (26) is also useful because it leads to a closed-form expression for Q_{vib} . Infinite sums of the form $x^n \exp(-x)$ have closed-form expressions for finite x values, and Eq. (26) is reducible to three sums of this form.

The approximation given in Eq. (26) is valid for this particular application, in part, because x ($= \omega_e x_e / \omega_e$) is always a small number. Now Eq. (26) can be simplified and used to calculate the vibrational contribution to the free-energy function:

$$Q_{\text{vib}} = [1 - \exp(-u)]^{-1} \left\{ 1 + \frac{2ux}{[\exp(u) - 1]^2} \right\}. \quad (27)$$

If we now substitute Eq. (27) into Eq. (18), we obtain two terms for the free-energy function.

$$\begin{aligned} \text{fef}_{\text{vib}} &= R \ln Q_{\text{vib}} \\ &= -R \ln[1 - \exp(-u)] + R \ln \left\{ 1 + \frac{2ux}{[\exp(u) - 1]^2} \right\} \end{aligned} \quad (28)$$

The first term is identical to the harmonic-oscillator contribution given in Eq. (22), and the second term can be identified as the correction term for anharmonicity.

It is particularly important to reactor-safety analysis to examine the limitations of approximations such as Eq. (28), because of the extremes of temperature needed for the analysis of some hypothetical accidents. Attempts to use algebra to find the domain of validity of Eq. (28), in terms of the variables x and u were not successful. Results are shown in Fig. 3 of some numerical evaluations of the vibrational contribution to the free-energy function for a range u and x values. The ordinate is the ratio of the contribution of the first term in Eq. (28), to the total of Eq. (28), and provides a measure of the contribution of vibrational anharmonicity to the free-energy function.

Fig. 3. The Ratio of the Harmonic-oscillator Contribution to the Total Contribution for $-(G^0 - H_0^0)/T$ as a Function of $u = 1.4387\omega_0/T$ for Some Values of $x = \omega_e x_e / \omega_e$

Some typical values of u and x are given in Table 1 for O_2 , UO , and several molecules with smaller vibrational frequencies. The vibrational contribution to the free-energy function for each of the molecules in Table 1 was obtained at 298, 2000, and 6000 K in two ways. If it is assumed that the vibrational energy levels are exactly represented by two terms in Eq. (16), then an exact vibrational contribution to the free-energy function can be obtained

by summation to the maximum vibrational level. This value is compared in Table 1 to the value obtained from Eq. (28). Two of the important conclusions from these results may be summarized as follows:

1. The range of u and x values for which Eq. (28) is both a necessary and a valid approximation, is very limited. There is a "physical" breakdown of Eq. (28) because more terms are needed to describe the physical situation--i.e., a single term for anharmonicity is not sufficient. There is also a "mathematical" breakdown of the approximation of Eq. (28) that occurs in about the same range of u and x values as the physical breakdown--i.e., replacing $v_{\max}$ by ∞ results in divergence of the summation in Eq. (25).

2. It is important to consider anharmonic effects at 6000 K for frequencies of about 150 cm^{-1} or less and at 2000 K for frequencies of about 50 cm^{-1} or less. (This conclusion is implicitly extended to polyatomic molecules even though the analysis of data is limited to diatomic molecules.)

TABLE 1. Calculated Vibrational Contributions to the Free-energy Functions of Selected Molecules (Data from Ref. 2)

Molecule	ω_e^a	$\omega_e x_e^a$	x_e^b	T, K	u^c	$-(G^v - H_0^v)/T^d$			Total ^g	Ratio ^h	% Error ⁱ
						Exact ^e	Harmonic Oscillator	Correction Term ^f			
O ₂	1580.36	12.07	0.0078	298	7.5	0.0	0.0	0.0	0.0	--	0.0
				2000	1.1	3.3	3.3	0.0	3.3	1.000	0.0
				6000	0.37	10.0	9.7	0.25	9.9	0.979	-0.4
UO	825.0	2.5	0.0030	298	4.0	0.2	0.2	0.0	0.2	1.000	0.0
				2000	0.59	6.8	6.7	0.0	6.8	0.993	0.0
				6000	0.20	14.6	14.3	0.2	14.5	0.986	-0.3
PbTe	211.8	0.12	0.00057	298	1.0	3.7	3.7	0.0	3.7	1.000	0.0
				2000	0.15	16.3	16.3	0.0	16.3	0.997	0.0
				6000	0.051	25.2	25.0	0.2	25.2	0.992	0.0
BiI	163.9	0.31	0.0019	298	0.79	5.1	5.1	0.0	5.1	1.000	0.0
				2000	0.12	18.5	18.3	0.2	18.5	0.986	0.0
				6000	0.039	28.2	27.1	0.8	27.9	0.973	-1.3
CsI	142	1.2	0.0086	298	0.67	6.0	5.9	0.1	6.0	0.986	0.0
				2000	0.10	21.3	19.5	1.3	20.8	0.938	-2.2
				6000	0.034	28.7	27.1	4.1	32.5	0.834	+13.1
Rb ₂	57.28	0.96	0.017	298	0.27	13.3	13.0	0.8	12.9	0.935	3.1
				2000	0.040	24.9	26.9	6.9	33.9	0.794	+36.1

^aUnits of cm^{-1} .

^b $x = \omega_0 x_0 / \omega_0 = \omega_e x_e / \omega_e$.

^c $u = 1.4387 \omega_0 / T$.

^dIn $\text{J K}^{-1} \text{mol}^{-1}$.

^eAssuming $G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$ is exact.

^fApproximate formula for anharmonicity.

^gHarmonic-oscillator contribution plus approximated correction term.

^hHarmonic-oscillator term to total.

ⁱTotal compared to exact.

These general conclusions are useful for the calculation of the thermodynamic functions of thorium, uranium, and plutonium oxides. In particular, the observed stretching modes are at sufficiently high frequencies that anharmonicity should not make an important contribution to the thermodynamic functions in the temperature range of interest to reactor safety analysis and, therefore, can be neglected. However, the unobserved bending modes of PuO_2 or ThO_2 could

be at frequencies that are in the range of values for which anharmonicity is important at high temperatures. The low-frequency vibrational modes of UO_2 and UO_3 are sufficiently close to the 150-cm^{-1} limit that uncertainty about anharmonicity is an important factor in the overall uncertainty. These possibilities are examined in Section III-E.

D. Polyatomic Molecules

The vibrational energy levels for a bent triatomic molecule (e.g., ThO_2) neglecting anharmonicity, are given by three vibrational constants, ω_1 , ω_2 , and ω_3 , and the corresponding three quantum numbers, v_1 , v_2 , and v_3 , analogous to the first term in Eq. (16) for a diatomic molecule,

$$\epsilon_i/hc = G(v_i) = \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2) + \omega_3(v_3 + 1/2). \quad (29)$$

We may proceed to calculate the vibrational partition function from this energy-level expression and the general formula for Q given in Eq. (2). There is no vibrational degeneracy, and thus:

$$\begin{aligned} Q_{\text{vib}} &= \sum_{\substack{\text{all} \\ \text{states}}} \exp(-\epsilon_i/kT) \\ &= \sum_{v_1} \sum_{v_2} \sum_{v_3} \exp[-hcG(v_i)/kT] \\ &= \sum_{v_1} \sum_{v_2} \sum_{v_3} \exp(-u_1v_1 - u_2v_2 - u_3v_3) \end{aligned} \quad (30)$$

where $u_i = hc\omega_i/kT = 1.4387\omega_i/T$. Because v_1 , v_2 , and v_3 are independent quantum numbers, the expression for Q_{vib} becomes the product of three sums and each sum has a form identical to that of Eq. (20), the harmonic-oscillator approximation for a diatomic molecule.

Thus, in the case of the bent molecule ThO_2 , we may refer to a symmetric-stretching-mode (the v_1 mode with harmonic frequency ω_1 and quantum number v_1) contribution to the calculated thermodynamic functions. Similarly, we have a bending-mode contribution (v_2) and an antisymmetric-stretching-mode contribution (v_3).

The free-energy function becomes:

$$\begin{aligned} f_{\text{ef}, \text{vib}} &= R \ln Q_{\text{vib}} \\ &= -R \{ \ln[1 - \exp(-u_1)] + \ln[1 - \exp(-u_2)] \\ &\quad + \ln[1 - \exp(-u_3)] \} \end{aligned} \quad (31)$$

In the case of a linear triatomic molecule, e.g., UO_2 , there are four vibrational degrees of freedom. This additional degree of vibrational freedom compared to a bent triatomic molecule occurs as a degeneracy in the bending-mode vibration (v_2). Physically, there are two mutually perpendicular, thus independent, bending motions that are identical in their atomic displacements and in their frequencies. The energy-level expression for a nonlinear triatomic molecule, Eq. (29), is equally valid for a linear triatomic molecule, however in the latter case the bending mode (v_2) is degenerate.

One way to treat this degeneracy is to add an additional term, $\omega_2'(v_2' + 1/2)$, to Eq. (29) to represent the additional vibrational degree of freedom. Now v_2' and v_2 are independent, but $\omega_2 = \omega_2'$. The degeneracy is the result of multiple ways of obtaining the same energy in Eq. (29). The vibrational partition function becomes:

$$\begin{aligned} Q_{\text{vib}} &= \sum_{\text{all states}} \exp(-\epsilon_i/kT) \\ &= \sum_{v_1} \sum_{v_2} \sum_{v_3} \sum_{v_2'} \exp(-u_1 v_1 - u_2 v_2 - u_3 v_3 - u_2' v_2') \\ &= \left[\sum_{v_1} \exp(-u_1 v_1) \right] \left[\sum_{v_2} \exp(-u_2 v_2) \right]^2 \left[\sum_{v_3} \exp(-u_3 v_3) \right] \end{aligned} \quad (32)$$

where $u_i = hc\omega_i/kT = 1.4387\omega_i/T$.

Alternatively, the degeneracy of the vibrational level $v_2 = n$ can be shown to be $n + 1$. (There are $n + 1$ ways of obtaining the same energy with $v_2 = 0, 1, \dots, n$ subject to the constraint that $v_2 + v_2' = n$.) In this case, the vibrational partition function is:

$$Q_{\text{vib}} = \sum_{v_1} \sum_{v_2} \sum_{v_3} (v_2 + 1) \cdot \exp(-u_1 v_1 - u_2 v_2 - u_3 v_3) \quad (33)$$

This expression for Q_{vib} can be shown to be mathematically equivalent to Eq. (32).

The free-energy function that is calculated for the case of a linear triatomic molecule from Eq. (32) is identical to that for a bent triatomic molecule as given in Eq. (31) except that the bending-mode contribution is larger by a factor of two.

For molecules with more than three atoms, our procedure is the same. The UO_3 molecule is the only example of interest to the calculation of thermodynamic properties of fuel-vapor species. This molecule has six vibrational degrees of freedom which could lead to four vibrational frequencies (two modes are doubly degenerate) if the geometry were either C_{3v} (pyramidal) or D_{3h} (symmetric planar). The molecule is known to have a planar C_{2v} structure

(T-shaped), and thus, UO_3 has six nondegenerate vibrational frequencies. The form of the appropriate energy-level expression would be identical to that of Eq. (29) with six harmonic frequencies and the corresponding six vibrational quantum numbers. The free-energy function expression for UO_3 is similar to Eq. (31) with six terms now contributing.

The energy-level expression of Eq. (29), or the corresponding expressions for molecules with four or more atoms, is valid provided anharmonicity can be neglected. If we consider anharmonicity, in the general case² we have:

$$\begin{aligned} \epsilon_i/hc &= G(v_i) \\ &= \sum_i \omega_i(v_i + 1/2) + \sum_i \sum_{j>i} x_{ij} \left(v_i + \frac{g_i}{2}\right) \left(v_j + \frac{g_j}{2}\right) \\ &\quad + \text{other terms} \end{aligned} \tag{34}$$

where g_i and g_j are the degeneracies, x_{ij} are the values of the anharmonic correction terms, and the "other terms" arise from a breakdown of degeneracies due to vibration-vibration interactions. In the case of a bent triatomic molecule, there are nine anharmonic constants ($x_{11}, x_{12}, \dots, x_{33}$). We will assume for polyatomic molecules that anharmonicity can be neglected at $T < 6000 \text{ K}$ for $\omega > 150 \text{ cm}^{-1}$ as was shown to be the case for diatomic molecules. This assumption is made because: (1) we expect that the conclusions for a diatomic molecule can reasonably be extended to small polyatomic molecules; and (2) the absence of experimental data makes it difficult to do otherwise. It must be remembered, however, that the neglect of anharmonicity creates an uncertainty in the calculated thermodynamic functions when very high temperatures and very low frequencies are combined.

E. Numerical Results, Errors, and Estimations

This section reports some results of the application of the vibrational energy formulas to the cases of uranium, thorium and plutonium oxides. The purpose of these calculations is to obtain numerical results for the molecules of interest so that the sensitivity of the calculated thermodynamic functions to input molecular parameters can be determined. In addition, parameters must be estimated for some of the molecules of interest. The contributions of these estimated parameters to the calculated functions will be numerically evaluated, compared with alternatives, and examined for uncertainties.

Table 2 compares the observed vibrational frequencies of uranium, plutonium and thorium oxides in Ar and Kr matrices. In all cases, the difference between the observed transition in Ar and the corresponding transition in Kr is less than 8.1 cm^{-1} . Some correlations among the observed gas-phase vibrational frequency and the frequencies measured in Ar, Kr, and other matrices^{7,8} suggest that the frequencies given in Table 2 should be no more than 1% different from the gas-phase values. In the case of UO , for example, the data in

Table 3 show that a 1% uncertainty in frequency does not substantially affect the vibrational contribution to the free-energy function in the temperature range of interest. Thus, "matrix-shifts" are not a major source of error in the resultant calculated thermodynamic functions. It should be possible to calculate a "gas-phase" value for each vibrational frequency of interest based on measured frequencies in Ar and Kr matrices of all known molecules and a correlation of these vibrational frequencies of the same molecules in different media including the gas phase. The vibrational frequencies of a number of molecules are now known from both experimental gas-phase studies and matrix-isolation studies and such a correlation seems feasible. The use of such calculated values would be expected to result in less uncertainty in calculated thermodynamic functions than would the direct use of measured frequencies from matrix-isolation studies. However, the data in Table 3 show that this is not a necessary step because the uncertainties that result from the direct use of Ar matrix data are small relative to other sources. Similarly, the experimental uncertainty³⁻⁵ of 0.1 cm^{-1} or less in the frequency measurement is negligible.

TABLE 2. Observed Vibrational Frequencies in cm^{-1} of the Stretching Modes of Matrix-isolated Uranium and Plutonium Oxides

	Ar Matrix	Kr Matrix	Δ
Pu^{16}O	822.3 ^a	817.3 ^a	5.0
$\text{Pu}^{16}\text{O}_2\nu_3$	794.3 ^a	786.8 ^a	7.5
U^{16}O	820.0 ^b	819.3, 815.5 ^b	0.7, 4.5
$\text{U}^{16}\text{O}_2\nu_3$	776.1 ^b	768.0 ^b	8.1
$\text{U}^{16}\text{O}_3\nu_4$	852.5 ^b	848.1 ^b	4.4
Th^{16}O	879.2, 876.1 ^c	874.3 ^c	4.9, 1.8
$\text{Th}^{16}\text{O}_2\nu_3$	786.6 ^c	779.8 ^c	6.8

^aRef. 3.

^bRef. 4.

^cRefs. 5 and 6.

TABLE 3. Vibrational Contribution in $\text{J K}^{-1} \text{ mol}^{-1}$ to the Free-energy Function for $\text{UO}(\text{g})$ Calculated from the Experimental Frequency and from a Frequency That Is 1.0% Larger than the Experimental Frequency

T, K	$f_{\text{ef}, \text{vib}}$	
	$\omega_0 = 820.0 \text{ cm}^{-1}$	$\omega_0 = 828.2 \text{ cm}^{-1}$
298	0.16	0.15
2000	6.72	6.66
6000	14.33	14.25

Molecules of the form X-M-X belong either to the symmetry group $D_{\infty h}$ (linear) or C_{2v} (bent) and, in either case, have three vibrational modes (see Section III-D of this report for an explanation of the nomenclature). In the case of linear MX_2 , both ν_2 and ν_3 are infrared active whereas ν_1 is only Raman active; but for bent MX_2 , all three modes are both infrared and Raman active. However, it is possible to accurately calculate the ν_1 mode frequency of a linear MX_2 molecule with data obtained from isotopic substitution and infrared spectroscopy alone.

The stretching modes of PuO_2 ($D_{\infty h}$)³, UO_2 ($D_{\infty h}$)⁴, and ThO_2 (C_{2v})⁵, have been observed or calculated from force constants that were derived from measured frequencies, but the bending modes were not observed in these studies. A value of $\nu_2 = 82 \text{ cm}^{-1}$ has been reported⁹ for UO_2 , but this value has been questioned¹⁰ because it could not be reproduced.¹¹ More recently the bending mode of UO_2 in Ar matrices has been identified and its frequency measured.¹² For ThO_2 , a value of $\nu_2 = 124 \text{ cm}^{-1}$ has been estimated¹³ and used to calculate thermodynamic functions.¹⁴ There is reason* to question the accuracy of this estimate for ThO_2 because it is based on the observed stretching-mode frequencies of isotopomers of ThO_2 , and it is not possible to accurately obtain ν_2 from these data. Thus, we conclude that for ThO_2 , no reliable empirical value exists for the bending-mode frequency. No data exist for PuO_2 despite attempts³ to observe the far-infrared spectrum. Only for UO_2 has a reliable frequency for the ν_2 mode been established.¹²

A correlation of empirical data for all molecules of the type X-M-X was undertaken to determine whether the bending-mode frequencies of PuO_2 and ThO_2 can be estimated by analogy. For this purpose it is useful to treat UO_2 as an unknown to see if the measured frequency of ν_2 can be predicted from the correlation. A complete literature evaluation has not been attempted; however, for 51 molecules of the form X-M-X, data on all three vibrational modes have been compiled. For three of these molecules ($PbCl_2$, $BaCl_2$, and $HgCl_2$) there are conflicting data. Twenty-five of the 51 molecules are reported to be linear, but there are conflicting data for one of these (MgF_2). No attempt has been made to evaluate the experimental data to determine whether errors exist.

The parameters chosen for correlation of MX_2 molecules are: (1) the mass ratio, R_M , of the X atom to the M atom; (2) the frequency ratio of ν_2 to ν_3 ; and (3) the frequency ratio of ν_2 to ν_1 . Because the dioxides of interest have relatively small mass ratios and because the set of collected data shows that the frequency ratios do appear to depend upon the mass ratio, only data for MX_2 -type molecules with R_M equal to 1.0 or more were correlated. These data are given in Table 4; and the ν_2/ν_3 frequency ratio, R_V , is plotted in Fig. 4 as a function of the mass ratio, R_M .

*Numerical calculations based on estimated force constants show that the stretching and bending mode frequencies are essentially independent even when interaction force constants are nonzero.

TABLE 4. Data for Molecules of the Type MX_2 for Which the Mass Ratio, X/M , is Less than 1.0

Molecule	Observed Frequencies			Calculated Ratios			θ	Reference Number
	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}	Mass X/M	Freq. ν_2/ν_1	Freq. ν_2/ν_3		
GeF_2	685	263	655	0.26	0.38	0.40	94	15
SnF_2	593	197	571	0.16	0.33	0.35	94	16
PbF_2	531	165	507	0.09	0.31	0.33	90	16
GeCl_2	390	163	362	0.48	0.42	0.45	95	17
SnCl_2	341	124	320	0.29	0.36	0.39	95	17
PbCl_2	326	81	304	0.17	0.25	0.27	96	18
PbCl_2	322	103	300	0.17	0.32	0.34	-	17
SnBr_2	244	82	231	0.67	0.34	0.35	-	17
H_2O	3657	1595	3756	0.06	0.44	0.42	105	19
H_2S	2615	1183	2628	0.03	0.45	0.45	92	19
SO_2	1151	518	1362	0.50	0.45	0.38	120	19
ClO_2	946	447	1101	0.46	0.47	0.41	118	19
MgF_2	552	247	851	0.79	0.45	0.29	180	20
CaF_2	485	163	554	0.48	0.34	0.30	140	21
CaCl_2	243	63.6	402	0.88	0.26	0.16	180	22
SrF_2	441	82.0	442	0.22	0.19	0.19	108	21
SrCl_2	269	43.7	300	0.40	0.16	0.15	120	22
BaF_2	390	64	413	0.14	0.16	0.15	100	21
BaCl_2	255	36	260	0.26	0.14	0.14	100	22
BaCl_2	262	62	268	0.26	0.24	0.23	120	18
ZnF_2	600	151	758	0.30	0.25	0.20	180	23
ZnCl_2	351	102	509	0.55	0.29	0.20	180	23
CdF_2	572	123	662	0.17	0.21	0.19	180	23
CdCl_2	327	88.5	419	0.31	0.27	0.21	180	23
CdBr_2	205	62.0	319	0.70	0.30	0.19	180	23
HgF_2	588	172	642	0.10	0.29	0.27	180	23
HgCl_2	348	107	407	0.17	0.31	0.26	180	17
HgCl_2	363	75	413	0.17	0.21	0.18	180	19
HgBr_2	219	73.0	294	0.40	0.33	0.25	180	23
HgI_2	158	63.0	238	0.64	0.40	0.27	180	23
H_2Se	2260	1074	2350	0.01	0.48	0.46	90	24
D_2Se	1630	745	1696	0.02	0.46	0.44	90	24
NiCl_2	360	85	521	0.60	0.24	0.16	180	25
SiF_2	843	343	855	0.68	0.41	0.40	101	26

Fig. 4

Correlation of the Frequency Ratio, ν_2/ν_3 , with the Mass Ratio, X/M , for Linear (squares) and Bent (circles) Molecules of the Type $X-M-X$. (The darkened squares and circles are for the alkaline-earth dihalides.)

The alkaline-earth dihalides are shown as darkened squares and circles in Fig. 4 because these data appear to deviate slightly from the remainder of the data. The data for linear molecules were least-squares fitted in four ways:

1. All data (13 molecules):

$$R_v = 0.22 - 0.021R_M \quad (1\sigma = 0.04) \quad (35)$$

2. All data except MgF_2 and HgI_2 (the two largest errors from the first fit):

$$R_v = 0.24 - 0.090R_M \quad (1\sigma = 0.03) \quad (36)$$

3. Alkaline-earth dihalides only:

$$R_v = 0.19 + 0.032R_M \quad (1\sigma = 0.05) \quad (37)$$

4. All data except alkaline-earth dihalides:

$$R_v = 0.24 - 0.057R_M \quad (1\sigma = 0.04) \quad (38)$$

Similarly, the bent molecules were least-squares fitted (irrespective of bond angle) in four ways:

1. All data (21 molecules):

$$R_v = 0.34 - 0.017R_M \quad (1\sigma = 0.10) \quad (39)$$

2. All data except SrF_2 , SrCl_2 , BaF_2 and BaCl_2 (the four largest errors from the first fit):

$$R_v = 0.39 - 0.041R_M \quad (1\sigma = 0.06) \quad (40)$$

3. Alkaline-earth dihalides only:

$$R_v = 0.11 + 0.29R_M \quad (1\sigma = 0.05) \quad (41)$$

4. All data except alkaline earth dihalides:

$$R_v = 0.039 - 0.001R_M \quad (1\sigma = 0.05) \quad (42)$$

We may now apply these equations to the molecules of interest-- ThO_2 , UO_2 , and PuO_2 . Both UO_2 and PuO_2 are linear with known values^{3,4} of ν_3 (776 and 794 cm^{-1} , respectively). Using Eqs. (35), (36), and (38) we calculate $R_v = 0.22$, 0.23, and 0.24, respectively, for both UO_2 and PuO_2 with $1\sigma = 0.04$. If we take $R_v = 0.23 \pm 0.04$, then the bending-mode frequencies are:

$$\text{UO}_2\nu_2 = 178 \pm 31 \text{ cm}^{-1}$$

$$\text{PuO}_2\nu_2 = 183 \pm 32 \text{ cm}^{-1}$$

For the bent ThO_2 molecule,⁵ which has $\nu_3 = 735 \text{ cm}^{-1}$, we use $R_v = 0.34$, 0.39, and 0.39 from Eqs. (39), (40), and (42), respectively, to obtain ν_2 in

the range between 287 and 250 cm^{-1} . The large value of σ in the equation that fits all data is caused by the alkaline-earth dihalides, which can be seen in Fig. 4 to be different from other bent MX_2 molecules. If we take $\sigma = 0.05$ from the equation which fits all data except the alkaline-earth dihalides, we have an uncertainty of about 38 cm^{-1} in ν_2 .

The true uncertainty in this method of estimating ν_2 must take into account several factors for which no quantitative data are available including:

1. Can a correlation of R_ν with R_M be justified?
2. Are the molecules given in Table 4 sufficiently similar to ThO_2 , PuO_2 , and UO_2 that a prediction based on this correlation is reasonable?
3. What factors cause deviations for some molecules that are outside the standard deviation (σ)?
4. Are the data given in Table 4 free from errors in assignment?

No complete discussion of the answers to these questions can be given here; however, some estimate of the uncertainty of these correlations is obtained by comparing the estimated ν_2 of UO_2 to the measured¹² value. This comparison will be made, but let us first consider an alternative to the correlations given in Eqs. (35)-(42).

Twenty-five linear molecules, including all those in Table 4, were used to see if a correlation could be obtained between the mass ratio, R_M , and a force-constant ratio, $R_f \equiv (f_\theta/r^2)/f_r$. This correlation is similar to that shown in Fig. 4, except that the mass dependence of R_ν is not present in R_f (ν_1 depends on the masses and, $(f_r + f_{rr})$; ν_2 depends on the masses and, f_θ/r^2 ; and ν_3 depends on the masses and $(f_r - f_{rr})$ where r is the bond distance and f_r , f_{rr} , and f_θ are the three valence force constants). This correlation between R_M and R_f did not prove useful and will not be discussed further.

The measured¹² bending-mode frequency of 225 cm^{-1} for UO_2 in Ar matrices is higher than the estimated value of 178 cm^{-1} that is obtained from the correlation based on the data in Table 4. It is also higher than the 150- cm^{-1} estimate used by Gabelnick²⁷ and very much higher than the reported⁹ measurement of 82 cm^{-1} by Abramowitz *et al.* The measured $\nu_2 = 225 \text{ cm}^{-1}$ is close to that of the uranyl ion, UO_2^{2+} , which has been observed²⁸ in aqueous solution ($\nu_1 = 860$; $\nu_2 = 210$; $\nu_3 = 930 \text{ cm}^{-1}$) and in several solids.^{29,30} Consideration³¹ of the uranyl data alone led to the prediction of $\nu_2 \approx 175 \text{ cm}^{-1}$ for UO_2 . A value of 190 cm^{-1} for ν_2 of UO_2 has been used³² by Ackermann *et al.* In summary, the measured bending-mode frequency for UO_2 of 225 cm^{-1} is somewhat higher than expected (support for the idea that empirical data are better than even the most reasonable estimates).

The prediction, which resulted from the correlation of R_V with R_M , of a slightly higher ν_2 frequency for PuO_2 than for UO_2 (183 cm^{-1} compared with 178 cm^{-1}) is expected to be valid. Thus, we estimate $\nu_2 = 230 \text{ cm}^{-1}$ for PuO_2 from this correlation and the measured ν_2 frequency of UO_2 . The correlations clearly suggest a higher ν_2 frequency for bent molecules than for linear molecules. We use the estimate of 250 cm^{-1} for ν_2 of ThO_2 that was obtained from the correlation equations, Eqs. (39), (40), and (42). There is reason to believe that the estimated ν_2 of PuO_2 is close to the true value because of the great similarity of the UO_2 and PuO_2 vibrations. The uncertainty for ThO_2 is probably greater because the estimated ν_2 values from the correlation equations, Eqs. (35)–(42), have been shown (for the case of UO_2) to have relatively large uncertainties. We shall take ν_2 to be uncertain by $\pm 40 \text{ cm}^{-1}$ for both ThO_2 and PuO_2 , although this may be too large an uncertainty for PuO_2 .

We would like to know how the uncertainty of $\pm 40 \text{ cm}^{-1}$ in ν_2 for PuO_2 and ThO_2 (approximate value obtained from R_V versus R_M correlation) affects the calculation of thermodynamic functions. For the case of PuO_2 we can determine this uncertainty from the data in Table 5. For the higher temperatures an uncertainty of $\pm 3.1 \text{ J K}^{-1} \text{ mol}^{-1}$ can be attributed to the uncertainty of $\pm 40 \text{ cm}^{-1}$ in ν_2 . The calculated vibrational contributions to the free-energy function of PuO_2 are given in Table 6. It is clear that the bending mode does make a large contribution and that the uncertainty in ν_2 results in a relatively large uncertainty in the vibrational contribution to the free-energy function.

TABLE 5. Calculated Bending-mode Contribution to the Free-energy Function of PuO_2 at Three Temperatures for Three Estimated Values of the Bending-mode Frequency (Units are $\text{J K}^{-1} \text{ mol}^{-1}$)

$\omega_2, \text{ cm}^{-1}$	fefvib		
	298 K	2000 K	6000 K
230	6.6	31.3	48.6
270	5.3	28.8	46.0
190	8.5	34.2	51.7

TABLE 6. Calculated Vibrational Contribution to the Free-energy Function of PuO_2 . (Data for stretching modes are measured³ and the bending mode is estimated. Units are $\text{J K}^{-1} \text{ mol}^{-1}$.)

Vibrational Mode	fefvib		
	298 K	2000 K	6000 K
$\nu_1 = 746.5 \text{ cm}^{-1}$	0.2	7.3	15.0
$\nu_2 = 230 \text{ cm}^{-1}$	6.6	31.3	48.6
$\nu_3 = 794.25 \text{ cm}^{-1}$	0.2	6.9	14.6
Total	8.0	45.5	78.2

It was previously determined (see Section III-C) that frequencies of 150 cm^{-1} or less may require some correction for anharmonicity at the highest temperatures of interest (6000 K). The cases of UO_2 , ThO_2 , and PuO_2 are not near this limit. However, it must be emphasized that the 150-cm^{-1} limit was obtained by considering only stretching modes of diatomic molecules and its application to the bending modes of triatomic molecules is assumed.

Plutonium and thorium have no trioxide, but uranium does, and the stretching-mode frequencies of matrix-isolated UO_3 have been measured,⁴ and more recently, the bending-mode frequencies were measured.¹² For thermodynamic calculations, all six vibrational-mode frequencies of UO_3 are needed.

The UO_3 molecule has a C_{2v} , "T-shaped" geometry.^{4,12} It has six normal modes of vibration ($3n - 6$) which have the symmetry $3A_1 + 2B_1 + B_2$ as shown in Fig. 5. If we use the three bond vectors as a basis, the irreducible representation is $2A_1 + B_1$; whereas if we use the three bond angles, it is $A_1 + 2B_1$.

Fig. 5. Coordinate Systems for UO_3 (top) and the Normal Modes of Vibration for UO_3

of which one B_1 is redundant because the three angles must sum to 2π for in-plane motions. An out-of-plane motion would be antisymmetric with respect to rotation about the C_2 axis as well as with respect to reflection in the molecular plane and symmetric with respect to other C_{2v} symmetry operations; therefore, it is of B_2 symmetry. Thus, for a T-shaped UO_3 molecule we expect three vibrational modes of $2A_1 + B_1$ symmetry in which the principal motion is bond stretching, two modes of $A_1 + B_1$ symmetry in which the principal motion consists of in-plane bond angle changes, and one mode of B_2 symmetry which is an out-of-plane bond angle change. The modes, their symmetries, their descriptions and their measured vibrational frequencies in Ar matrices are given in Table 7.

TABLE 7. Vibrational-mode Frequencies of UO_3

Mode	Symmetry	Description	$\bar{\nu}$, cm^{-1}
ν_1	A_1	Odd-O stretch	844 ^a
ν_2	A_1	Sym. stretch	746 ^a
ν_3	A_1	Uranyl bend	186 ^b
ν_4	B_1	Antisym. str.	853 ^a
ν_5	B_1	Deformation	212 ^b
ν_6	B_2	Out-of-plane	152 ^b

^aObserved, Ref. 4.

^bObserved, Ref. 12.

The only other T-shaped molecules whose vibrational frequencies are known are ClF_3 and BrF_3 .³³⁻³⁷ However, the mass ratio M/X for the MX_3 molecules significantly affects the relative nuclear motions (e.g., UO_2 vibrations are principally O-atom motions, whereas CO_2 vibrations involve all three atoms) so that the comparison of UO_3 to ClF_3 and BrF_3 must be done with extreme caution. In addition, the odd U-to-O bond in UO_3 is larger than the two equivalent U-to-O bonds whereas the opposite is true for the interhalogens.

The lowest UO_3 frequency is just above our limit of 150 cm^{-1} for which anharmonic corrections should be considered. Because the limit is based only on consideration of the stretching modes of diatomic molecules, the potential need for anharmonic corrections does contribute to the uncertainty in the vibrational contribution to the free-energy function of UO_3 . It is difficult to obtain a numerical estimate of this uncertainty because data on anharmonicity of polyatomic molecules are very incomplete. Anharmonicity should reduce the effective vibrational frequency (i.e., the frequency of each vibrational transition weighted by the thermal population of the lower state); thus if we assume it is reduced by no more than 10%, the contribution to the uncertainty in $f_{\text{vib}}(UO_3, g)$ is less than $0.9 \text{ J K}^{-1} \text{ mol}^{-1}$ (i.e., the difference in harmonic-oscillator contributions).

IV. ROTATIONAL CONTRIBUTION

A. Diatomic Molecules

The rotational contributions to the thermodynamic functions are calculated from the rotational partition function according to Eqs. (2)-(8). For these calculations we need a set of rotational energy levels and their corresponding degeneracies.

The degeneracy, g_i , of each rotational level is $2J + 1$, where J is the rotational quantum number. The rotational energy levels are given by³⁸:

$$\epsilon_i/hc = F(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 \quad (43)$$

The rotational constant D_v is due to centrifugal stretching and is small compared to the constant B_v . The effects of including D_v in the rotational energy level expression will be considered in Section VI-C; for the moment, we will neglect this term. We will also neglect the vibration-rotation interaction that is implicitly included in Eq. (43) and we will assume $B_v = B_e$ for all values of the vibrational quantum number v . The spectroscopic rotation constant, B_e , is related to the equilibrium internuclear distance, r_e ,

$$\begin{aligned} B_e &= \frac{h}{8\pi^2 c \mu} \cdot \left(\frac{1}{r_e^2} \right) \\ &= \frac{0.16858}{\mu r_e^2} \end{aligned} \quad (44)$$

for the reduced mass μ in amu, r_e in nm and B_e in cm^{-1} . For both PuO and UO, $\mu = 14.99$, so that $B_e = 0.01125/r_e^2$.

We now use Eqs. (43) and (44) in Eq. (2) to obtain the partition function. In general, for a diatomic molecule Eq. (2) should include the symmetry number (σ) which results from the equivalence of molecules that differ only by rotation ($\sigma = 1$ for a heteronuclear molecule and $\sigma = 2$ for a homonuclear molecule).

For the molecules of interest and the temperature range of interest, the summation in Eq. (2) over all rotational states can be replaced by an integral.

$$\begin{aligned}
 Q_{\text{rot}} &= \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) \exp[-hcBJ(J+1)/kT] \\
 &= \frac{1}{\sigma a} \int_0^{\infty} e^{-x} dx \\
 &= \frac{1}{\sigma a} = kT/\sigma hcB \quad (45)
 \end{aligned}$$

Where $a = hcB/kT = 1.4387B/T$ and $x = aJ(J + 1)$. The rotational contribution to the free-energy function can now be evaluated from Eq. (45) using Eq. (8):

$$f_{\text{ef rot}} = -R \ln(1.4387\sigma B/T) \quad (46)$$

To obtain an estimate of the rotational constant and, thus, the rotational contribution to Q , it is sufficient to estimate the equilibrium internuclear distance, r_e . Values of r_e for diatomic oxide molecules have been taken from compilations³⁹⁻⁴² of measured values and from tabulated estimates;⁴³ these are given in Fig. 6. From these tabulated data, the internuclear distances of UO and PuO may be estimated as 0.184 and 0.183 nm, respectively. The calculated rotational contributions to the free-energy functions are given in Table 8 for these two values of r_e as well as for $r_e = 0.180$ and 0.190 nm. The values 0.180 and 0.190 are taken as the limits of uncertainty in the estimated r_e values for UO and PuO based on the data in Fig. 6. From these values, it is concluded that the uncertainty in the free-energy function of either PuO or UO derived from the uncertainty in the rotational contribution is very small relative to uncertainties from other sources, provided that r_e can be estimated to the nearest 0.01 nm. This seems to be a reasonable expectation based on trends in the internuclear distances of diatomic oxides.

[illegible]

Fig. 6. Values of the Ground-state Equilibrium Internuclear Distances, r_e , in nm of Some Diatomic Oxides

TABLE 8. Rotational Contributions in $\text{J K}^{-1} \text{mol}^{-1}$ to the Free-energy Function at Three Temperatures as a Function of the Equilibrium Internuclear Distance, r_e , for PuO and UO

r_e , nm	B_e , cm^{-1}	f_{efrot}		
		298 K	2000 K	6000 K
0.180	0.347	53.1	68.9	78.0
0.183	0.336	53.3	69.2	78.3
0.184	0.332	53.4	69.3	78.4
0.190	0.312	54.0	69.8	78.9

corresponds to $r_e = 0.176$ nm. This value is probably less reliable than the value of $r_e = 0.184$ nm obtained previously.

Good spectroscopic data are available for ThO (Ref. 39) and no estimates are required.

B. Polyatomic Molecules

The rotational energy levels (in cm^{-1}) of a linear molecule, either diatomic or polyatomic, are given approximately by³⁸:

$$F(J) = \epsilon/hc = BJ(J + 1) \quad (47)$$

where the rotational constant B is the only spectroscopic constant required to represent the rotational energy levels in this approximation. (Centrifugal distortion effects can be considered but are not large relative to uncertainties in B for the cases of interest; similarly, the dependence of B on the vibrational quantum number will be neglected.) The value of B can be obtained experimentally by spectral analysis or from a knowledge of the atomic masses (m) and bond distances (r). For a linear molecule:

$$B = \frac{h}{8\pi^2 c I} \quad (48)$$

where, for a coordinate system whose origin is at the center of mass, the moment of inertia is

$$I = \sum_i m_i r_i^2 \quad (49)$$

A diatomic molecule can be considered a special case of a linear molecule, so that the I is mr^2 and Eq. (48) becomes the same as Eq. (44).

For the cases of UO_2 and PuO_2 (both linear), the center of mass is at the heavy-metal nucleus and:

$$I = mr^2 + mr^2 = 2mr^2 \quad (50)$$

An alternative approach to obtain the rotational constant is to use Badger's rule⁴⁴ to correlate vibrational and rotational data. The vibrational data are available for plutonium, thorium, and uranium oxides. This method has been used⁴⁵ for the UO bond in various compounds and has been extended⁴⁶ to gaseous UO and PuO . The value of B_e calculated by this method is 0.364 cm^{-1} which

where m is the mass of oxygen and r is the equilibrium internuclear distance between the oxygen atom and the heavy-metal atom. For PuO_2 and UO_2 (or any other linear dioxide) the partition function is:

$$\begin{aligned}
 Q_{\text{rot}} &= \sigma^{-1} \sum g_i \cdot \exp(-\epsilon_i/kT) \\
 &= \sigma^{-1} \sum_{J=1}^{\infty} (2J + 1) \exp[-hcBJ(J + 1)/kT] \\
 &= \sigma^{-1} \int_0^{\infty} (2J + 1) \cdot \exp[-hcBJ(J + 1)/kT] dJ \\
 &= kT/\sigma hcB \\
 &= 131.9 \text{Tr}^2/\sigma
 \end{aligned} \tag{51}$$

for r in nm where σ is the symmetry number ($\sigma = 2$ for UO_2 and PuO_2).

The rotational contribution to the free-energy function is:

$$\begin{aligned}
 f_{\text{ef,rot}} &= R \ln Q_{\text{rot}} \\
 &= R \ln(131.9 \text{Tr}^2/\sigma).
 \end{aligned} \tag{52}$$

Thus, we need only a method to estimate the U-O (and Pu-O) bond distance, r , in UO_2 (and PuO_2) to obtain an estimate of the calculated rotational contribution to the thermodynamic functions.

The following relationship between the stretching force constant, f in $\text{N}\cdot\text{m}^{-1}$, and bond distance, r in nm has been derived⁴⁵ for uranyl complexes:

$$r = 0.0501f^{-1/3} + 0.117. \tag{53}$$

The force constants for UO_2 (Ref. 4) and PuO_2 (Ref. 3) are 0.5260 and 0.5248 $\text{N}\cdot\text{m}^{-1}$, respectively, which give, from Eq. (53), both the U-O and Pu-O bond distances as 0.175 nm. For the UO molecule, $r = 0.184$ nm was estimated in the preceding section by comparison with other metal oxides, although other estimates of 0.176,⁴⁵ 0.1764,²⁷ and 0.180 nm⁴⁷ have been made. There is reason to expect that the U-O bond distance in UO_2 is similar to that in UO based on comparison⁴⁸ of other MO_2/MO pairs. From these values, we estimate that $r = 0.179 \pm 0.005$ nm for the UO bond distance in UO_2 and for the PuO bond distance in PuO_2 . The uncertainty in the calculated free-energy function is similar to that previously discussed in Section IV-A for the cases of PuO and UO .

The general case of polyatomic rotation is for an unsymmetrical top molecule (three unequal principal moments of inertia, I_x , I_y , and I_z). Each moment of inertia defines a rotational constant by a relationship of the form given by Eq. (48). The relationship between the moments of inertia and the rotational partition function is given⁴⁹ by

$$Q_{\text{rot}} = \sigma^{-1} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (\pi I_x I_y I_z)^{1/2} \quad (54)$$

where σ is the symmetry number [$\sigma = 2$ for both ThO_2 and UO_3 because both have a two-fold (C_2) axis of symmetry]. We will consider the cases of the two unsymmetrical tops of interest-- ThO_2 and UO_3 .

The bond angle of ThO_2 is calculated as 122.5° from vibrational spectral data,⁵ and the bond distance is 0.184 nm if it is the same as that observed³⁹ for ThO . From these values, the principal moments of inertia are (z is the symmetry axis and the x axis is the molecular plane):

$$I_x = 36.6 \times 10^{-40} \text{ g}\cdot\text{cm}^2$$

$$I_y = 174.8 \times 10^{-40} \text{ g}\cdot\text{cm}^2$$

$$I_z = 138.2 \times 10^{-40} \text{ g}\cdot\text{cm}^2$$

From Eq. (48) we obtain rotational constants of 0.766 cm^{-1} , 0.212 cm^{-1} , and 0.167 cm^{-1} .

TABLE 9. Calculated Rotational Contributions in $\text{J K}^{-1} \text{ mol}^{-1}$ to the Free-energy Function of ThO_2 for Two Values of the Th-O Bond Distance

r , nm	f_{rot}		
	298 K	2000 K	6000 K
0.184	80.9	104.6	118.3
0.180	80.3	104.1	117.8

The resultant calculated values of the free-energy function are compared in Table 9 to the values obtained with $r = 0.180 \text{ nm}$. The uncertainty in the calculated free-energy function caused by the uncertainty in r is small relative to other sources of error.

The geometry of UO_3 has been determined^{4,12} to be T-shaped (C_{2v}), and the bond distances have been estimated assuming the derived force constants are correlated with the U-O bond distances. The two equivalent oxygens are estimated to be 0.176 nm from the uranium; whereas, the nonequivalent oxygen is estimated to be 0.179 nm from the uranium. From these values, the principal moments of inertia are (z is the symmetry axis and the x axis is in the molecular plane):

$$I_x = 80.3 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

$$I_y = 244.9 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

$$I_z = 164.5 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

From these moments of inertia we obtain with Eq. (48) rotational constants of 0.348 cm^{-1} , 0.170 cm^{-1} , and 0.114 cm^{-1} .

Uncertainties in the thermodynamic functions of UO_3 arise from uncertainties in the two U-O bond distances. The sensitivity of the calculated free-energy function to each of these bond distances is similar to that of ThO_2 (as shown in Table 9). Roughly then, the uncertainty in the rotational contribution to the free-energy function of UO_3 is about twice that of the dioxides or about $1.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

C. Molecular Geometry

The molecular geometry is a required parameter for thermodynamic calculations. The bond distances and bond angles together with the atomic masses determine the molecular moments of inertia which, in turn, fix the rotational contribution to the partition function (Section IV-B). The symmetry and bond angles of uranium, plutonium, and thorium oxide vapor species have been determined and are given in Table 10. Bond distances can be estimated with sufficient accuracy for thermodynamic calculations as shown in Section IV-B. We consider here the sensitivity of the calculated rotational contribution (to the free-energy function) to the experimentally determined bond angle(s).

TABLE 10. Bond Angles and Symmetry Groups of Plutonium, Uranium, and Thorium Oxide Vapor Species

Molecule	Symmetry Group	Bond Angle	Geometric Description	Reference
PuO_2	$D_{\infty h}$	180°	Linear	3
UO_2	$D_{\infty h}$	180°	Linear	4
ThO_2	C_{2v}	$122.5 \pm 2^\circ$	Bent	5
UO_3	C_{2v}	-	T-shaped	4

For any molecule of the form MX_2 , there are either 2 rotational and 4 vibrational or 3 rotational and 3 vibrational degrees of freedom depending on whether the molecule is linear ($D_{\infty h}$) or nonlinear (C_{2v}), respectively. Thus, a full consideration of the effects of bond angle on calculated thermodynamic functions must consider both rotational and vibrational contributions. Table 11 compares the rotational and vibrational contributions to the free-energy function for the linear (real) UO_2 and the bent (hypothetical) UO_2 with both

120° or 150° bond angles. These results show that the determination of an accurate molecular geometry is vital. A total lack of knowledge about the O-U-O bond angle results in an uncertainty of approximately 12 J K⁻¹ mol⁻¹ at 6000 K for this particular set of molecular parameters.

TABLE 11. Calculated Rotational and Vibrational Contributions in J K⁻¹ mol⁻¹ to the Free-energy Function of UO₂(g) for Three Bond Angles at Three Temperatures

T, K =	Bond Angle = 180°			Bond Angle = 150°			Bond Angle = 120°		
	298	2000	6000	298	2000	6000	298	2000	6000
Rotation ^a	53.6	69.4	78.5	75.4	99.1	112.8	79.6	103.6	117.3
Bending Vibration ^b	6.8	31.6	49.0	3.4	15.8	24.5	3.4	15.8	24.5
Total	60.4	101.0	127.5	78.8	114.9	137.3	83.0	119.4	141.8

^aUsing $r = 0.179$ nm.

^b $\nu_2 = 225$ cm⁻¹ is two-fold degenerate for $\theta = 180^\circ$.

It is important to note that the comparison made in Table 11 assumes that all parameters remain constant except the O-U-O bond angle. This is not expected to be a completely fair basis for comparison because the data in Fig. 4 suggest that ν_2 will be larger for a bent molecule than for a linear molecule. Thus, the difference between the calculated thermodynamic functions for these bond angles would be less. Nevertheless, the calculated thermodynamic functions are very dependent on the molecular geometry.

Because, in fact, the bond angles of all plutonium, uranium, and thorium oxide vapor species are well determined (Table 10), there is no appreciable uncertainty in the rotational contribution to the free-energy function attributable to bond-angle uncertainty. For example, the rotational contributions at 6000 K to the free-energy functions for ThO₂ with $\theta = 122.5^\circ$ and 120.5° are 117.8 and 117.4 J K⁻¹ mol⁻¹, respectively. The difference between these values is a small uncertainty relative to other sources.

The geometry of an excited electronic state is not necessarily the same as that of the ground state. The effects of this possibility are related to the discussion given here and will be considered in Section V-D.

V. ELECTRONIC CONTRIBUTION

A. General

The electronic contribution to each of the thermodynamic functions can be calculated using Eqs. (2)-(8) from the set of electronic energies, ϵ_i , and their corresponding degeneracies, g_i . The electronic partition function is:

$$Q_{el} = g_0 + g_1 \exp(-\epsilon_1/kT) + g_2 \exp(-\epsilon_2/kT) + \dots \quad (55)$$

In the case of a relatively low-molecular weight molecule at a relatively low temperature, Eq. (55) can often be accurately evaluated because few electronic states make an appreciable contribution to the sum. In many cases $Q_{el} = g_0$ is an adequate approximation where g_0 is the degeneracy of the electronic ground state. In other cases a limited amount of electronic spectroscopy serves to determine the energies and degeneracies of all expected low-lying electronic states. In the cases of some transition-metal oxides, theoretical calculations are of sufficient quality to establish the thermodynamic functions even though the experimental data are incomplete.

The cases of uranium and plutonium oxides, however, as well as other actinide oxides, nitrides, and carbides, are particularly troublesome because: (1) the large number of atomic states for the metal atoms implies a large number of low-lying molecular electronic states for the oxides; (2) experimental information is either totally lacking or insufficient; (3) for these molecules, the high temperature range of interest means many electronic states contribute to the calculated functions; (4) theoretical self-consistent field calculations cannot be done with sufficient accuracy because of the large number of electrons involved; and (5) no simple model of electronic structure exists with the exception of ThO .⁵⁰

B. Atomic States Model

The electronic states of a diatomic molecule, AB, can be constructed conceptually according to certain rules³⁸ from the electronic states of A and B atoms. Alternatively, A^{n+} and B^{n-} could be the conceptual starting point so that, in the case of the ionic molecule UO, for example, we can consider, the U^{2+} and O^{2-} states as the basis for constructing the molecular electronic states. For either starting basis, the total degeneracy of the molecular states must be equal to the product of the degeneracies of the two atoms or ions.

The U^{2+} ion is isoelectronic with Th, whereas O^{2-} is isoelectronic with Ne; and data are available for both Th and Ne. Because Ne has a nondegenerate ground state ($1S$) and no low-lying excited states, the states of UO can be considered, in this approximation, to be dependent only on the electronic states of Th. The experimental Th levels^{51,52} have been used directly²⁷ to compute an electronic contribution to thermodynamic functions for UO. The implicit

assumptions in this approximation are that: (1) both the molecular electronic-state density and distribution are similar to those of the appropriate ion; (2) the experimental data are sufficiently complete to avoid substantial errors; and (3) Th states are similar to those of U^{2+} . The effects of these assumptions on the calculated thermodynamic functions should be examined.

The atomic-states model has been previously applied⁴³ to a number of high-temperature molecules for which adequate experimental data are unavailable. It is believed⁴³ that this model overestimates the number of low-lying electronic states for most molecules.

The density of atomic levels (sum of degeneracies divided by cm^{-1} interval) for atomic thorium (Th I) is given in Table 12 for known^{51,52} levels, although analysis of the spectrum is incomplete. These results show that the calculated density of states of Th I is dependent upon the limit to which the summation of degeneracies is taken. If we use Th I levels or some function of Th I levels as a basis for modeling the UO electronic state density, then some interpretation is required to select the appropriate value of the density of states.

TABLE 12. Density of States (Nondegenerate States per cm^{-1}) for Selected Atoms and Ions Calculated from Known Spectroscopic Data to 10,000, 20,000, and 30,000 cm^{-1}

Atomic Levels ^a	Model for	Density of States		
		To 10,000	To 20,000	To 30,000
Th III	UO ₂	0.0160	0.0128	0.0101
Th I	UO, PuO ₂	0.0093	0.0258	0.0552
U I	PuO	0.0214	0.0739	0.209
Pu I	Pu	0.0069	0.0322	0.124

^aI stands for neutral, II for singly ionized, etc.

A dependence on the limit is also seen in Table 12 for Th III,⁵¹ U I,⁵³ and Pu I,⁵⁴ although there are differences in the nature of the variation of the density of states with the summation limit. These results indicate the difficulty encountered in applying the atomic states model to the molecules of interest at high temperatures, even if we accept the assumptions involved.

The electronic ground states of some atoms and ions of interest are given in Table 13. If we combine³⁸ the ground states of U I and O I, we obtain 765 nondegenerate molecular electronic states of UO. If we assume arbitrarily that all these states lie within a 5000 cm^{-1} interval, the energy-level density is 0.15. There are a number of U I excited states that have components with energies less than 5000 cm^{-1} , so the molecular energy-level density would be increased if these were considered in addition to the states from ground-state atoms. This is, very roughly, in agreement with the density of states given in Table 12. However, without additional information, these values are not sufficiently fixed by either method to allow the calculation of a reliable electronic contribution to the thermodynamic functions.

TABLE 13. Electronic Ground State Identity and Degeneracy for Selected Atoms and Ions

Atom or Ion	Ground State	Degeneracy
O I	3p	9
Th III	3F	21
Th I	3F	21
U I	5L ^o	85
O ²⁻	1s	1

It is useful to consider the case of ThO in some detail because empirical data are available.³⁹ The comparison of the atomic states model, other models, and empirical data for ThO is done in Section V-E of this report.

C. Other Models

To make some numerical comparisons, the free-energy function will be calculated from Eqs. (2) and (8) for several different models of the electronic structure. These models will then be compared with experimental data and evaluated. We use PuO(g) and UO₂(g) as examples.

A simple, potentially useful model of the electronic structure of heavy-metal oxide molecules will be considered first. Let us approximate the set of molecular electronic energy levels of the molecule by assuming a uniform "level density" or a constant "density of states." Specifically, assume the molecule has a set of nondegenerate ($g_i = 1$), equally spaced electronic states—one every $x \text{ cm}^{-1}$. The single adjustable parameter in the model, x , can be determined, in principle, by one of several different empirical or theoretical methods. For example, in the case of thorium, uranium, and plutonium oxides, experimental data on vapor pressures are available at temperatures between 1000 and 3000 K. Provided other contributions (translational, rotational, and vibrational) can be accurately determined and provided the empirical data are accurate, the value of x can be calculated from these data. It should be clear that this density-of-states model is applicable only to those cases for which a large number of electronic states make an appreciable contribution to the partition function. This is the case for heavy-metal-containing molecules at high temperatures.

With this model, the partition function can be evaluated from Eq. (55)

$$Q_{el} = 1 + \exp(-cx/T) + \exp(-2cx/T) + \exp(-3cx/T) + \dots \quad (56)$$

where

$c = 1.4387 \text{ K} \cdot \text{cm}$, a constant

$x = \text{level spacing in cm}^{-1}$

$T = \text{temperature in K}$

The infinite sum for Q_{el} has a closed-form solution

$$Q_{el} = [1 - \exp(-cx/T)]^{-1} \quad (57)$$

and thus, from Eq. (8)

$$f_{el} = -R \ln[1 - \exp(-cx/T)]. \quad (58)$$

The electronic contributions to the free-energy function are given in lines I and II of Table 14 for the illustrative choices of $x = 1000$ and 100 , respectively.

TABLE 14. Electronic Contributions (in $J K^{-1} mol^{-1}$) to the Free-energy Function of PuO Gas at Three Temperatures for Several Models of the Electronic Structure

Description of Electronic Structure	f_{el}		
	298 K	2000 K	6000 K
I $g_i = 1; \epsilon_i = 1000i$	0.1	5.6	12.8
II $g_i = 1; \epsilon_i = 100i$	8.0	22.2	31.1
III U I atomic levels ^a	21.7	26.2	39.7
IV $g_i = 5; \epsilon_i = 5000i$	13.4	13.6	16.4
V $g_i = 5; \epsilon_i = 500i$	14.1	23.3	31.5

^aReference 53.

Let us consider a modification of this model to give some improvement without loss of mathematical simplicity. Assume $g_i = 5$ and $\epsilon_i = 5000i$ --i.e. the same overall level density as for $g_i = 1$ with $\epsilon_i = 1000i$ (line I) but with a modified distribution of the levels. The formula for the free-energy function, Eq. (58), still applies with $x = 5000$, but now $R \ln 5$ must be added because the new Q_{el} is g times the Q_{el} given in Eq. (57). Line IV in Table 14 gives the results for this choice of x and g . This modification of the density-of-states model should yield improved results because the set of degenerate levels is almost certainly a better approximation to the actual physical situation. However, a second parameter has been introduced, namely, an average degeneracy, g . Now both g and x could be evaluated for each of the thorium, uranium, and plutonium oxides by fitting to the empirical data at two or more temperatures. The application of this model to the molecules of interest requires that reliable data (e.g., vapor pressure) be available from which the values of g and x could be derived.

The model in line V in Table 14 has the same level density as that in line II, but the levels are grouped differently. By comparing these two lines, it is seen that as the temperature increases, the details of the distribution of the levels become less important than the level density itself.

The atomic states model, which was described in Section V-B, has been applied⁵⁵ to PuO. Spectroscopic data for neutral uranium⁵³ (U I) have been used to approximate the states of Pu²⁺ (Pu III) and the results are given on line III in Table 14. These values should be considered as the upper limit⁴³ of the electronic contribution to the free-energy function of PuO. The various values in Table 14 serve to compare the magnitude and temperature-dependence of f_{el} calculated with the atomic states model and the density-of-states model. More specific comparison for all the molecules of interest will be made after some alternative models are considered.

Another model of electronic structure,⁵⁶ which has been applied to UO₂, is based on Rydberg-series¹⁹ representation of the electronic states. The derived electronic partition function is:

$$Q_{el} = \exp(-A_1/kT) \int_{n_0}^{n_{\max}} \exp\left[\frac{Ry}{(n - \delta)^2 kT}\right] \left[2n^2 + 2n + \frac{1}{3}\right] dn \quad (59)$$

where

A_1 = ionization energy

n = quantum number

Ry = Rydberg constant (12.6 eV)

δ = quantum defect.

The adequacy of this model is questionable for several reasons. Not all electronic states of small molecules can be represented as members of a Rydberg series. In particular, the valence states are not, in general, part of a Rydberg series in which the electronic ground state is the first member. It is this set of low-lying valence states that would be expected to make the largest contribution to Q_{el} . The justification for modifying the Rydberg model to account for degeneracy is probably valid; however, the particular choice given in Eq. (59) is not based on physical evidence. Furthermore, some arbitrary choices are made to determine the limits of integration in Eq. (59). However, if we view this model as simply an equation whose parameters must be determined from empirical data, then it may prove to be a useful tool and should be compared numerically to alternative models.

Unfortunately the integral in Eq. (59) cannot be evaluated analytically; and the internal energy, $E - E(0 \text{ K})$, is the only thermodynamic function that is evaluated numerically from Eq. (59) by the author.⁵⁶ Comparison will be made to the density-of-states model with the parameters listed on line V in Table 14 and to the model used by Gabelnick²⁷ for the case of UO₂(g).

For the constant density-of-states model we obtain from Eqs. (2)-(4):

$$Q = g/[1 - \exp(-cx/T)] \quad (60)$$

$$Q' = g(cx/T)[\exp(cx/2T) - \exp(-cx/2T)]^2 \quad (61)$$

$$Q'' = g\left(\frac{cx}{T}\right)^2 \frac{[\exp(cx/2T) + \exp(-cx/2T)]}{[\exp(cx/2T) - \exp(-cx/2T)]^3} \quad (62)$$

where $c = 1.4387 \text{ K} \cdot \text{cm}^{-1}$ (a constant) and T is in K.

Now Eqs. (60) and (61) may be used in Eq. (6) to obtain:

$$[E - E(0)]_{el} = \frac{Rcx \exp(-cx/T)}{1 - \exp(-cx/T)} \quad (63)$$

The comparison in Table 15 shows that the model used by Karow⁵⁶ gives an electronic contribution to the internal energy that is somewhat higher than for the model listed on line V of Table 14. Furthermore, Gabelnick yields a higher contribution to the internal energy than Karow's model except near 5000 K.

TABLE 15. Comparison of the Electronic Contributions to the Internal Energy of UO_2 for Karow's Model, Gabelnick's Model, and That Developed Here [Energy Units are J mol^{-1} and (eV)].

Model	T, K				
	3130	3600	4000	4400	5000
Karow ^a	25.1 (0.26)	32.7 (0.339)	37.8 (0.392)	42.6 (0.447)	50.1 (0.519)
Model ^b	23.1 (0.240)	27.0 (0.280)	30.3 (0.315)	33.7 (0.349)	38.7 (0.401)
Gabelnick ^c	30.5 (0.316)	-	40.0 (0.415)	-	49.0 (0.500)

^aReference 56, Table 7, p. 25.

^bThis report, Table 14, line V.

^cReference 27.

The model used by Gabelnick, the atomic states model discussed in Section V-B, is based on the approximation that Th III electronic states are the same as those of UO_2 . This model has no adjustable parameters, and values for $[E - E(0)]$ in Table 15 are fixed by the empirical spectroscopic data. Karow's model, as given in Eq. (59), makes use of one fixed empirical value, A , and several adjustable ones, n_0 , $n_{\max}$, and δ . Physical arguments are given⁵⁶ to justify the particular values of n_0 , $n_{\max}$, and δ used for the calculations in Table 15. Other choices of these parameters could be made. The model parameters g and x given on the fifth line of Table 14 are an arbitrary choice to illustrate the behavior of the model. Other values of g and x for UO_2 as well as the other oxides of interest will be considered after comparing the observed and calculated vapor pressures.

Another model of electronic structure has been discussed by Bogensberger et al.⁵⁷ in which a constant level density, $D(E)$, has been assumed. The sum,

similar to Eq. (56), is replaced by an integral between the "threshold" energy, E_e , and the ionization energy, E_i .

$$Q_{el} = g_0 + g_0 \int_{E_e}^{E_i} D(E) \exp(-E/RT) dE. \quad (64)$$

The use of an integral to replace the sum is valid only if the energy-level spacing is small compared to kT .

To compare this model to ours, we must consider a threshold energy in our model. If we modify Eq. (55) to do this, we obtain:

$$Q_{el} = g_0 + \sum_{i=1}^{\infty} g_0 \exp(-cxi/T). \quad (65)$$

We make use of the following two series expansions, which are valid for $r^2 < 1$,

$$\sum_{i=0}^{n-1} ar^i = a \left(\frac{r^n - 1}{r - 1} \right) \quad (66)$$

$$\sum_{i=0}^{\infty} ar^i = \frac{a}{1 - r} \quad (67)$$

where a is a constant, to obtain

$$\sum_{i=n}^{\infty} ar^i = \frac{ar^n}{1 - r} \quad (68)$$

and Eq. (65) becomes

$$Q_{el} = g_0 + g_0 \frac{\exp(-ncx/T)}{1 - \exp(-cx/T)} \quad (69)$$

The model of Bogensberger et al. has been used assuming $E_e \ll E_i$ so that Eq. (64) becomes:

$$Q_{el} = g_0 [1 + DRT \exp(-E_e/RT)]. \quad (70)$$

They choose the parameters $E_e = 8000 \text{ cal mol}^{-1}$ (2800 cm^{-1}), $D = 5 \times 10^{-4} \text{ mol cal}^{-1}$ (equivalent to $x = 700 \text{ cm}^{-1}$) and $g_0 = 7$ for UO_2 . The values of Q_{el} and f_{el} obtained are close to those obtained with the same parameters but not approximating the sum with an integral [i.e. Eq. (69)] and to our model without a threshold energy. Their physical model has more parameters and a somewhat different temperature dependence than ours. A choice between Eq. (70) and Eq. (69) may be possible from the comparison of the temperature dependence of the Q_{el} that can be derived from empirical vapor pressures.

Let us consider another modification of the constant-density-of-states model to see if further improvements are possible. To do this, let us consider a Rydberg series whose term values are given by:¹⁹

$$\epsilon_n = A - \frac{Ry}{(n - \delta)^2} \quad (71)$$

where A is the ionization limit, Ry is the Rydberg constant ($109\,737\text{ cm}^{-1}$), δ is the quantum defect and n is the quantum number ($n > 1$). For Rydberg terms, the density-of-states increases with energy, particularly near $\epsilon \approx A$.

In contrast, the model of electronic structure that has been described in Eqs. (56)-(58) assumes a constant density of states. One consequence of this assumption is a high-temperature limit for the electronic contribution to the heat capacity. It can be shown from Eqs. (2)-(5) that this limit is R . The experimental Th III levels, which have been used as a model for UO_2 electronic states,²⁷ result in a maximum for the electronic contribution to the heat capacity near 2000 K. A constant or decreasing heat capacity for uranium or plutonium oxide vapor species is not intuitively appealing because the density of states should increase with energy. Similarly, a density of states based purely on Eq. (71), such as Eq. (59), is unlikely to satisfactorily represent the low-lying electronic states, which are of particular importance to the calculated thermodynamic functions.

We consider here some modifications of the two-parameter, constant density-of-states model that will allow for an increasing electronic contribution to C_p^0 .

Either the energy-level spacing, x , or the degeneracy, g_0 , can be modified to make them functions of the quantum number, n , in the density-of-states model. These two approaches yield almost identical results provided a large number of states at an energy ϵ and g states at an average energy ϵ have equal densities-of-states. Some trial calculations were done with $g_n = c_0 - c_1/n^2$ (analogous to Eq. (71) where c_0 and c_1 are constants) and $x = \text{a constant}$. This revised model includes three adjustable parameters that could be determined from empirical data. The good fit obtained with a constant density of states, equivalent to $c_1 = 0$ in the revised model, shows that c_1 is small (see Section V-D).

A more attractive alternative is to use the known ionization potentials of the oxide vapor species.⁵⁸ If we let

$$g_n = g_0 / (1 - \epsilon_n / A) \quad (72)$$

where A is the ionization potential, then the degeneracy of states increases with energy in a manner similar to Eq. (71). If the energy levels remain equally-spaced,

$$\epsilon_n = nx \quad (73)$$

then the constant density-of-states model has been modified to allow for an increasing density-of-states without introduction of an additional adjustable parameter.

The increasing-density-of-states model, which is defined by Eqs. (72) and (73), is intended to retain some of the advantages of the constant-density-of-states model yet allow for an expected increase in the heat capacity at high temperatures. The heat capacity, C_p^0 , depends upon the second temperature derivative of the partition function and, thus, would be more sensitive to both small changes in the energy levels and to higher energy states. The density of states and the heat capacity would be expected to increase as the ionization limit is approached.

Some small discontinuities in the values of C_p^0 as a function of temperature result for:

ThO(g)	5500 < T < 5600
UO(g)	4700 < T < 4800
UO ₂ (g)	5000 < T < 5100
PuO(g)	5500 < T < 5600

There are no discontinuities in other thermodynamic functions, such as f_{ef} , nor in the calculated C_p^0 for ThO₂(g), UO₃(g), and PuO₂(g). This problem of discontinuities arises because Eq. (72) increases too rapidly ($g_n \rightarrow \infty$) near the ionization limit and, thus, the partition function sum begins to diverge as $\epsilon_n \rightarrow A$. This mathematical problem is easily solved without sacrificing advantages of the model by limiting the partition function sum to $n \leq A/x$ and by altering the degeneracy, Eq. (72), to:

$$g_n = g_0 / (1 - 0.9\epsilon_n/A) \quad (74)$$

Thus, g may increase by a factor of ten at most as $\epsilon_n \rightarrow A$. The model defined by Eqs. (73) and (74) now has one empirical parameter (the ionization potential) and two adjustable parameters. The mathematical forms of Eqs. (73) and (74) have been chosen to allow for an increasing C_p^0 near $kT \approx A$ while retaining the advantages of extrapolation from temperatures near 2000 K (where vapor pressures have been measured) to those near 6000 K (the highest temperature of interest). The methods of choosing the two adjustable parameters, g_0 and x are discussed in Sections V-D and V-E.

D. Numerical Results--UO₂

The increasing-density-of-states model of electronic structure that was discussed in Section V-C has two adjustable parameters (g_0 --an average electronic degeneracy; and x --an average energy-level spacing) and one fixed empirical parameter (A --the ionization energy). The values of these parameters for UO₂(g) have been determined from a fit to the vapor-pressure data over the temperature range of experimental measurement. A "best vapor pressure equation" for UO₂ ($1800 < T < 2600$ K) that was derived³² from all experimental data has been used in Table 16 to compare with the pressures that were calculated from the following input data:

Vibrational frequencies: 765.4, 225.2, 776.1 cm⁻¹

Rotational data: U-O bond distance = 0.179 nm

Electronic data: $g_0 = 1$; $x = 230$ cm⁻¹, $A = 45\,000$ cm⁻¹ for model

TABLE 16. Comparison for UO₂ of Calculated Vapor Pressures with Experimental Values

T, K	Calc ^a p, MPa	Exp ^b p, MPa
1800	2.2×10^{-10}	2.0×10^{-10}
2000	1.2×10^{-8}	1.1×10^{-8}
2200	2.8×10^{-7}	2.7×10^{-7}
2400	3.8×10^{-6}	3.9×10^{-6}
2600	3.3×10^{-5}	3.6×10^{-5}

^aCondensed-phase data from Ref. 27.

^bFrom Eq. (1) of Ref. 32.

If we assume g_0 is integer (the degeneracy of any electronic state is an integer; however, an average g may not be), then $g_0 = 1$ is required to avoid a systematic temperature-dependent error in Table 16 provided we assume the experimental pressure equation is accurate.

The calculation of g_0 and x is dependent upon thermodynamic quantities for the condensed phase. Because

there has not previously been agreement on all condensed-phase thermodynamic data, the relationship between the model parameters, g_0 and x , is presented here so that revisions in data will lead to improved values of g_0 and x .

For the sublimation reaction:

we have

$$\begin{aligned} R \ln p(\text{UO}_2) &= \text{fef}'(\text{UO}_2, \text{g}) - \text{fef}'(\text{UO}_2, \text{s}) \\ &= [\text{H}^\circ(\text{UO}_2, \text{g}, \mathcal{T}) - \text{H}^\circ(\text{UO}_2, \text{s}, \mathcal{T})]/T.* \end{aligned} \quad (76)$$

*The symbol $\mathcal{T}$ indicates standard temperature (298.15 K).

Thus, both the temperature-dependent free-energy function of the condensed phase and the value of the enthalpy of sublimation of UO_2 at T are needed to solve Eq. (76) for $\text{fef}'(\text{UO}_2, \text{g})$ if the values of $p(\text{UO}_2)$ are known as a function of temperature. The tabulated^{27,59} values of the free-energy function for solid UO_2 are in good agreement; however, there is a range of values that have been reported for $\Delta H_{\text{sub}}^0(\text{UO}_2, T)$. We have used the value³² of $618.4 \text{ kJ mol}^{-1}$ ($147.8 \text{ kcal mol}^{-1}$) because it is more in accord with spectroscopic data.⁶⁰ Values of $643.9 \text{ kJ mol}^{-1}$ (Ref. 27) ($153.9 \text{ kcal mol}^{-1}$ from⁵⁹ $\Delta H_f^0(\text{UO}_2, \text{s}, T) = -259.3 \text{ kcal mol}^{-1}$), $636.4 \text{ kJ mol}^{-1}$ (Ref. 61) ($152.1 \text{ kcal mol}^{-1}$ from $H^0(T) - H^0(0 \text{ K}) = 2.7 \text{ kcal mol}^{-1}$ for the solid and 3.1 for the gas) and 699 kJ mol^{-1} ($167 \text{ kcal mol}^{-1}$)⁶² have also been reported.

This wide range of values for $\Delta H_{\text{sub}}^0(T)$ results not from a wide range of values for $\Delta H_{\text{sub}}^0(T)$ for $1800 \leq T \leq 2600 \text{ K}$ but primarily from differences in heat capacity data between T and 1800 K or from differences in the third-law treatment [*i.e.*, the free-energy functions used in Eq. (76)].

If we choose the value $636.4 \text{ kJ mol}^{-1}$ for $\Delta H_{\text{sub}}^0(\text{UO}_2, T)$, the electronic contribution to fef exceeds that calculated from the atomic states model (our upper limit) and is rejected for that reason. However, we can use this ΔH_{sub}^0 to derive $g_0 = 17.7$ and $x = 3300 \text{ cm}^{-1}$ from Eq. (76) with the vapor pressures of Ackermann *et al.*,³² $r = 0.179 \text{ nm}$, and the measured^{4,12} vibrational frequencies. The other (higher) values of $\Delta H_{\text{sub}}^0(\text{UO}_2, T)$ are inconsistent with the data (*i.e.*, modification would be required in either the model of electronic structure, in the experimental vapor-pressure data, or in a molecular parameter such as the bond distance). Similarly, values for $\Delta H_{\text{sub}}^0(T)$ less than the $618.4 \text{ kJ mol}^{-1}$ value that we have used³² are also inconsistent.

Vapor pressures have been calculated to 6000 K from these two sets of data for the model. In each case the condensed-phase data are identical. We conclude from these calculations:

1. The value of $\Delta H_{\text{sub}}^0(T)$ makes little difference in the calculated UO_2 vapor pressure for $T \leq 6000 \text{ K}$. More specifically, the model parameters, g_0 and x , can vary widely without affecting the vapor pressures for $T \leq 6000 \text{ K}$ provided a reasonably good fit to experimental pressures is obtained for $1800 \leq T \leq 2600 \text{ K}$.

2. The recommended vapor pressures are lower than those of Gabelnick²⁷ by about a factor of four at high temperatures because of a lower electronic contribution to the free-energy function [see Eq. (76)].

The principal sources of uncertainty in the electronic contribution to the calculated thermodynamic functions of UO_2 are:

1. The question of the applicability of this model of electronic structure to UO_2 ; and
2. The uncertainty in other molecular parameters (these do affect the apparent electronic contribution because the experimental vapor pressures are fit by the data).

For the case of UO_2 , we conclude that the increasing density-of-states model, which is defined by Eqs. (73) and (74), provides an adequate method to obtain an electronic contribution to the calculated thermodynamic functions. The empirical vapor pressure equation,³² in combination with measured and estimated molecular parameters, yields the numerical values: $g_0 = 1$ and $x = 230 \text{ cm}^{-1}$. The $\Delta H_{\text{sub}}^{\circ}(\text{UO}_2, \text{T})$ must be near $618.4 \text{ kJ mol}^{-1}$ (Ref. 32) for this method to work.

E. Numerical Results--Other Molecules

The UO_2 molecule has been well studied by a variety of experimental techniques. The derived thermodynamic data are extensive and have been evaluated.³² The other molecules of interest to reactor safety analysis, UO , UO_3 , ThO , ThO_2 , PuO , and PuO_2 , have been studied less extensively and the derived thermodynamic data have had less experimental verification. Careful examination⁶⁰ of the recommended values of the thermodynamic functions leads to the conclusion that the case of UO_2 is the only one for which reliable values of the parameters g_0

and x may be derived from recommended values of the thermodynamic functions or from the vapor pressure. The recommended values of the model parameters for all oxide molecules of interest are given in Table 17. The reasons for these choices are summarized here.

TABLE 17. Model Parameters for Uranium, Plutonium, and Thorium Oxides

	g_0	$x, \text{ cm}^{-1}$	$A, \text{ cm}^{-1} \text{ }^a$
UO	1	920	45 000
UO_2	1	230	45 000
UO_3	1	2300	85 000
ThO	1	430	49 000
ThO_2	1	2300	70 000
PuO	1	260	47 000
PuO_2	1	670	75 000

^aReference 58.

The relationship between the "best" spectroscopic data and the "best" thermodynamic data has been discussed⁶⁰ by treating the electronic contribution to the free-energy function, fef_{el} , as an unknown that must fall between zero and the upper limit that is given by the atomic states model

(see Section V-B). It was concluded that the thermodynamic and spectroscopic data were consistent for the cases of UO , UO_2 , UO_3 , and PuO provided that certain choices were made among alternative thermodynamic values. However, the thermodynamic and spectroscopic data were not consistent for the cases of PuO_2 , ThO , and ThO_2 , and no reasonable changes in estimated parameters could account for the observed discrepancies.

The data of Pattoret et al.⁶¹ [vapor pressure of UO over the two-phase system $\text{UO}_2(\text{s}) + \text{U}(\text{l})$] can be fit very well by the parameters $g_0 = 7$, $x = 1040 \text{ cm}^{-1}$, and $A = 45,000 \text{ cm}^{-1}$ for $1700 < T < 2100 \text{ K}$. However, the calculated electronic contribution to the free-energy function exceeds our assumed upper limit⁴³--the contribution from the Th I states⁵¹--and can be rejected for that reason.

The recommended⁶³ free-energy of formation of $\text{UO}(\text{g})$ in J mol^{-1} for $1500 < T < 2600 \text{ K}$

$$\Delta G_f^{\circ}(\text{UO}, \text{g}) = -21\,700 - 51.09T \quad (77)$$

can be used to find the free-energy function from the following relationship:

$$\text{fef}(\text{UO}, \text{g}) = 1/2 \text{fef}(\text{O}_2, \text{g}) + \text{fef}(\text{U}, \text{l}) - \Delta G_f^{\circ}(\text{UO}, \text{g})/T + \Delta H_f^{\circ}(\text{UO}, \text{g}, 0 \text{ K})/T \quad (78)$$

The free-energy functions of O_2 (Ref. 64) and U (Ref. 65) are known, the enthalpy of formation of $\text{UO}(\text{g})$ can be obtained from the cycle given in Fig. 7, and with Eq. (77) we can use Eq. (78) to obtain $\text{fef}(\text{UO}, \text{g})$. To obtain $\Delta H_f^{\circ}(\text{UO}, \text{g}, 0 \text{ K})$ by the cycle in Fig. 7 we must have all the appropriate data. The dissociation energy of UO has been reported as⁶¹ $759.0 \text{ kJ mol}^{-1}$ ($181.4 \text{ kcal mol}^{-1}$) and as⁶⁶ $757.3 \text{ kJ mol}^{-1}$ ($181.0 \text{ kcal mol}^{-1}$) each with an uncertainty of 17 kJ mol^{-1} (4 kcal mol^{-1}). The evaluated⁶⁵ enthalpy of sublimation of U of $531.4 \text{ kJ mol}^{-1}$ ($127.0 \text{ kcal mol}^{-1}$) and the dissociation energy⁶⁷ of $\text{O}_2(\text{g})$ of $246.8 \text{ kJ mol}^{-1}$ ($58.99 \text{ kcal mol}^{-1}$) are known and were used with this cycle to obtain $\Delta H_f^{\circ}(\text{UO}, \text{g}, 0 \text{ K}) = 19.2 \text{ kJ mol}^{-1}$ ($4.6 \text{ kcal mol}^{-1}$). The best fit of these data to the increasing-density-of-states model gives $g_0 = 0.5$ and $x = 290 \text{ cm}^{-1}$. The measured⁴ vibrational frequency (820 cm^{-1}) and estimated $r = 0.184 \text{ nm}$ were used to calculate the vibrational and rotational contributions to the free-energy function. This mathematical fit has no physical meaning at low temperatures because a negative contribution to the free-energy function results from $g_0 = 0.5$. This lack of meaning is expected because the use of the model is valid only if a large number of electronic states contribute to the thermodynamic functions. The best fit to the data with $g_0 = 1.0$ (the smallest meaningful value) gives $x = 920 \text{ cm}^{-1}$. These values of the model parameters give reasonable--i.e. between 0 and our assumed⁴³ upper limit obtained from Th III states--values of the electronic contribution.

Fig. 7. A Thermodynamic Cycle That Can Be Used to Determine the Standard Enthalpy of Formation of $\text{UO}(\text{g})$ at 0 K

The methods used for $\text{UO}(\text{g})$ were also applied to $\text{UO}_3(\text{g})$. In this case the atomic states model (Section V-B) predicts that UO_3 electronic states can be approximated by those of U^{6+} . This ion is isoelectronic with Rn for which no low-lying electronic states exist. Thus, no electronic contribution to the thermodynamic functions would be expected from this model. The recommended⁶³ free-energy of formation (in J mol^{-1})

$$\Delta G_f^{\circ}(\text{UO}_3, \text{g}) = -829\,000 + 78.28T \quad (79)$$

was used with $\Delta H_f^\circ(\text{UO}_3, \text{g}, 0 \text{ K}) = -841 \text{ kJ mol}^{-1}$ ($-201 \text{ kcal mol}^{-1}$). The latter value was derived from the cycle in Fig. 8 with data for O_2 (Ref. 67) and U (Ref. 65) and the enthalpy of atomization of $\text{UO}_3(\text{g})$ (Ref. 61) of 2110 kJ mol^{-1} ($505 \text{ kcal mol}^{-1}$). These values together with the spectroscopic data and thermodynamic functions for O_2 (Ref. 64) and U (Ref. 65) lead to a physically impossible situation,⁶⁰ namely a negative electronic contribution to the free-energy function. Therefore, we estimate that the electronic contribution to the free-energy function of UO_3 is very small (from the atomic states model) and can be approximated by the model parameters given in Table 17. The value $x = 2300 \text{ cm}^{-1}$ is an estimate obtained from the assumption that the model spacing for UO_3 is ten times greater than that for UO_2 . This assumption should avoid large errors in the electronic contribution to the thermodynamic functions of UO_3 at higher temperatures because it was also used (Section VII of this report) to derive a consistent $\Delta H_f^\circ(\text{U})$.

Fig. 8. A Thermodynamic Cycle That Can Be Used to Determine the Standard Enthalpy of Formation of $\text{UO}_3(\text{g})$ at 0 K

The evaluated thermodynamic data for $\text{PuO}(\text{g})$ (Ref. 68) have been used with the analog of Eq. (78) to calculate the values of the parameters given in Table 17. For PuO_2 , however, the same procedure fails⁶⁰ to give reasonable results.

The atomic states model (see Section V-B) predicts the electronic states of PuO_2 to be like those of Pu^{4+} , which is isoelectronic with Th . Similarly, UO electronic states should be like those of U^{2+} , which is also isoelectronic with Th . Although we expect^{43,69} that this model overestimates the electronic contribution, the predicted similarity of electronic states of UO and PuO_2 will be useful. For the best available $\Delta G_f^\circ(\text{UO}, \text{g})$, this model overestimates the electronic contribution by about a factor of two at $T = 2000 \text{ K}$ as shown previously. If we assume that PuO is also overestimated by a factor of two at 2000 K and we set $g_0 = 1$, we obtain $x = 670 \text{ cm}^{-1}$ as shown in Table 17.

For both ThO and ThO_2 , like PuO_2 , it is not possible to fit the evaluated⁷⁰ thermodynamic data with reasonable choices of the model parameters because these data are not consistent⁶⁰ with spectroscopic data.

The atomic states model⁴³ for ThO_2 uses Th V (Th^{4+}) states as an approximation of those of ThO_2 because ThO_2 can be considered as $(\text{Th}^{4+})(\text{O}^{2-})_2$. The Th^{4+} ion is isoelectronic with Rn so there should be no low-lying electronic states and, thus, no electronic contribution to the calculated thermodynamic functions. However, the Th atom in ThO_2 is probably better represented as Th^{3+} or Th^{2+} and there are low-lying states of these ions. Thus, we would expect some nonzero electronic contribution to the ThO_2 thermodynamic functions. The U^{6+} ion is also isoelectronic with Rn; however, through similar reasoning we would also expect small electronic contributions to the thermodynamic functions of UO_3 . The increasing-density-of-states model parameters for ThO_2 that are given in Table 17 are the same as those for UO_3 . Although these parameters are rather uncertain, the effect on the calculated thermodynamic functions at high temperature will be small because the parameters will be used only with a value of $\Delta H_f^0(\text{Th})$ that is consistent with the parameter values.

Some experimental data are available³⁹ for the ThO electronic states although there is reason⁵⁰ to believe that unobserved low-lying states exist which could affect the calculated thermodynamic properties. Calculated electronic contributions to the free-energy function of ThO at three temperatures are given in Table 18 for different methods and models. We shall examine the electronic contribution for ThO in more detail than for other molecules because there are more spectroscopic data available.

TABLE 18. Calculated Electronic Contributions to the Free-energy Function of $\text{ThO}(\text{g})$ in $\text{J K}^{-1} \text{mol}^{-1}$

T, K	Known ^a					
	ThO	Ra I ^b	Th III ^c	Th I ^d	Rand ^e	Model ^f
298.15	0.0	0.0	13.7	13.4	0.0	1.1
2000	0.4	0.0	22.4	16.3	0.8	11.2
6000	5.4	5.3	32.8	30.5	9.6	20.1

^aReference 39.

^bReference 71.

^cReference 52.

^dReference 51.

^eReference 70.

^fWith $g_0 = 1$, $x = 430 \text{ cm}^{-1}$.

The known ThO electronic states³⁹ are singlets, but a large number of triplet states would be expected.⁵⁰ Thus, column 2 of Table 18 is a lower limit to f_{el} for ThO.

The atomic states model⁴³ uses Th III as an approximation for the electronic states of ThO. Both Th III and Ra I electronic states⁷¹ (they are isoelectronic) were used to calculate approximations to f_{el} for ThO. This comparison is useful as a test of the validity of the isoelectronic approximation because U electronic states were used for Pu^{2+} and Th states were used for Pu^{4+} in the cases of PuO and PuO_2 , respectively.

A comparison of columns 3 and 4 of Table 18 shows that Ra and Th III electronic states do not give similar results despite the fact that they are isoelectronic. Part of the reason for this difference is that 5f, 6d, and 7s orbitals are nearly degenerate (the differences in ground-state configurations shown in Table 19 is a consequence of this near degeneracy). The density of electronic states is very sensitive to the relative energies of these orbitals. It is also clear that as the nuclear charge increases in an isoelectronic series, the orbitals with lower principal quantum number are stabilized relative to those with higher principal quantum number. The effect of this stabilization on the density of states is seen in Table 20 by comparing, as an example, the states arising for s^2 , sd , and d^2 configurations. For the atoms and ions of interest, the stabilization of 5f and 6d orbitals over the 7s results in a greater density of states. Thus, it would be expected that Th III ($[Rn] 6d^2$), would have a larger density of states than the isoelectronic Ra ($[Rn] 7s^2$), and the results in columns 3 and 4 of Table 18 are expected. The increase in the density of states resulting from the stabilization of the 5f and 6d orbitals in Th III compared to Th I would be counteracted by the two additional electrons in Th I. Columns 4 and 5 in Table 18 show that these effects approximately cancel each other.

TABLE 19. Ground Electronic-state Configurations of Atoms and Ions of Thorium and Uranium

Species	Ground-state Configuration	Species	Ground-state Configuration
Th I	$[Rn] 6d^2 7s^2$	Th IV	$[Rn] 5f$
Th II	$[Rn] 6d 7s^2$	U I	$[Rn] 5f^3 6d 7s^2$
Th III	$[Rn] 6d^2$	U II	$[Rn] 5f^3 7s^2$

TABLE 20. Number of Electronic States and Total Degeneracy Resulting from Three Electronic Configurations

Configuration	States	Total Degeneracy
s^2	1	1
sd	2	20
d^2	5	45

The last column in Table 18 is the fef_{el} obtained by Rand⁷⁰ who included some low-lying triplet states. This contribution is certainly more realistic than that obtained only from analyzed electronic states, but is also probably lower than the true fef_{el} .

We conclude that it is not possible to obtain a reliable fef_{el} for ThO from measured spectroscopic data even though, relative to PuO and UO, it is a well studied molecule.

We choose an electronic contribution that seems reasonable for ThO similar to the method used for ThO₂ and for PuO₂. We arbitrarily set $g_0 = 1$ and, with the assumption that the set of known Th III states overestimates the value of f_{el} by a factor of 2 at 2000 K, we determine $x = 430 \text{ cm}^{-1}$ as shown in Table 17.

The process of deriving values of the model parameters for the increasing-density-of-states model from the empirical thermodynamic data for UO, UO₂, and UO₃ has shown that there are some problems. The consistency of the "best" thermodynamic data with spectroscopic data has been examined in detail.⁶⁰ The results suggest that new values of $\Delta H_f^0(T)$ should be derived so that consistent values are used in all results. This has been done and is the subject of Section VII of this report.

F. Conclusions

Complete empirical data on the electronic states of the molecules of interest are unavailable. It is unlikely that ab initio calculations of sufficient accuracy will be available in the near future. There appears to be no accurate method of modeling the electronic structures of these molecules without the use of empirical data such as the vapor pressure as a function of temperature. Of the models considered, the density-of-states model with a degeneracy that increases with energy and converges at the ionization limit seems to be a reasonable way to extrapolate both the free-energy function and the heat capacity from temperatures less than 3000 to 6000 K. Parameter values for this model are given in Table 17.

It is also concluded that some revision is required in $\Delta H_f^0(T)$ values in order to obtain thermodynamic functions that are consistent with spectroscopic data. This revision is the subject of Section VII.

VI. BETTER APPROXIMATIONS

A. Introduction

We have approximated the basic equation for the internal partition function,

$$Q_{\text{int}} = \sum_{\substack{\text{all} \\ \text{states}}} g_i \exp(-\epsilon_i/kT), \quad (80)$$

in two basic ways. We have assumed that Q_{int} can be separated into rotational, vibrational, and electronic parts, i.e. Eq. (1). We have also made various approximations for the set of energy levels, ϵ_i . The correction to the harmonic-oscillator approximation for vibrational energy levels, has been examined in detail in Section III-C. We consider here three other possible corrections and determine their importance for the cases of interest.

B. Vibration-Rotation Interaction

The rotational and vibrational contributions to calculated thermodynamic functions were previously considered as separate. The vibration-rotation interaction is most conveniently treated as a correction to the equilibrium rotational constant, B_e :

$$B_v = B_e - \alpha_e(v + 1/2) \quad (81)$$

where v is the vibrational quantum number and α_e is a spectroscopic constant that represents the vibration-rotation interaction. Thus, each vibrational level is characterized by a different rotational constant,

$$B_v \text{ (e.g., } B_0 = B_e - \alpha_e/2; B_1 = B_e - 3\alpha_e/2; \text{ etc.)}.$$

The vibration-rotation interaction prevents the factoring of the internal partition function, Q_{int} , which may be treated as the product of a separable electronic part, Q_{el} , and a rotational-vibrational part, Q_{rv} . Now Q_{rv} includes: (1) the rigid-rotator rotational part; (2) the vibrational part; and (3) an interaction part that was not previously considered:

$$Q_{\text{int}} = Q_{\text{el}} \cdot Q_{\text{rv}} \quad (82)$$

If we neglect anharmonicity,

$$Q_{\text{rv}} = \sigma^{-1} \sum_{v=0}^{v_{\text{max}}} \sum_{J=0}^{\infty} (2J + 1) \exp \left\{ - \left[\frac{F(J) + G(v) - G(0)}{kT} \right] \right\} \quad (83)$$

where

$$\begin{aligned} F(J) &= B_v J(J+1) \\ &= [B_e - \alpha_e(v+1/2)]J(J+1) \\ &= [B_0 - \alpha_e v]J(J+1); \end{aligned}$$

$$G(v) - G(0) = \omega_0 v;$$

and σ is the symmetry number.

Let

$$u = \omega_0/kT;$$

$$y = B_0/kT;$$

$$q = \alpha_e/kT;$$

$$z = J(J+1); \text{ so } dz = (2J+1)dJ,$$

$$Q_{rv} = \sigma^{-1} \sum_{v=0}^v e^{-uv} \sum_{J=0}^{\infty} (2J+1) e^{-yz} e^{qvz}. \quad (84)$$

We replace the sum over J by an integral because the rotational energy spacing is small compared to the kT values of interest; we expand $\exp(qvz)$ in a manner similar to that used for vibrational anharmonicity (see Section III-C) and we sum to $v = \infty$. Thus,

$$\begin{aligned} Q_{rv} &= \sigma^{-1} \sum_{v=0}^v e^{-uv} \int_0^{\infty} e^{-yz} (1 + qvz) dz \\ &= \sigma^{-1} y^{-1} \sum_{v=0}^{\infty} e^{-uv} + \sigma^{-1} q y^{-2} \sum_{v=0}^{\infty} v e^{-uv} \\ &= \frac{1}{\sigma y [1 - \exp(-u)]} \left[1 + \frac{q}{y [\exp(u) - 1]} \right] \quad (85) \end{aligned}$$

TABLE 21. Ratio of the Spectroscopic Constants B_e and α_e for Heteronuclear Diatomic Oxide Molecules (Data are taken from Refs. 40 and 42)

Molecule	B_e/α_e	Molecule	B_e/α_e
AlO	111	NbO	205
AsO	147	PO	133
BO	107	PbO	160
BaO	266	PtO	135
BeO	87	SO	126
BiO	138	SbO	351
CO	110	ScO	156
CaO	133	SeO	145
CeO	199	SiO	144
CrO	106	SnO	162
FeO	135	SrO	154
GeO	132	TaO	221
HfO	224	TeO	150
IO	128	ThO	255
LaO	251	TiO	176
MgO	115	VO	156
NO	96	ZrO	184

0.00008057, and $u = 0.1972$; and the values of $f_{\text{f}_{\text{rv}}}$ calculated are 92.68 or 92.93 J K⁻¹ mol⁻¹ depending, respectively, on whether the correction term is omitted or included. This difference is a relatively minor uncertainty in the calculated thermodynamic function.

If we neglect the term involving q (i.e., the vibration-rotation interaction), then Q_{rv} reduces to the product of Q_{rotation} and $Q_{\text{vibration}}$. Thus, the size of the term involving q must be less than 1.0 for vibration-rotation interaction to be neglected. The data in Table 21 and Fig. 9 show that for UO and PuO it can be expected that $B_e/\alpha_e = 150$ so that $q/y = 1/150$. If we consider PuO as an example, $\omega_0 = 922.3 \text{ cm}^{-1}$ and $B_e = 0.336 \text{ cm}^{-1}$ (see Section IV-A), and for $T = 6000 \text{ K}$, the term involving q in Eq. (85) becomes 0.03 and can be neglected without significant errors (at lower temperatures the correction term is even less important). With these values for PuO, the parameters in Eq. (85) are: $\sigma = 1$, $y =$

Fig. 9
Ratio of the Spectroscopic Constants B_e and α_e for Heteronuclear Diatomic Oxide Molecules, MO, as a Function of the Mass of M

Even for a vibrational frequency of 150 cm^{-1} , the uncertainty is only about $1.2 \text{ J K}^{-1} \text{ mol}^{-1}$ at 6000 K. Thus, we conclude that vibration-rotation interactions are not a major source of uncertainty provided vibrational frequencies are 150 cm^{-1} or greater.

As was the case with vibrational anharmonicity, the conclusions are strictly valid only for the diatomic molecules of interest. The extension of these conclusions to the other molecules is itself a source of uncertainty. In particular, the interaction between rotation and a bending vibration, e.g. in UO_2 , may be different than the interaction between rotation and a stretching vibration.

C. Centrifugal Stretching

A centrifugal-distortion correction to the rotational energy can become important at large values of the rotational quantum number J . Physically this correction arises because the centrifugal force of rotation increases the bond length and, thus, the moment of inertia. The result of this effect on the spectrum is to decrease the effective rotational constant, B_v , at large values of J . This can be treated by adding a correction term to the rotational energy-level expression:

$$F(J) = B_v J(J + 1) - DJ^2(J + 1)^2 \quad (86)$$

(Note: the sign in Eq. (86) is chosen to give D a positive value). If we let:

$$y = B_v/kT$$

$$p = D/kT$$

$$z = J(J + 1)$$

$$\begin{aligned} Q_{\text{rot}} &= \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J + 1) \exp\left[\frac{-hcF(J)}{kT}\right] \\ &= \frac{1}{\sigma} \int_0^{\infty} \exp(-yz) \exp(pz^2) dz \end{aligned} \quad (87)$$

where the sum has been replaced by an integral. We may expand the exponential involving the correction term to obtain integrals that have closed-form expressions. Thus,

$$Q_{\text{rot}} = \frac{1}{y\sigma} \left[1 + \frac{2p}{y^2} \right] \quad (88)$$

It can be shown³⁸ that

$$D = \frac{4B_e^3}{\omega_e^2} \quad (89)$$

For PuO, we obtain $D = 2.2 \times 10^{-7} \text{ cm}^{-1}$.

Numerical evaluation of the centrifugal distortion term in Eq. (88) shows that at 6000 K for the case of PuO, this correction to Q is less than 2% and can be neglected. Another way to arrive at the same conclusion is to say that an error of $1.2 \text{ J K}^{-1} \text{ mol}^{-1}$ in f_{ef} is the maximum tolerable uncertainty. It is easy to show that this corresponds to $2p/y^2 = 0.16$ or a temperature of 60,000 K for PuO. This temperature is well beyond the temperature region of interest so that the second term in Eq. (88) can be neglected.

D. Excited-state Geometry

The sensitivity of the calculated thermodynamic functions to bond angles and bond distances was considered in Section IV. It was shown that for all thorium, uranium, and plutonium oxide vapor species the calculated thermodynamic functions are relatively insensitive to small errors in bond angles. Because the bond angles for the molecules of interest are well known and the bond distances can be estimated with sufficient accuracy, it was concluded that the molecular geometries of the species of interest are sufficiently well-established for the purpose of calculation of thermodynamic functions. This conclusion is valid for the electronic ground-state only. It would be expected that some low-lying electronic states of UO_2 and PuO_2 would be nonlinear and some of the available experimental data⁷² can be interpreted as evidence of thermally-populated, bent electronic states of UO_2 .

The method of calculation of the electronic contribution, which is described in Section V-B, circumvents the problem of low-lying nonlinear electronic states. The parameters g_0 and x are determined from empirical vapor pressure data or other means and, thus, include the effects of nonlinear, thermally-populated electronic states.

It is important, however, to recognize that other methods of determining the electronic contribution to the thermodynamic functions may require consideration of the geometries of low-lying electronic states.

E. Electronic-state Separation

The separation of the internal partition function into electronic, vibrational, and rotational factors, Eq. (1), is an approximation that assumes the rotational constant, B , and the vibrational constant, ω_e , are the same for excited electronic states as for the ground state. We consider here the errors

involved in this approximation and their effects on the calculation of the thermodynamic functions of uranium, plutonium, and thorium oxides.

We will consider the case of UO as an example for the purpose of obtaining numerical results. Other monoxides of interest will be similar. For the dioxides of interest and for UO_3 the molecular geometry of excited electronic states is a factor which cannot be separated, but this topic has been previously considered (Section VI-D). We may expect our conclusions for UO to apply to the other molecules of interest.

A particular internal energy level of UO, for example, may conveniently be considered as the sum of three parts:

$$\epsilon_i = \epsilon_e + \epsilon_{ev} + \epsilon_{evr} \quad (90)$$

Here ϵ_e is the term value of the electronic state (i.e. the difference between the potential energy minimum of the electronic state of interest and that of the ground electronic state); ϵ_{ev} is the vibrational energy and $\epsilon_{ev} = hc[G_e(v) - G_e(0)]$ where the subscript e is to designate a dependence upon the electronic state; and $\epsilon_{evr} [= hcF(J)]$ is the rotational energy where the subscripts designate a dependence of the rotational term value on both the electronic state and the vibrational level.

Let us neglect both anharmonicity (Section III-C) and vibration-rotation interaction (Section VI-B) so that:

$$\epsilon_{ev}/hc = \omega_0 \cdot v \quad (91)$$

$$\epsilon_{evr}/hc = hcBJ(J + 1) \quad (92)$$

Both spectroscopic constants, ω_0 and B, are dependent upon the electronic state but, in this approximation, neither is dependent on the quantum numbers v and J. Now Eq. (90) may be used in the general expression for the internal partition function,

$$\begin{aligned} Q_{\text{int}} &= \sum_{\text{all states}} g_i \cdot \exp(-\epsilon_i/kT) = \sum_{\text{elect states}} \sum_v \sum_J g_e \cdot (2J + 1) \cdot \exp(-\epsilon_e/kT) \\ &\quad \cdot \exp(-hc\omega_0 v/kT) \cdot \exp[-hcBJ(J + 1)/kT] \\ &= \sum_{\text{elect states}} g_e \cdot \exp(-\epsilon_e/kT) \sum_v \exp(-hc\omega_0 v/kT) \\ &\quad \cdot \sum_J (2J + 1) \exp[-hcBJ(J + 1)/kT] \end{aligned} \quad (93)$$

where g_e = electronic degeneracy.

If we assume that the vibrational and rotational constants of all excited electronic states are identical to those of the ground electronic state, then Eq. (93) becomes three independent summations and each summation can be evaluated by methods that were discussed previously. Let us assume, for purposes of numerical comparison, that $r = 0.184$ nm for the ground state of UO and 0.190 nm for an excited state at 1000 cm^{-1} and furthermore, that both electronic states are nondegenerate ($g = 1$). We can compare the (exact) combined rotational-electronic contribution to the free-energy function calculated from Eq. (93) to the approximate contribution obtained by separating the rotational and electronic contributions. If $Q_0 = kT/hcB_0$ for the ground electronic state ($Q_0 = 2.092$ T for the example considered) and $Q_1 = kT/hcB_1$ for the excited electronic state ($Q_1 = 2.231$ T) then from Eq. (4),

$$Q_{\text{total}} = Q_0 + Q_1 \exp(-1438.7/T) \quad (94)$$

and the approximation gives

$$Q_{\text{total}} = Q_{\text{el}} \cdot Q_{\text{rot}} = [1 + \exp(-1438.7/T)] \cdot Q_0 \quad (95)$$

The numerical results are presented in Table 22. The differences between the approximate and exact results are negligible even at high temperature. The

TABLE 22. Calculated Rotational-electronic Contribution to the Free-energy Function for the Exact [Eq. (94)] and Approximate [Eq. (95)] Equations (Units are J K^{-1} and mol^{-1})

T, K	Eq. (94)	Eq. (95)
298	53.6	53.6
2000	72.8	72.6
6000	83.5	83.3

cumulative effect of a large number of relatively low-lying electronic states could become important if the bond distances of the excited states differ appreciably, and in the same direction, from that of the ground electronic state. This is not expected to be the case for the molecules of interest because the low-lying electronic states are largely the result of the rearrangement of electrons in molecular orbitals without major changes in the force constant or internuclear distance. Thus, both the vibrational constants, ω_0 , and rotational

constants, B , of excited electronic states are expected to be sufficiently close to those of the ground state to allow an accurate separation of electronic, vibrational, and rotational contributions to the calculated thermodynamic functions. For the relatively highly excited electronic states the bond distances would be expected to be larger and the vibrational frequencies lower, however, the weighting of these vibrational and rotational contributions becomes very small because $\exp(-\epsilon_e/kT)$ is very small.

VII. DERIVATION OF $\Delta H_f^0(T)$ VALUES

The increasing-density-of-states model, which is described in Section V, has two adjustable parameters, g_0 and x , that could be determined, in principle, from the evaluated $\Delta H_f^0(T)$ and the temperature-dependent ΔG_f^0 . This process was not successful for some of the molecules of interest because the ΔG_f^0 and ΔH_f^0 are not consistent⁶⁰ with spectroscopic data. The results of the consistency checks are summarized in Table 23. In order to obtain a consistent set of thermodynamic data it is necessary to derive a new value of $\Delta H_f^0(T)$ for some of the molecules of interest. It seems reasonable to apply the same methods to all molecules so we derive here a new value of $\Delta H_f^0(T)$ for each of the oxides of thorium, uranium, and plutonium.

TABLE 23. Summary of the Results of Consistency Checks between Spectroscopic and Thermodynamic Data for Gaseous Thorium, Uranium, and Plutonium Oxides

Consistent	Inconsistent
UO_2 : $p(UO_2)$ and $\Delta H_{sub}^0(UO_2, T)$	UO_3 : $\Delta G_f^0(UO_3, g)$ and $D^0(UO_3, g, 0 K)$
UO : $\Delta G_f^0(UO, g)$ and $\Delta H_f^0(UO, g, T)$	PuO_2 : $\Delta G_f^0(PuO_2, g)$ and $\Delta H_f^0(PuO_2, g, T)$
UO_3 : $\Delta G_f^0(UO_3, g)$ and new $\Delta H_f^0(UO_3, g, 0 K)$	ThO : $\Delta G_f^0(ThO, g)$ and $\Delta H_f^0(ThO, g, T)$
PuO : $\Delta G_f^0(PuO, g)$ and $\Delta H_f^0(PuO, g, T)$	ThO_2 : $p(ThO_2)$ and $\Delta H_{sub}^0(ThO_2, T)$

Several experimental methods (e.g., mass spectroscopy, transpiration, mass deposition, torsion effusion) are available to determine the temperature dependence of the ΔG_f^0 . The physically measured quantity (e.g., ion current) is generally converted to a pressure value by an appropriate method, which may involve calibration of the experimental apparatus as well as assumptions (e.g.-- UO_2 is the predominant vapor species). There are potential sources of error in the process to obtain pressures that depend upon the temperature range, the particular apparatus, the experimental method, and the particular system under study.

The "third-law method" of determining ΔH_f^0 requires knowledge of the free-energy functions, f_{ef}' , for each species in the formation reaction. For example, for $UO_2(g)$:

$$\Delta H_f^0(UO_2, g, T) = \Delta G_f^0(UO_2, g) + T[f_{ef}'(UO_2, g) - f_{ef}'(U, ref) - f_{ef}'(O_2, g)] \quad (96)$$

For each data point (a derived p and a measured T) a value of ΔG_f^0 and a value of $\Delta H_f^0(T)$ would be obtained provided ΔG_f^0 are known for other species in the reaction. The values of ΔG_f^0 as a function of T are often fit to an equation of the form

$$\Delta G_f^0 = a + bT \quad (97)$$

where $a \approx \Delta H_f^\circ$ and $b \approx -\Delta S_f^\circ$ over a small temperature range. For a set of n temperatures, n values of $\Delta H_f^\circ(\text{UO}_2, g, T)$ would be determined. Assuming there is no systematic trend of $\Delta H_f^\circ(T)$ values with T , these n values would be averaged to give the "third-law" value of $\Delta H_f^\circ(T)$.

A value of $\Delta H^\circ(T_a)$ is determined with the "second-law method" from the measured data, where T_a is the average temperature at which data were measured. "The second-law method" requires a knowledge of $H^\circ(T_a) - H^\circ(T)$ for each species involved in the reaction studied. For example, for UO_2 sublimation:

$$\frac{\partial R \ln p(\text{UO}_2)}{\partial (1/T)} = -\Delta H_{\text{sub}}^\circ \quad (98)$$

From the enthalpy increments, $H^\circ(T_a) - H^\circ(T)$ for $\text{UO}_2(g)$ and $\text{UO}_2(s)$ we can obtain $\Delta H_{\text{sub}}^\circ(T)$. Then,

$$\Delta H_f^\circ(\text{UO}_2, g, T) = \Delta H_{\text{sub}}^\circ(\text{UO}_2, T) + \Delta H_f^\circ(\text{UO}_2, s, T) \quad (99)$$

It is not possible to give a general statement that will apply to all cases, however, we will assume that the inconsistencies given in Table 23 are due entirely to errors in the derivation of ΔH_f° from the experimental data, with the exception of $\text{ThO}(g)$. We will derive new values of $\Delta H_f^\circ(T)$ for all gaseous oxides of thorium, uranium, and plutonium based on the ΔG_f° equations. The numerical results from this process have been reported⁷³ and summarized here.

The ΔG_f° equations, which are given in the second column of Table 24, are all evaluated (i.e. come from more than one set of experimental data) and are of the form of Eq. (97). To obtain $\Delta H_f^\circ(T)$ by the third-law method we use free-energy functions for O_2 ,⁶⁴ the metal in the reference state,⁶⁵ and the metal oxide molecule. This was done at the lower temperature limit of the ΔG_f° equation, the upper limit and a middle temperature for each of the seven molecules. These values, columns 4-6 in Table 24 were averaged, column 7, to obtain a "best" third-law ΔH_f° value. The three values that were averaged for ThO_2 show a temperature dependence and, thus, the average $\Delta H_f^\circ(T)$ values should be viewed with caution.

A second-law value of $\Delta H_f^\circ(T)$ was calculated from the constant term in the ΔG_f° equation assuming this term is $\Delta H_f^\circ(T_a)$ where T_a is the average temperature for which the ΔG_f° equation is valid. The enthalpy increments, $H^\circ(T_a) - H^\circ(T)$, were obtained from published data^{64,65} for each reactant in the formation reaction and were calculated for the products. These second-law values of ΔH_f° at T and at 0 K are given in columns 8 and 9 of Table 24. The new second- and third-law values of $\Delta H_f^\circ(T)$, columns 7 and 8 of Table 24, agree within 10 kJ for UO , UO_2 , UO_3 , and PuO . For these molecules we give the two values equal weight and recommend the values given in the last column in Table 24. The estimated uncertainty that is given is no less than twice the

TABLE 24. Free Energies of Formation and Enthalpies of Formation at 298.15 K, $\bar{T}$, for Gaseous Uranium, Plutonium, and Thorium Oxide Species

Molecule	ΔG_f° , J mol ⁻¹	ΔH_f° , kJ mol ⁻¹							
		Old Values	Third-law Values at $\bar{T}$				Second-law Values		New Values
							Avg of 3	T = $\bar{T}$	T = 0
UO	-21670 - 51.09T ^a 1500 < T < 2600	19.2 ^b T = 0	16.7 T = 1500	17.1 T = 2100	14.6 T = 2600		16.1	23.6	25.3
UO ₂	-500 030 + 14.88T ^c 1300 < T < 2400	-468 ^d T = $\bar{T}$	-465.3 T = 1800	-464.2 T = 2100	-464.3 T = 2400		-464.6	-468.3	-466.5
UO ₃	-829 350 + 78.3T ^a 1200 < T < 1800	-841 ^e T = 0	-799.8 T = 1200	-796.5 T = 1500	795.7 T = 1800		-797.3	-802.8	-807.2
PuO	-121 000 - 50.6T ^f 1600 < T < 2100	-92.0 ^f T = $\bar{T}$	-91.0 T = 1600	-90.3 T = 1900	-90.1 T = 2100		-90.3	-91.6	-90.2
PuO ₂	-473 200 + 18.2T ^f 1600 < T < 2100	-422 ^f T = $\bar{T}$	-471.6 T = 1600	-475.2 T = 1900	-477.6 T = 2100		-474.8	-452.5	-448.8
ThO	-70 790 - 51.09T ^g 2023 < T < 3000	-28.5 ^h T = $\bar{T}$	-1.3 T = 2023	0.0 T = 2600	0.5 T = 3000		-1.0	-29.8	-28.5
ThO ₂	-546 800 + 27.87T ^h 2023 < T < 3000	-504.2 ^h T = $\bar{T}$	-462.4 T = 2100	-451.6 T = 2600	-444.2 T = 3000		-452.7	-502.9	-499.4

^aFrom Ref. 63.

^bDerived in Ref. 60.

^cFrom Ref. 48; consistent with p(UO₂) in Ref. 32.

^dFrom Ref. 32.

^eDerived in Ref. 60 from D^o in Ref. 61.

^fRecommended value in Ref. 68.

^gFrom Ref. 74; inconsistent with Ref. 70.

^hRecommended value in Ref. 70.

uncertainty from averaging. The new $\Delta H_f^{\circ}(T)$ values for UO , UO_2 , and PuO are in good agreement with the old recommended values, but the new value for UO_3 is substantially different from the old.

For PuO_2 the three third-law values are in reasonably good agreement so we give triple weight to the average third-law value and obtain the recommended value in the last column in Table 24. The recommended $\Delta H_f^{\circ}(PuO_2, g, T)$ value is more than 40 kJ smaller than the previously recommended⁶⁸ value.

For ThO and ThO_2 the second- and third-law values of $\Delta H_f^{\circ}(T)$ are not in good agreement. In addition the third-law values for ThO_2 that are derived at different temperatures have an unacceptable temperature dependence. These inconsistencies, which suggest the possibility of an error in the ΔG_f° equation, must be resolved before a value of $\Delta H_f^{\circ}(T)$ can be recommended with confidence. Comparison of Rand's evaluated equation⁷⁰ for $\Delta G_f^{\circ}(ThO, g)$ to other equations⁷⁴⁻⁷⁶ suggests some error. In Table 24 we use the more recent equation⁷⁴ of Ackermann and Tetenbaum.

The derivation of both the second- and third-law $\Delta H_f^{\circ}(ThO, g, T)$ values depends upon the electronic contribution to the thermodynamic functions of $ThO(g)$. The values of $\Delta H_f^{\circ}(ThO, g, T)$ given in Table 24 come from thermodynamic functions for ThO that use an electronic contribution calculated from the data in Table 17. A smaller electronic contribution was used by Rand,⁷⁰ and with this, functions for ThO $\Delta H_f^{\circ}(ThO, g, T) = -29.4 \text{ kJ mol}^{-1}$ (average third-law value) or $-26.9 \text{ kJ mol}^{-1}$ (second-law value) are derived.

To obtain a value of $\Delta H_f^{\circ}(ThO, g, T)$ that is consistent with all uncertainties including the electronic contribution we attach equal weight to each of the second- and third-law (averaged) values in Table 24 and to the value derived for the ΔG_f° equation in Table 24 and Rand's functions for ThO .⁷⁰ The average of these four values gives $\Delta H_f^{\circ}(ThO, g, T) = -21.8 \text{ kJ mol}^{-1}$ ($-5.2 \text{ kcal mol}^{-1}$).

For ThO_2 we accept the average third-law value of $\Delta H_f^{\circ}(ThO_2, g, T) = -451 \text{ kJ mol}^{-1}$. A large uncertainty must be attached to this value because of the apparent temperature dependence of the third-law values and because of the lack of agreement between second- and third-law values.

VIII. RESULTS AND UNCERTAINTIES

The thermodynamic functions for $\text{ThO}(\text{g})$, $\text{ThO}_2(\text{g})$, $\text{UO}(\text{g})$, $\text{UO}_3(\text{g})$, $\text{PuO}(\text{g})$, and $\text{PuO}_2(\text{g})$, which were calculated from the data given in Fig. 10, are given in Appendix B.

Fig. 10. Summary of Data for Uranium, Plutonium, and Thorium Oxide Vapor Species

	UO	UO ₂	UO ₃	PuO	PuO ₂	ThO	ThO ₂
Rotation ^a	$r = 0.184 \text{ nm}$	linear $r = 0.179 \text{ nm}$	T-shaped $2r = 0.176 \text{ nm}$ $r = 0.179 \text{ nm}$	$r = 0.183 \text{ nm}$	linear $r = 0.179 \text{ nm}$	$r = 0.184 \text{ nm}$	$\theta = 122.5^\circ$ $r = 0.180 \text{ nm}$
Vibration ^b (frequency in cm^{-1})	820.0	765.4 225.2 (2), 776.1	843.5, 745.7, 186.2, 852.6, 211.6, 151.5	822.3	746.50, 230 (2), 794.25	890.99	787.40, 250, 735.35
Electronic ^c	$g = 1$, $x = 920 \text{ cm}^{-1}$, IP = 45,000 cm^{-1}	$g = 1$, $x = 230$, IP = 45,000	$g = 1$, $x = 2300$, IP = 85,000	$g = 1$, $x = 260$, IP = 47,000	$g = 1$, $x = 670$, IP = 75,000	$g = 1$, $x = 430$, IP = 49,000	$g = 1$, $x = 2300$, IP = 70,000
ΔH_f° (°) in kJ and (kcal)	19.9 (4.8)	-466.5 (-111.5)	-800.1 (-191.2)	-91.0 (-21.8)	-469.2 (-112.1)	-21.8 (-5.2)	-453 (-108)

^aBond angles are measured;³⁻⁵ bond distances are estimated, except for ThO.³⁹

^bAll frequencies above 300 cm^{-1} are measured;^{3-5,39} those below are measured¹² for UO₂ and UO₃; others are estimated.

^cModel parameters are derived; ionization potentials are measured.⁵⁸

All functions except ΔH_f° and ΔG_f° are dependent solely on the properties of the gaseous molecule. The ΔH_f° values are calculated from a $\Delta H_f^\circ(\text{F})$ input value and $H^\circ(\text{T}) - H^\circ(\text{F})$ for each element in the formation reaction in its standard state. Thermodynamic functions for the elements are given in Appendix A. The ΔG_f° values are calculated from the $\Delta H_f^\circ(\text{F})$ values and an equation like Eq. (96) which required the free-energy function for each element in the formation reaction.

In general, the uncertainties in the thermodynamic functions that are given in Appendix B are less than previously available. The results of Section V-E, indicate that the best available thermodynamic data are not consistent with spectroscopic data and that new $\Delta H_f^\circ(\text{F})$ values are required; this was done in Section VII. The uncertainties in $\Delta H_f^\circ(\text{F})$ values, as shown in Table 24, are the minimum uncertainties in ΔH_f° and ΔG_f° in Appendix C.

The uncertainties in the calculated thermodynamic functions of UO, UO₂, UO₃, and PuO are relatively small. The uncertainties for ThO are tolerable for most applications and those for ThO₂ and PuO₂ indicate the need for better data. The lack of consistency between spectroscopic data and the evaluated ΔG_f° equations⁶⁰ cannot reasonably be attributed to uncertainties in spectroscopic data.

APPENDIX A

Thermodynamic Functions of the Elements

The free-energy functions of Th, U, Pu, and O₂ in their reference states as functions of temperature are required to calculate ΔG_f° for each of the metal oxide vapor species. The appropriate tables of data were least-squares fitted and the coefficients are given in Table A.1. Similarly, the enthalpy increments, $H^\circ(T) - H^\circ(298.15 \text{ K})$, for the same elements are required to calculate ΔH_f° for each of the metal oxide vapor species. Coefficients for these equations are given in Table A.2.

TABLE A.1. Coefficients of the Equations (in cal mol⁻¹ K⁻¹)
 $= [C^\circ - H^\circ(T)]/T = A + BT + C/T + D \cdot \log_{10}(T)$ Fitted from
 Data in Reference 65 for the Reference State of
 the Metals and from JANAF Tables⁶⁴ for O₂

Element	T-range, K	A	B	C	D
Th	0-1633	-27.938	9.807×10^{-4}	1874.6	13.788
	1633-2023	18.048	2.4608×10^{-3}	-4823.1	0
	2023-4900	-65.100	0	4080.1	25.325
	5000-6000	-16.536	2.4655×10^{-4}	-137320.6	19.549
U	0-942	-18.517	3.4631×10^{-3}	1563.8	9.7956
	1000	15.942	0	0	0
	1049-1408	16.579	3.7423×10^{-3}	-4435.2	0
	1408-4400	-67.481	-2.7086×10^{-6}	2453.4	26.817
	4500-6000	-81.415	-3.8588×10^{-4}	-101 396	37.524
Pu	0-300	13.42	0	0	0
	400	13.769	0	0	0
	500	14.813	0	0	0
	600-700	9.983	9.760×10^{-3}	0	0
	800-900	10.782	8.70×10^{-3}	0	0
	1000-3600	-52.043	-5.8717×10^{-7}	1742.2	23.258
	3700-6000	-93.588	-2.9675×10^{-4}	-58935	39.970
O ₂	0-1400	4.2602	8.6662×10^{-4}	2053.9	15.194
	1400-6000	-8.0698	1.9907×10^{-4}	3267.0	19.137

TABLE A.2. Coefficients of the Equations (in kcal mol⁻¹) [$H^{\circ}(T) - H^{\circ}(298.15 \text{ K})$] =
 $A + BT + CT^2 + DT^3 + E \cdot \log_{10}(T) + FT^4 + G/T$ Fitted from Data in Reference 65
for the Reference State of the Metals and from JANAF Tables⁶⁴ for O₂

Element	T-range, K	A	B	C	D	E	F	G
Th	8-1633	-1.6322	6.1412×10^{-3}	9.2807×10^{-7}	0	-0.11369	0	0
	1633-2023	1.4307	3.7476×10^{-3}	1.4307×10^{-6}	0	0	0	0
	2023-4900	-4.086	0.011	0	0	0	0	0
	5000-6000	321.184	0.021089	-4.6044×10^{-7}	0	-61.957	0	0
U	8-942	-1.8357	5.792×10^{-3}	8.4408×10^{-7}	1.1069×10^{-9}	0	3.485×10^{-13}	0
	1000	6.835	0	0	0	0	0	0
	1049-1408	-1.1235	9.1503×10^{-3}	0	0	0	0	0
	1408-4400	-2.430	0.01163	0	0	0	0	0
	4500-6000	-946.521	-1.7844×10^{-3}	0	0	290.318	0	273920
Pu	300	0.015	0	0	0	0	0	0
	400	1.683	0	0	0	0	0	0
	500	2.653	0	0	0	0	0	0
	600-700	-1.65	8.879×10^{-3}	0	0	0	0	0
	800-900	-0.71	8.23×10^{-3}	0	0	0	0	0
	1000-3600	-1.7427	0.0101	0	0	0	0	0
	3700-6000	-17.458	0.033602	-1.43752×10^{-6}	0	0	0	118673
O ₂	8-1400	-1.9359	6.0133×10^{-3}	1.7198×10^{-6}	-37171×10^{-10}	0	0	0
	1400-6000	-2.5262	7.5478×10^{-3}	4.4248×10^{-7}	-2.414×10^{-11}	0	0	0

APPENDIX B

Tables of Thermodynamic Functions for Gaseous Thorium,
Uranium, and Plutonium Oxides

TABLE B.1. Thermodynamic Functions for ThO(g); Units for Columns 2-5 are cal K⁻¹ mol⁻¹ and for Columns 6-9 are kcal mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-2.29	-4.9	-4.9
298.15	8.89	58.20	50.53	58.20	2.29	0.0	-5.2	-11.5
300.00	8.90	58.26	50.58	58.20	2.30	0.02	-5.2	-11.5
400.00	9.51	60.91	52.84	58.56	3.23	0.94	-5.3	-13.6
500.00	9.91	63.08	54.68	59.25	4.20	1.91	-5.4	-15.6
600.00	10.18	64.91	56.24	60.05	5.20	2.92	-5.5	-17.7
700.00	10.36	66.49	57.59	60.86	6.23	3.94	-5.6	-19.7
800.00	10.50	67.89	58.79	61.65	7.27	4.99	-5.7	-21.7
900.00	10.59	69.13	59.87	62.41	8.33	6.04	-5.8	-23.7
1000.00	10.66	70.25	60.86	63.14	9.39	7.11	-5.9	-25.7
1100.00	10.72	71.27	61.76	63.84	10.46	8.18	-6.1	-27.7
1200.00	10.77	72.20	62.59	64.49	11.54	9.25	-6.2	-29.6
1300.00	10.80	73.07	63.36	65.12	12.62	10.33	-6.4	-31.6
1400.00	10.84	73.87	64.08	65.72	13.70	11.41	-6.6	-33.5
1500.00	10.86	74.62	64.76	66.29	14.78	12.50	-6.9	-35.4
1600.00	10.88	75.32	65.40	66.83	15.87	13.59	-7.1	-37.3
1700.00	10.91	75.98	66.00	67.35	16.96	14.68	-8.2	-39.1
1800.00	10.92	76.61	66.58	67.85	18.05	15.77	-8.4	-40.9
1900.00	10.94	77.20	67.12	68.32	19.15	16.86	-8.7	-42.7
2000.00	10.95	77.76	67.64	68.78	20.24	17.96	-9.0	-44.5
2100.00	10.97	78.29	68.13	69.22	21.34	19.05	-12.7	-46.2
2200.00	10.98	78.81	68.61	69.64	22.44	20.15	-13.2	-47.7
2300.00	10.99	79.29	69.06	70.05	23.54	21.25	-13.6	-49.3
2400.00	11.00	79.76	69.50	70.45	24.64	22.35	-14.1	-50.9
2500.00	11.01	80.21	69.92	70.83	25.74	23.45	-14.5	-52.4
2600.00	11.03	80.64	70.32	71.20	26.84	24.56	-15.0	-53.9
2700.00	11.04	81.06	70.71	71.56	27.95	25.66	-15.5	-55.4
2800.00	11.05	81.46	71.09	71.90	29.05	26.76	-15.9	-56.8
2900.00	11.06	81.85	71.45	72.24	30.16	27.87	-16.4	-58.3
3000.00	11.07	82.23	71.80	72.57	31.26	28.98	-16.9	-59.7
3100.00	11.08	82.59	72.15	72.88	32.37	30.08	-17.3	-61.1
3200.00	11.09	82.94	72.48	73.19	33.48	31.19	-17.8	-62.5
3300.00	11.09	83.28	72.80	73.49	34.59	32.30	-18.3	-63.9
3400.00	11.10	83.62	73.11	73.79	35.70	33.41	-18.8	-65.3
3500.00	11.11	83.94	73.42	74.07	36.81	34.53	-19.2	-66.7
3600.00	11.12	84.25	73.72	74.35	37.93	35.64	-19.7	-68.0
3700.00	11.13	84.56	74.00	74.62	39.04	36.75	-20.2	-69.4
3800.00	11.14	84.85	74.29	74.89	40.16	37.87	-20.7	-70.7
3900.00	11.15	85.14	74.56	75.15	41.27	38.98	-21.1	-72.0
4000.00	11.16	85.43	74.83	75.40	42.39	40.10	-21.6	-73.3
4100.00	11.17	85.70	75.09	75.65	43.51	41.22	-22.1	-74.6
4200.00	11.18	85.97	75.35	75.89	44.62	42.34	-22.6	-75.9
4300.00	11.19	86.24	75.60	76.13	45.74	43.46	-23.1	-77.1
4400.00	11.20	86.49	75.84	76.36	46.87	44.58	-23.5	-78.4
4500.00	11.21	86.75	76.08	76.59	47.99	45.70	-24.0	-79.6
4600.00	11.22	86.99	76.32	76.81	49.11	46.82	-24.5	-80.8
4700.00	11.23	87.23	76.55	77.03	50.24	47.95	-25.0	-82.1
4800.00	11.25	87.47	76.77	77.25	51.36	49.08	-25.5	-83.3
4900.00	11.26	87.70	76.99	77.46	52.49	50.20	-25.9	-84.5
5000.00	11.27	87.93	77.21	77.67	53.62	51.33	-161.5	-84.9
5100.00	11.28	88.16	77.42	77.87	54.75	52.46	-161.9	-83.4
5200.00	11.29	88.37	77.63	78.07	55.88	53.59	-162.4	-81.8
5300.00	11.31	88.59	77.83	78.27	57.01	54.72	-162.9	-80.3
5400.00	11.32	88.80	78.03	78.46	58.14	55.85	-163.4	-78.7
5500.00	11.33	89.01	78.23	78.65	59.28	56.99	-163.9	-77.1
5600.00	11.35	89.22	78.43	78.84	60.41	58.13	-164.4	-75.5
5700.00	11.36	89.42	78.62	79.02	61.55	59.26	-164.9	-74.0
5800.00	11.38	89.62	78.81	79.20	62.69	60.40	-165.4	-72.4
5900.00	11.39	89.81	78.99	79.38	63.83	61.54	-165.8	-70.7
6000.00	11.41	90.00	79.17	79.55	64.97	62.69	-166.3	-69.1

TABLE B.2. Thermodynamic Functions for ThO₂(g): Units for Columns 2-5 are cal K⁻¹ mol⁻¹ and for Columns 6-9 are kcal mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-2.79	-107.4	-107.4
298.15	11.15	67.00	57.65	67.00	2.79	0.0	-108.3	-109.8
300.00	11.17	67.07	57.71	67.00	2.81	0.02	-108.3	-109.8
400.00	12.05	70.41	60.48	67.45	3.97	1.18	-108.5	-110.3
500.00	12.67	73.17	62.75	68.33	5.21	2.42	-108.7	-110.8
600.00	13.16	75.53	64.69	69.34	6.50	3.71	-108.8	-111.2
700.00	13.56	77.59	66.39	70.37	7.84	5.05	-109.0	-111.6
800.00	13.89	79.42	67.90	71.39	9.21	6.42	-109.2	-111.9
900.00	14.16	81.07	69.28	72.37	10.62	7.83	-109.4	-112.2
1000.00	14.40	82.58	70.53	73.32	12.04	9.26	-109.5	-112.5
1100.00	14.59	83.96	71.69	74.23	13.49	10.70	-109.7	-112.8
1200.00	14.76	85.24	72.77	75.09	14.96	12.17	-109.9	-113.1
1300.00	14.90	86.42	73.77	75.92	16.44	13.66	-110.2	-113.4
1400.00	15.02	87.53	74.71	76.71	17.94	15.15	-110.4	-113.6
1500.00	15.12	88.57	75.60	77.46	19.45	16.66	-110.6	-113.8
1600.00	15.21	89.55	76.45	78.19	20.97	18.18	-110.9	-114.0
1700.00	15.29	90.47	77.24	78.88	22.49	19.70	-112.0	-114.2
1800.00	15.36	91.35	78.00	79.55	24.02	21.23	-112.2	-114.3
1900.00	15.42	92.18	78.73	80.20	25.56	22.77	-112.5	-114.4
2000.00	15.47	92.97	79.42	80.81	27.11	24.32	-112.7	-114.5
2100.00	15.51	93.73	80.08	81.41	28.66	25.87	-116.5	-114.5
2200.00	15.56	94.45	80.72	81.99	30.21	27.42	-116.9	-114.4
2300.00	15.59	95.15	81.33	82.55	31.77	28.98	-117.4	-114.2
2400.00	15.63	95.81	81.92	83.08	33.33	30.54	-117.8	-114.1
2500.00	15.66	96.45	82.49	83.61	34.89	32.10	-118.3	-113.9
2600.00	15.69	97.06	83.04	84.11	36.46	33.67	-118.8	-113.7
2700.00	15.71	97.66	83.57	84.60	38.03	35.24	-119.2	-113.5
2800.00	15.73	98.23	84.08	85.08	39.60	36.81	-119.7	-113.3
2900.00	15.76	98.78	84.58	85.54	41.18	38.39	-120.2	-113.1
3000.00	15.78	99.32	85.06	85.99	42.75	39.97	-120.7	-112.8
3100.00	15.79	99.83	85.53	86.43	44.33	41.54	-121.1	-112.5
3200.00	15.81	100.34	85.99	86.86	45.91	43.13	-121.6	-112.3
3300.00	15.83	100.82	86.43	87.27	47.50	44.71	-122.1	-112.0
3400.00	15.84	101.29	86.86	87.68	49.08	46.29	-122.6	-111.6
3500.00	15.86	101.75	87.28	88.07	50.67	47.88	-123.1	-111.3
3600.00	15.87	102.20	87.69	88.46	52.25	49.46	-123.6	-111.0
3700.00	15.89	102.64	88.08	88.84	53.84	51.05	-124.1	-110.6
3800.00	15.90	103.06	88.47	89.21	55.43	52.64	-124.6	-110.3
3900.00	15.91	103.47	88.85	89.57	57.02	54.23	-125.1	-109.9
4000.00	15.92	103.88	89.22	89.92	58.61	55.82	-125.6	-109.5
4100.00	15.94	104.27	89.58	90.26	60.21	57.42	-126.1	-109.1
4200.00	15.95	104.65	89.94	90.60	61.80	59.01	-126.6	-108.6
4300.00	15.96	105.03	90.29	90.93	63.40	60.61	-127.1	-108.2
4400.00	15.97	105.40	90.62	91.26	64.99	62.21	-127.6	-107.8
4500.00	15.98	105.76	90.96	91.58	66.59	63.80	-128.1	-107.3
4600.00	15.99	106.11	91.28	91.89	68.19	65.40	-128.6	-106.9
4700.00	16.00	106.45	91.60	92.20	69.79	67.00	-129.1	-106.4
4800.00	16.01	106.79	91.91	92.50	71.39	68.60	-129.6	-105.9
4900.00	16.02	107.12	92.22	92.79	72.99	70.20	-130.1	-105.4
5000.00	16.03	107.44	92.52	93.08	74.60	71.81	-265.7	-104.1
5100.00	16.03	107.76	92.82	93.37	76.20	73.41	-266.2	-100.9
5200.00	16.05	108.07	93.11	93.64	77.80	75.01	-266.7	-97.6
5300.00	16.05	108.38	93.39	93.92	79.41	76.62	-267.2	-94.4
5400.00	16.06	108.68	93.67	94.19	81.01	78.22	-267.8	-91.1
5500.00	16.07	108.97	93.95	94.46	82.62	79.83	-268.3	-87.8
5600.00	16.08	109.26	94.22	94.72	84.23	81.44	-268.8	-84.6
5700.00	16.09	109.55	94.49	94.98	85.84	83.05	-269.4	-81.3
5800.00	16.10	109.83	94.75	95.23	87.45	84.66	-269.9	-77.9
5900.00	16.10	110.10	95.01	95.48	89.06	86.27	-270.4	-74.6
6000.00	16.11	110.37	95.26	95.73	90.67	87.88	-270.9	-71.3

TABLE B.3. Thermodynamic Functions for UO(g); Units for Columns 2-5 are cal K⁻¹ mol⁻¹ and for Columns 6-9 are kcal mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	9.0	0.0	INF	INF	0.0	-2.15	5.2	5.2
298.15	8.05	57.59	50.38	57.59	2.15	0.0	4.8	-1.5
300.00	8.07	57.64	50.42	57.59	2.17	0.01	4.8	-1.6
400.00	8.84	60.07	52.54	57.92	3.01	0.86	4.6	-3.6
500.00	9.40	62.11	54.25	58.56	3.93	1.78	4.4	-5.7
600.00	9.78	63.86	55.71	59.30	4.89	2.74	4.2	-7.7
700.00	10.06	65.39	56.99	60.06	5.88	3.73	3.9	-9.6
800.00	10.25	66.74	58.12	60.81	6.90	4.74	3.6	-11.5
900.00	10.39	67.96	59.15	61.54	7.93	5.78	3.1	-13.4
1000.00	10.50	69.06	60.09	62.24	8.97	6.82	2.0	-15.2
1100.00	10.59	70.07	60.95	62.90	10.03	7.88	0.6	-16.8
1200.00	10.65	70.92	61.75	63.54	11.09	8.94	0.3	-18.4
1300.00	10.71	71.85	62.49	64.15	12.16	10.01	0.0	-19.9
1400.00	10.75	72.64	63.19	64.73	13.23	11.08	-0.3	-21.4
1500.00	10.79	73.38	63.84	65.28	14.31	12.16	-3.0	-22.8
1600.00	10.83	74.08	64.46	65.81	15.39	13.24	-3.5	-24.1
1700.00	10.85	74.74	65.05	66.31	16.48	14.32	-4.0	-25.4
1800.00	10.88	75.36	65.60	66.80	17.56	15.41	-4.5	-26.6
1900.00	10.90	75.95	66.13	67.26	18.65	16.50	-5.0	-27.8
2000.00	10.92	76.51	66.64	67.71	19.74	17.59	-5.6	-29.0
2100.00	10.94	77.04	67.12	68.14	20.84	18.69	-6.1	-30.2
2200.00	10.96	77.55	67.58	68.56	21.93	19.78	-6.6	-31.3
2300.00	10.98	78.04	68.03	68.96	23.03	20.88	-7.1	-32.4
2400.00	10.99	78.51	68.45	69.35	24.13	21.98	-7.6	-33.5
2500.00	11.00	78.96	68.87	69.73	25.23	23.08	-8.2	-34.6
2600.00	11.02	79.39	69.26	70.09	26.33	24.18	-8.7	-35.6
2700.00	11.03	79.81	69.64	70.44	27.43	25.28	-9.2	-36.6
2800.00	11.05	80.21	70.02	70.78	28.54	26.39	-9.8	-37.6
2900.00	11.06	80.60	70.37	71.11	29.64	27.49	-10.3	-38.6
3000.00	11.07	80.97	70.72	71.44	30.75	28.60	-10.8	-39.6
3100.00	11.08	81.33	71.06	71.75	31.86	29.71	-11.4	-40.5
3200.00	11.09	81.69	71.38	72.06	32.97	30.82	-11.9	-41.5
3300.00	11.11	82.03	71.70	72.35	34.00	31.93	-12.4	-42.4
3400.00	11.12	82.36	72.01	72.64	35.19	33.04	-13.0	-43.3
3500.00	11.13	82.68	72.31	72.92	36.30	34.15	-13.5	-44.2
3600.00	11.14	83.00	72.60	73.20	37.42	35.27	-14.0	-45.0
3700.00	11.15	83.30	72.89	73.47	38.53	36.38	-14.6	-45.9
3800.00	11.16	83.60	73.17	73.73	39.65	37.50	-15.1	-46.7
3900.00	11.18	83.89	73.44	73.99	40.77	38.62	-15.7	-47.6
4000.00	11.19	84.17	73.70	74.24	41.89	39.73	-16.2	-48.4
4100.00	11.20	84.45	73.96	74.49	43.01	40.85	-16.7	-49.2
4200.00	11.21	84.72	74.21	74.73	44.13	41.98	-17.3	-50.0
4300.00	11.23	84.98	74.46	74.96	45.25	43.10	-17.8	-50.7
4400.00	11.24	85.24	74.70	75.19	46.37	44.22	-18.4	-51.5
4500.00	11.25	85.50	74.94	75.42	47.50	45.35	-189.9	-50.5
4600.00	11.27	85.74	75.17	75.64	48.63	46.48	-136.6	-48.6
4700.00	11.28	85.99	75.40	75.86	49.76	47.60	-137.2	-46.7
4800.00	11.30	86.22	75.62	76.07	50.89	48.73	-137.8	-44.8
4900.00	11.31	86.46	75.84	76.28	52.02	49.87	-138.5	-42.8
5000.00	11.32	86.69	76.06	76.49	53.15	51.00	-139.1	-40.9
5100.00	11.34	86.91	76.27	76.69	54.28	52.13	-139.7	-38.9
5200.00	11.36	87.13	76.47	76.89	55.42	53.27	-140.3	-36.9
5300.00	11.38	87.35	76.68	77.08	56.56	54.41	-140.9	-34.9
5400.00	11.39	87.56	76.88	77.27	57.70	55.55	-141.5	-32.9
5500.00	11.41	87.77	77.07	77.46	58.84	56.69	-142.1	-30.9
5600.00	11.42	87.98	77.27	77.65	59.98	57.83	-142.7	-28.9
5700.00	11.44	88.18	77.46	77.83	61.12	58.97	-143.2	-26.8
5800.00	11.45	88.38	77.64	78.01	62.27	60.11	-143.8	-24.8
5900.00	11.47	88.57	77.83	78.19	63.41	61.26	-144.3	-22.7
6000.00	11.48	88.77	78.01	78.36	64.56	62.41	-144.9	-20.7

TABLE B.4. Thermodynamic Functions for $\text{UO}_2(\text{g})$; Units for Columns 2-5 are $\text{cal K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kcal mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{C_p^\circ - H_f^\circ}{T}\right)$	$-\left(\frac{C_p^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_f^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-3.16	-111.1	-111.1
298.15	13.77	63.66	53.05	63.66	3.16	0.0	-111.5	-112.3
300.00	13.79	63.74	53.11	63.66	3.19	0.03	-111.5	-112.3
400.00	14.79	67.86	56.30	64.21	4.62	1.46	-111.5	-112.6
500.00	15.41	71.23	58.96	65.29	6.14	2.97	-111.4	-112.8
600.00	15.81	74.08	61.25	66.52	7.70	4.53	-111.4	-113.1
700.00	16.08	76.54	63.26	67.78	9.29	6.13	-111.5	-113.4
800.00	16.27	78.70	65.06	69.02	10.91	7.75	-111.6	-113.7
900.00	16.40	80.63	66.69	70.20	12.55	9.38	-111.8	-113.9
1000.00	16.51	82.36	68.17	71.33	14.19	11.03	-112.7	-114.1
1100.00	16.58	83.94	69.53	72.41	15.85	12.68	-114.0	-114.2
1200.00	16.65	85.39	70.79	73.43	17.51	14.35	-114.1	-114.2
1300.00	16.70	86.72	71.97	74.40	19.18	16.01	-114.2	-114.2
1400.00	16.74	87.96	73.07	75.33	20.85	17.69	-114.3	-114.2
1500.00	16.77	89.12	74.10	76.21	22.53	19.36	-116.9	-114.0
1600.00	16.80	90.20	75.07	77.05	24.21	21.04	-117.2	-113.8
1700.00	16.83	91.22	75.99	77.85	25.89	22.73	-117.6	-113.6
1800.00	16.85	92.18	76.86	78.62	27.57	24.41	-117.9	-113.4
1900.00	16.87	93.10	77.69	79.36	29.26	26.10	-118.3	-113.1
2000.00	16.89	93.96	78.49	80.07	30.95	27.79	-118.7	-112.8
2100.00	16.91	94.79	79.24	80.75	32.64	29.48	-119.1	-112.5
2200.00	16.92	95.57	79.97	81.41	34.33	31.17	-119.4	-112.2
2300.00	16.94	96.33	80.66	82.04	36.03	32.86	-119.8	-111.9
2400.00	16.95	97.05	81.33	82.65	37.72	34.56	-120.2	-111.5
2500.00	16.97	97.74	81.97	83.24	39.42	36.26	-120.6	-111.2
2600.00	16.98	98.41	82.59	83.81	41.12	37.96	-121.0	-110.8
2700.00	16.99	99.05	83.19	84.36	42.82	39.65	-121.4	-110.4
2800.00	17.00	99.67	83.77	84.90	44.52	41.36	-121.8	-109.9
2900.00	17.02	100.27	84.33	85.42	46.22	43.06	-122.2	-109.5
3000.00	17.03	100.84	84.87	85.92	47.93	44.76	-122.6	-109.1
3100.00	17.04	101.40	85.39	86.41	49.63	46.47	-123.1	-108.6
3200.00	17.05	101.94	85.90	86.89	51.34	48.17	-123.5	-108.1
3300.00	17.06	102.47	86.40	87.35	53.04	49.88	-123.9	-107.7
3400.00	17.07	102.98	86.88	87.81	54.75	51.59	-124.3	-107.2
3500.00	17.08	103.48	87.34	88.25	56.46	53.30	-124.8	-106.6
3600.00	17.09	103.96	87.80	88.68	58.17	55.01	-125.2	-106.1
3700.00	17.11	104.43	88.24	89.10	59.88	56.72	-125.6	-105.6
3800.00	17.12	104.88	88.67	89.51	61.60	58.43	-126.1	-105.0
3900.00	17.13	105.33	89.09	89.91	63.31	60.15	-126.5	-104.5
4000.00	17.14	105.76	89.51	90.30	65.03	61.86	-126.9	-103.9
4100.00	17.15	106.19	89.91	90.68	66.74	63.58	-127.4	-103.3
4200.00	17.16	106.60	90.30	91.05	68.46	65.30	-127.8	-102.7
4300.00	17.18	107.01	90.68	91.42	70.18	67.02	-128.3	-102.1
4400.00	17.19	107.40	91.06	91.78	71.90	68.74	-128.7	-101.5
4500.00	17.20	107.79	91.43	92.13	73.62	70.46	-246.2	-99.2
4600.00	17.21	108.17	91.79	92.47	75.35	72.18	-246.7	-95.9
4700.00	17.23	108.54	92.14	92.81	77.07	73.91	-247.3	-92.6
4800.00	17.24	108.90	92.48	93.14	78.80	75.63	-247.8	-89.4
4900.00	17.25	109.26	92.82	93.47	80.52	77.36	-248.4	-86.0
5000.00	17.27	109.61	93.16	93.79	82.25	79.09	-248.9	-82.7
5100.00	17.28	109.95	93.48	94.10	83.98	80.82	-249.4	-79.4
5200.00	17.30	110.29	93.80	94.41	85.71	82.55	-249.9	-76.1
5300.00	17.31	110.62	94.12	94.71	87.45	84.28	-250.5	-72.7
5400.00	17.33	110.94	94.42	95.01	89.18	86.02	-251.0	-69.4
5500.00	17.35	111.26	94.73	95.30	90.92	87.76	-251.5	-66.0
5600.00	17.37	111.57	95.03	95.59	92.66	89.50	-251.9	-62.6
5700.00	17.38	111.88	95.32	95.87	94.40	91.24	-252.4	-59.2
5800.00	17.41	112.18	95.61	96.15	96.15	92.98	-252.9	-55.8
5900.00	17.43	112.48	95.89	96.43	97.90	94.73	-253.3	-52.4
6000.00	17.46	112.78	96.17	96.70	99.65	96.49	-253.8	-49.0

TABLE B.5. Thermodynamic Functions for $\text{UO}_3(\text{g})$: Units for Columns 2-5 are $\text{cal K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kcal mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-3.62	-193.2	-190.2
298.15	15.43	74.66	61.85	73.99	3.62	0.0	-191.2	-187.8
300.00	15.46	74.69	61.93	73.99	3.65	0.03	-191.2	-187.8
400.00	16.79	78.73	65.57	74.62	5.26	1.64	-191.4	-186.6
500.00	17.74	82.58	68.60	75.84	6.99	3.37	-191.5	-185.4
600.00	18.44	85.88	71.21	77.24	8.80	5.18	-191.6	-184.2
700.00	18.99	88.77	73.52	78.69	10.68	7.06	-191.8	-182.9
800.00	19.43	91.33	75.58	80.11	12.60	8.98	-192.0	-181.6
900.00	19.79	93.64	77.47	81.49	14.56	10.94	-192.3	-180.3
1000.00	20.08	95.74	79.19	82.81	16.55	12.93	-193.3	-179.0
1100.00	20.32	97.67	80.78	84.07	18.57	14.95	-194.6	-177.5
1200.00	20.52	99.45	82.27	85.28	20.62	17.00	-194.8	-175.9
1300.00	20.68	101.10	83.65	86.44	22.68	19.06	-194.9	-174.3
1400.00	20.82	102.63	84.95	87.54	24.75	21.13	-195.0	-172.7
1500.00	20.95	104.07	86.18	88.59	26.84	23.22	-197.6	-171.0
1600.00	21.05	105.43	87.34	89.60	28.94	25.32	-198.0	-169.2
1700.00	21.14	106.71	88.44	90.57	31.05	27.43	-198.3	-167.4
1800.00	21.22	107.92	89.49	91.50	33.17	29.55	-198.7	-165.5
1900.00	21.28	109.07	90.49	92.40	35.29	31.67	-199.1	-163.7
2000.00	21.34	110.16	91.45	93.26	37.42	33.80	-199.5	-161.8
2100.00	21.39	111.20	92.36	94.09	39.56	35.94	-199.9	-159.9
2200.00	21.44	112.20	93.24	94.89	41.70	38.08	-200.2	-158.0
2300.00	21.48	113.15	94.09	95.66	43.85	40.23	-200.6	-156.1
2400.00	21.52	114.07	94.90	96.41	46.00	42.38	-201.0	-154.1
2500.00	21.55	114.95	95.69	97.13	48.15	44.53	-201.4	-152.2
2600.00	21.58	115.80	96.44	97.84	50.31	46.69	-201.8	-150.2
2700.00	21.61	116.61	97.18	98.52	52.47	48.85	-202.3	-148.2
2800.00	21.64	117.40	97.88	99.18	54.63	51.01	-202.7	-146.2
2900.00	21.66	118.16	98.57	99.82	56.80	53.18	-203.1	-144.2
3000.00	21.68	118.89	99.24	100.44	58.97	55.35	-203.5	-142.1
3100.00	21.70	119.60	99.88	101.05	61.14	57.51	-203.9	-140.1
3200.00	21.72	120.29	100.51	101.64	63.31	59.69	-204.4	-138.0
3300.00	21.74	120.96	101.12	102.21	65.46	61.86	-204.8	-135.9
3400.00	21.75	121.61	101.71	102.78	67.65	64.03	-205.3	-133.8
3500.00	21.77	122.24	102.29	103.32	69.83	66.21	-205.7	-131.7
3600.00	21.78	122.85	102.85	103.86	72.01	68.39	-206.2	-129.6
3700.00	21.80	123.45	103.40	104.38	74.19	70.57	-206.6	-127.5
3800.00	21.81	124.03	103.94	104.89	76.37	72.75	-207.1	-125.3
3900.00	21.82	124.60	104.46	105.39	78.55	74.93	-207.5	-123.2
4000.00	21.83	125.15	104.97	105.87	80.73	77.11	-208.0	-121.0
4100.00	21.85	125.69	105.47	106.35	82.92	79.30	-208.5	-118.8
4200.00	21.86	126.22	105.95	106.82	85.10	81.48	-209.0	-116.6
4300.00	21.86	126.73	106.43	107.27	87.29	83.67	-209.4	-114.4
4400.00	21.88	127.24	106.90	107.72	89.48	85.86	-209.9	-112.2
4500.00	21.88	127.73	107.36	108.16	91.66	88.04	-327.4	-108.3
4600.00	21.89	128.21	107.80	108.59	93.85	90.23	-328.0	-103.4
4700.00	21.90	128.68	108.24	109.01	96.04	92.42	-328.6	-98.5
4800.00	21.91	129.14	108.67	109.43	98.24	94.61	-329.2	-93.6
4900.00	21.92	129.59	109.10	109.84	100.43	96.81	-329.8	-88.7
5000.00	21.93	130.04	109.51	110.24	102.62	99.00	-330.3	-83.8
5100.00	21.94	130.47	109.92	110.63	104.81	101.19	-330.9	-78.8
5200.00	21.94	130.90	110.32	111.01	107.01	103.39	-331.5	-73.9
5300.00	21.95	131.31	110.71	111.39	109.20	105.58	-332.0	-68.9
5400.00	21.96	131.73	111.09	111.77	111.40	107.78	-332.6	-64.0
5500.00	21.97	132.13	111.47	112.13	113.59	109.97	-333.2	-59.0
5600.00	21.97	132.52	111.85	112.49	115.79	112.17	-333.7	-54.0
5700.00	21.98	132.91	112.21	112.85	117.99	114.37	-334.2	-49.0
5800.00	21.99	133.30	112.57	113.20	120.19	116.57	-334.7	-44.0
5900.00	22.00	133.67	112.93	113.54	122.39	118.77	-335.3	-38.9
6000.00	22.00	134.04	113.28	113.88	124.59	120.97	-335.8	-33.9

TABLE B.6. Thermodynamic Functions for PuO(g); Units for Columns 2-5 are cal K⁻¹ mol⁻¹ and for Columns 6-9 are kcal mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-2.42	-21.4	-21.4
298.15	9.33	59.12	51.01	59.12	2.42	0.0	-21.8	-28.1
300.00	9.34	59.18	51.06	59.12	2.43	0.02	-21.8	-28.1
400.00	9.83	61.94	53.45	59.49	3.39	0.98	-22.8	-30.2
500.00	10.15	64.17	55.38	60.21	4.39	1.98	-23.2	-32.0
600.00	10.36	66.04	57.00	61.03	5.42	3.00	-23.5	-33.7
700.00	10.50	67.65	58.41	61.86	6.46	4.05	-23.8	-35.4
800.00	10.61	69.06	59.66	62.68	7.52	5.10	-24.0	-37.0
900.00	10.68	70.31	60.77	63.46	8.59	6.17	-24.2	-38.6
1000.00	10.74	71.44	61.78	64.20	9.66	7.24	-25.6	-40.1
1100.00	10.78	72.47	62.71	64.91	10.73	8.32	-25.9	-41.5
1200.00	10.82	73.41	63.56	65.57	11.82	9.40	-26.3	-42.9
1300.00	10.85	74.27	64.35	66.21	12.90	10.48	-26.6	-44.3
1400.00	10.88	75.08	65.09	66.82	13.99	11.57	-27.0	-45.7
1500.00	10.90	75.83	65.78	67.39	15.08	12.66	-27.4	-47.0
1600.00	10.92	76.54	66.43	67.94	16.17	13.75	-27.7	-48.3
1700.00	10.93	77.20	67.05	68.47	17.26	14.84	-28.1	-49.5
1800.00	10.95	77.82	67.63	68.97	18.35	15.94	-28.4	-50.8
1900.00	10.96	78.42	68.18	69.45	19.45	17.03	-28.8	-52.0
2000.00	10.97	78.98	68.71	69.91	20.55	18.13	-29.1	-53.2
2100.00	10.99	79.52	69.21	70.36	21.65	19.23	-29.5	-54.4
2200.00	11.00	80.03	69.69	70.79	22.75	20.33	-29.9	-55.6
2300.00	11.01	80.52	70.15	71.20	23.85	21.43	-30.2	-56.8
2400.00	11.02	80.99	70.59	71.60	24.95	22.53	-30.6	-57.9
2500.00	11.03	81.44	71.02	71.98	26.06	23.64	-31.0	-59.1
2600.00	11.04	81.87	71.42	72.35	27.16	24.74	-31.4	-60.2
2700.00	11.05	82.29	71.82	72.71	28.27	25.85	-31.7	-61.3
2800.00	11.06	82.69	72.20	73.06	29.37	26.96	-32.1	-62.4
2900.00	11.07	83.08	72.57	73.40	30.48	28.06	-32.5	-63.4
3000.00	11.08	83.46	72.93	73.73	31.59	29.17	-32.9	-64.5
3100.00	11.09	83.82	73.27	74.05	32.70	30.28	-33.2	-65.5
3200.00	11.10	84.17	73.61	74.36	33.81	31.39	-33.6	-66.6
3300.00	11.11	84.52	73.93	74.66	34.92	32.50	-34.0	-67.6
3400.00	11.12	84.85	74.25	74.96	36.03	33.62	-34.4	-68.6
3500.00	11.13	85.17	74.56	75.25	37.15	34.73	-34.8	-69.6
3600.00	11.14	85.48	74.86	75.53	38.26	35.85	-35.1	-70.6
3700.00	11.15	85.79	75.15	75.80	39.38	36.96	-119.2	-69.4
3800.00	11.16	86.09	75.43	76.07	40.50	38.08	-120.0	-68.0
3900.00	11.16	86.38	75.71	76.33	41.61	39.20	-120.8	-66.7
4000.00	11.18	86.66	75.98	76.58	42.73	40.32	-121.7	-65.3
4100.00	11.19	86.94	76.24	76.83	43.85	41.44	-122.5	-63.8
4200.00	11.20	87.21	76.50	77.08	44.97	42.56	-123.4	-62.4
4300.00	11.21	87.47	76.75	77.31	46.10	43.68	-124.2	-60.9
4400.00	11.22	87.73	77.00	77.55	47.22	44.80	-125.1	-59.5
4500.00	11.23	87.98	77.24	77.78	48.34	45.93	-125.9	-58.0
4600.00	11.24	88.23	77.48	78.00	49.47	47.05	-126.8	-56.4
4700.00	11.25	88.47	77.71	78.22	50.60	48.18	-127.6	-54.9
4800.00	11.26	88.71	77.93	78.44	51.72	49.31	-128.5	-53.3
4900.00	11.28	88.94	78.16	78.65	52.85	50.44	-129.3	-51.8
5000.00	11.29	89.17	78.38	78.86	53.98	51.57	-130.2	-50.2
5100.00	11.30	89.40	78.59	79.06	55.12	52.70	-131.0	-48.6
5200.00	11.31	89.62	78.80	79.26	56.25	53.83	-131.8	-47.0
5300.00	11.33	89.83	79.01	79.46	57.38	54.97	-132.6	-45.3
5400.00	11.34	90.05	79.21	79.66	58.52	56.10	-133.4	-43.7
5500.00	11.36	90.25	79.41	79.85	59.66	57.24	-134.1	-42.0
5600.00	11.37	90.46	79.60	80.03	60.80	58.38	-134.9	-40.3
5700.00	11.39	90.66	79.79	80.22	61.94	59.52	-135.6	-38.6
5800.00	11.41	90.86	79.98	80.40	63.08	60.67	-136.3	-36.9
5900.00	11.42	91.06	80.17	80.58	64.23	61.81	-137.0	-35.2
6000.00	11.44	91.25	80.35	80.76	65.38	62.96	-137.7	-33.4

TABLE B.7. Thermodynamic Functions for $\text{PuO}_2(\text{g})$; Units for Columns 2-5 are $\text{cal K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kcal mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-2.91	-111.3	-111.3
299.15	12.84	62.05	52.29	62.05	2.91	0.0	-112.1	-112.0
300.00	12.87	62.13	52.35	62.05	2.93	0.02	-112.1	-112.0
400.00	14.15	66.02	55.30	62.57	4.29	1.38	-113.2	-112.0
500.00	14.95	69.27	57.78	63.60	5.75	2.84	-113.4	-111.6
600.00	15.47	72.05	59.93	64.78	7.27	4.36	-113.7	-111.3
700.00	15.82	74.46	61.84	65.99	8.84	5.93	-113.8	-110.8
800.00	16.06	76.59	63.55	67.19	10.43	7.52	-113.9	-110.4
900.00	16.23	78.45	65.11	68.34	12.04	9.14	-113.9	-109.9
1000.00	16.35	80.21	66.53	69.44	13.67	10.76	-115.2	-109.3
1100.00	16.45	81.77	67.85	70.49	15.31	12.41	-115.4	-108.8
1200.00	16.53	83.21	69.07	71.49	16.96	14.06	-115.6	-108.1
1300.00	16.59	84.53	70.21	72.45	18.62	15.71	-115.8	-107.5
1400.00	16.64	85.76	71.28	73.35	20.28	17.37	-116.0	-106.9
1500.00	16.68	86.91	72.28	74.22	21.95	19.04	-116.2	-106.2
1600.00	16.71	87.99	73.23	75.05	23.62	20.71	-116.4	-105.5
1700.00	16.74	89.01	74.13	75.84	25.29	22.38	-116.6	-104.9
1800.00	16.77	89.96	74.98	76.60	26.97	24.06	-116.9	-104.2
1900.00	16.79	90.87	75.79	77.33	28.65	25.74	-117.1	-103.4
2000.00	16.81	91.73	76.57	78.02	30.33	27.42	-117.3	-102.7
2100.00	16.83	92.55	77.31	78.70	32.01	29.10	-117.6	-102.0
2200.00	16.84	93.34	78.02	79.34	33.69	30.78	-117.8	-101.2
2300.00	16.86	94.09	78.70	79.97	35.38	32.47	-118.0	-100.5
2400.00	16.87	94.80	79.36	80.57	37.06	34.15	-118.3	-99.7
2500.00	16.88	95.49	79.99	81.16	38.75	35.84	-118.5	-98.9
2600.00	16.89	96.16	80.60	81.72	40.44	37.53	-118.8	-98.1
2700.00	16.90	96.79	81.19	82.27	42.13	39.22	-119.0	-97.3
2800.00	16.91	97.41	81.76	82.80	43.82	40.91	-119.3	-96.5
2900.00	16.92	98.00	82.31	83.31	45.51	42.60	-119.6	-95.7
3000.00	16.93	98.58	82.84	83.81	47.21	44.30	-119.8	-94.9
3100.00	16.94	99.13	83.36	84.30	48.90	45.99	-120.1	-94.0
3200.00	16.94	99.67	83.86	84.77	50.60	47.69	-120.4	-93.2
3300.00	16.95	100.19	84.36	85.23	52.29	49.30	-120.7	-92.3
3400.00	16.96	100.70	84.82	85.67	53.99	51.08	-121.0	-91.5
3500.00	16.97	101.19	85.28	86.11	55.68	52.78	-121.2	-90.6
3600.00	16.97	101.67	85.73	86.54	57.38	54.47	-121.5	-89.7
3700.00	16.98	102.13	86.17	86.95	59.08	56.17	-120.5	-86.7
3800.00	16.99	102.59	86.59	87.36	60.78	57.87	-206.2	-83.4
3900.00	16.99	103.03	87.01	87.75	62.48	59.57	-206.9	-80.2
4000.00	17.00	103.46	87.41	88.14	64.18	61.27	-207.7	-76.9
4100.00	17.01	103.88	87.81	88.52	65.88	62.97	-208.5	-73.7
4200.00	17.01	104.29	88.20	88.89	67.58	64.67	-209.2	-70.4
4300.00	17.02	104.69	88.58	89.25	69.28	66.38	-210.0	-67.0
4400.00	17.02	105.08	88.95	89.61	70.99	68.08	-210.8	-63.7
4500.00	17.03	105.46	89.31	89.96	72.69	69.78	-211.6	-60.4
4600.00	17.04	105.84	89.67	90.30	74.40	71.49	-212.4	-57.0
4700.00	17.04	106.21	90.01	90.63	76.10	73.19	-213.1	-53.6
4800.00	17.05	106.56	90.35	90.96	77.81	74.90	-213.9	-50.2
4900.00	17.05	106.92	90.69	91.28	79.51	76.60	-214.7	-46.8
5000.00	17.06	107.26	91.02	91.60	81.22	78.31	-215.4	-43.4
5100.00	17.07	107.60	91.34	91.91	82.93	80.02	-216.2	-39.9
5200.00	17.07	107.93	91.65	92.21	84.63	81.72	-216.9	-36.4
5300.00	17.08	108.26	91.96	92.51	86.34	83.43	-217.7	-33.0
5400.00	17.08	108.58	92.27	92.81	88.05	85.14	-218.4	-29.5
5500.00	17.09	108.89	92.57	93.10	89.76	86.85	-219.1	-26.0
5600.00	17.10	109.20	92.86	93.38	91.47	88.56	-219.8	-22.5
5700.00	17.10	109.50	93.15	93.66	93.18	90.27	-220.5	-18.9
5800.00	17.11	109.80	93.44	93.94	94.89	91.98	-221.1	-15.4
5900.00	17.11	110.09	93.72	94.21	96.61	93.70	-221.8	-11.8
6000.00	17.12	110.38	93.99	94.48	98.32	95.41	-222.4	-8.2

TABLE B.8. Thermodynamic Functions for ThO(g); Units for Columns 2-5 are J K⁻¹ mol⁻¹ and for Columns 6-9 are kJ mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-9.6	-20.5	-20.5
298.15	37.17	243.5	211.4	243.5	9.6	0.0	-21.8	-47.9
300.00	37.23	243.8	211.6	243.5	9.6	0.1	-21.8	-48.1
400.00	39.78	254.8	221.1	245.0	13.5	3.9	-22.2	-56.8
500.00	41.47	263.9	228.8	247.9	17.6	8.0	-22.5	-65.4
600.00	42.59	271.6	235.3	251.2	21.8	12.2	-22.9	-73.9
700.00	43.37	278.2	241.0	254.6	26.1	16.5	-23.3	-82.4
800.00	43.92	284.0	246.0	257.9	30.4	20.9	-23.7	-90.8
900.00	44.31	289.2	250.5	261.1	34.9	25.3	-24.2	-99.2
1000.00	44.62	293.9	254.6	264.2	39.3	29.7	-24.7	-107.5
1100.00	44.86	298.2	258.4	267.1	43.8	34.2	-25.4	-115.7
1200.00	45.05	302.1	261.9	269.8	48.3	38.7	-26.1	-123.9
1300.00	45.20	305.7	265.1	272.5	52.8	43.2	-26.9	-132.0
1400.00	45.34	309.1	268.1	275.0	57.3	47.8	-27.8	-140.1
1500.00	45.44	312.2	271.0	277.3	61.9	52.3	-28.8	-148.1
1600.00	45.54	315.1	273.6	279.6	66.4	56.8	-29.8	-156.0
1700.00	45.63	317.9	276.2	281.8	71.0	61.4	-34.3	-163.7
1800.00	45.70	320.5	278.6	283.9	75.5	66.0	-35.3	-171.3
1900.00	45.77	323.0	280.8	285.9	80.1	70.5	-36.4	-178.8
2000.00	45.83	325.3	283.0	287.8	84.7	75.1	-37.6	-186.3
2100.00	45.89	327.6	285.1	289.6	89.3	79.7	-53.1	-193.2
2200.00	45.94	329.7	287.0	291.4	93.9	84.3	-55.0	-199.8
2300.00	45.99	331.8	288.9	293.1	98.5	88.9	-57.0	-206.3
2400.00	46.04	333.7	290.8	294.8	103.1	93.5	-58.9	-212.8
2500.00	46.08	335.6	292.5	296.4	107.7	98.1	-60.8	-219.1
2600.00	46.13	337.4	294.2	297.9	112.3	102.7	-62.8	-225.4
2700.00	46.18	339.2	295.9	299.4	116.9	107.4	-64.7	-231.6
2800.00	46.22	340.8	297.4	300.8	121.5	112.0	-66.7	-237.8
2900.00	46.26	342.5	299.0	302.3	126.2	116.6	-68.6	-243.9
3000.00	46.30	344.0	300.4	303.6	130.8	121.2	-70.6	-249.9
3100.00	46.34	345.6	301.9	304.9	135.4	125.9	-72.6	-255.8
3200.00	46.38	347.0	303.3	306.2	140.1	130.5	-74.5	-261.7
3300.00	46.42	348.5	304.6	307.5	144.7	135.2	-76.5	-267.5
3400.00	46.46	349.8	305.9	308.7	149.4	139.8	-78.5	-273.3
3500.00	46.50	351.2	307.2	309.9	154.0	144.5	-80.5	-279.0
3600.00	46.54	352.5	308.4	311.1	158.7	149.1	-82.5	-284.6
3700.00	46.58	353.8	309.6	312.2	163.3	153.8	-84.5	-290.2
3800.00	46.62	355.0	310.8	313.3	168.0	158.4	-86.5	-295.7
3900.00	46.66	356.2	312.0	314.4	172.7	163.1	-88.5	-301.2
4000.00	46.70	357.4	313.1	315.5	177.4	167.8	-90.5	-306.6
4100.00	46.75	358.6	314.2	316.5	182.0	172.5	-92.5	-312.0
4200.00	46.78	359.7	315.2	317.5	186.7	177.1	-94.5	-317.4
4300.00	46.83	360.8	316.3	318.5	191.4	181.8	-96.5	-322.7
4400.00	46.87	361.9	317.3	319.5	196.1	186.5	-98.5	-327.9
4500.00	46.91	362.9	318.3	320.4	200.8	191.2	-100.5	-333.1
4600.00	46.96	364.0	319.3	321.4	205.5	195.9	-102.5	-338.2
4700.00	47.01	365.0	320.3	322.3	210.2	200.6	-104.5	-343.3
4800.00	47.05	366.0	321.2	323.2	214.9	205.3	-106.5	-348.4
4900.00	47.10	367.0	322.1	324.1	219.6	210.0	-108.5	-353.4
5000.00	47.15	367.9	323.0	325.0	224.3	214.8	-675.5	-355.2
5100.00	47.20	368.8	323.9	325.8	229.1	219.5	-677.6	-348.8
5200.00	47.25	369.8	324.8	326.6	233.8	224.2	-679.6	-342.3
5300.00	47.30	370.7	325.7	327.5	238.5	229.0	-681.7	-335.8
5400.00	47.36	371.5	326.5	328.3	243.3	233.7	-683.7	-329.3
5500.00	47.41	372.4	327.3	329.1	248.0	238.4	-685.8	-322.7
5600.00	47.47	373.3	328.1	329.8	252.8	243.2	-687.8	-316.1
5700.00	47.54	374.1	328.9	330.6	257.5	248.0	-689.8	-309.4
5800.00	47.60	374.9	329.7	331.4	262.3	252.7	-691.9	-302.7
5900.00	47.67	375.8	330.5	332.1	267.1	257.5	-693.9	-296.0
6000.00	47.74	376.6	331.3	332.9	271.9	262.3	-695.9	-289.2

TABLE B.9. Thermodynamic Functions for $\text{ThO}_2(\text{g})$; Units for Columns 2-5 are $\text{J K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kJ mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-11.7	-449.5	-449.5
298.15	46.65	280.3	241.2	280.3	11.7	0.0	-453.0	-459.5
300.00	46.73	280.6	241.4	280.3	11.8	0.1	-453.0	-459.6
400.00	50.40	294.6	253.0	282.2	16.6	5.0	-453.9	-461.6
500.00	53.03	306.1	262.5	285.9	21.8	10.1	-454.7	-463.5
600.00	55.07	316.0	270.7	290.1	27.2	15.5	-455.4	-465.2
700.00	56.72	324.6	277.8	294.4	32.8	21.1	-456.1	-466.7
800.00	58.10	332.3	284.1	298.7	38.5	26.9	-456.8	-468.2
900.00	59.26	339.2	289.8	302.8	44.4	32.7	-457.5	-469.6
1000.00	60.24	345.5	295.1	306.8	50.4	38.7	-458.3	-470.9
1100.00	61.05	351.3	300.0	310.6	56.5	44.8	-459.1	-472.1
1200.00	61.76	356.6	304.5	314.2	62.6	50.9	-460.0	-473.3
1300.00	62.34	361.6	308.7	317.6	68.8	57.1	-460.9	-474.3
1400.00	62.84	366.2	312.6	320.9	75.1	63.4	-461.8	-475.3
1500.00	63.28	370.6	316.3	324.1	81.4	69.7	-462.9	-476.2
1600.00	63.65	374.7	319.8	327.1	87.7	76.1	-463.9	-477.1
1700.00	63.96	378.5	323.2	330.1	94.1	82.4	-464.5	-477.7
1800.00	64.25	382.2	326.4	332.8	100.5	88.8	-469.4	-478.3
1900.00	64.50	385.7	329.4	335.5	107.0	95.3	-470.5	-478.7
2000.00	64.71	389.0	332.3	338.1	113.4	101.7	-471.7	-479.1
2100.00	64.91	392.2	335.1	340.6	119.9	108.2	-487.3	-478.9
2200.00	65.08	395.2	337.7	343.0	126.4	114.7	-489.2	-478.5
2300.00	65.24	398.1	340.3	345.4	132.9	121.2	-491.1	-478.0
2400.00	65.38	400.9	342.8	347.6	139.4	127.8	-493.1	-477.3
2500.00	65.51	403.5	345.1	349.8	146.0	134.3	-495.0	-476.6
2600.00	65.63	406.1	347.4	351.9	152.6	140.9	-497.0	-475.9
2700.00	65.74	408.6	349.7	354.0	159.1	147.5	-498.9	-475.0
2800.00	65.83	411.0	351.8	356.0	165.7	154.0	-500.9	-474.1
2900.00	65.93	413.3	353.9	357.9	172.3	160.6	-502.9	-473.1
3000.00	66.01	415.5	355.9	359.8	178.9	167.2	-504.9	-472.0
3100.00	66.09	417.7	357.9	361.6	185.5	173.8	-506.9	-470.9
3200.00	66.17	419.8	359.8	363.4	192.1	180.4	-508.9	-469.7
3300.00	66.23	421.8	361.6	365.2	198.7	187.1	-510.9	-468.5
3400.00	66.29	423.8	363.4	366.8	205.4	193.7	-512.9	-467.1
3500.00	66.36	425.7	365.2	368.5	212.0	200.3	-515.0	-465.8
3600.00	66.42	427.6	366.9	370.1	218.6	207.0	-517.0	-464.3
3700.00	66.47	429.4	368.5	371.7	225.3	213.6	-519.1	-462.8
3800.00	66.53	431.2	370.2	373.2	231.9	220.3	-521.2	-461.3
3900.00	66.58	432.9	371.8	374.7	238.6	226.9	-523.2	-459.7
4000.00	66.63	434.6	373.3	376.2	245.2	233.6	-525.3	-458.1
4100.00	66.68	436.3	374.8	377.7	251.9	240.2	-527.4	-456.3
4200.00	66.72	437.9	376.3	379.1	258.6	246.9	-529.5	-454.6
4300.00	66.76	439.4	377.8	380.5	265.3	253.6	-531.6	-452.8
4400.00	66.81	441.0	379.2	381.8	271.9	260.3	-533.8	-450.9
4500.00	66.85	442.5	380.6	383.2	278.6	267.0	-535.9	-449.0
4600.00	66.89	444.0	381.9	384.5	285.3	273.6	-538.0	-447.1
4700.00	66.94	445.4	383.3	385.7	292.0	280.3	-540.2	-445.1
4800.00	66.97	446.8	384.6	387.0	298.7	287.0	-542.3	-443.0
4900.00	67.01	448.2	385.9	388.2	305.4	293.7	-544.4	-440.9
5000.00	67.06	449.5	387.1	389.4	312.1	300.4	-1111.5	-435.6
5100.00	67.09	450.9	388.4	390.6	318.8	307.1	-1113.7	-422.1
5200.00	67.13	452.2	389.6	391.8	325.5	313.9	-1115.9	-408.5
5300.00	67.17	453.5	390.8	393.0	332.2	320.6	-1118.1	-394.9
5400.00	67.20	454.7	391.9	394.1	339.0	327.3	-1120.3	-381.2
5500.00	67.24	455.9	393.1	395.2	345.7	334.0	-1122.5	-367.5
5600.00	67.28	457.2	394.2	396.3	352.4	340.7	-1124.8	-353.8
5700.00	67.31	458.3	395.3	397.4	359.1	347.5	-1127.0	-340.0
5800.00	67.35	459.5	396.4	398.4	365.9	354.2	-1129.2	-326.1
5900.00	67.38	460.7	397.5	399.5	372.6	360.9	-1131.4	-312.2
6000.00	67.41	461.8	398.6	400.5	379.4	367.7	-1133.5	-298.3

TABLE B.10. Thermodynamic Functions for UO(g); Units for Columns 2-5 are J K⁻¹ mol⁻¹ and for Columns 6-9 are kJ mol⁻¹

T(K)	C _p	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	H°-H ₀ °	H°-H ₂₉₈ °	ΔH _f °	ΔG _f °
0.0	0.0	0.0	INF	INF	0.0	-9.0	21.6	21.6
298.15	33.70	241.0	210.8	241.0	9.0	0.0	19.9	-6.4
300.00	33.77	241.2	211.0	241.0	9.1	0.1	19.9	-6.6
400.00	36.97	251.3	219.8	242.3	12.6	3.6	19.1	-15.2
500.00	39.31	259.9	227.0	245.0	16.4	7.4	18.3	-23.7
600.00	40.94	267.2	233.1	248.1	20.4	11.4	17.4	-32.1
700.00	42.08	273.6	238.4	251.3	24.6	15.6	16.3	-40.2
800.00	42.88	279.3	243.2	254.4	28.8	19.8	14.9	-48.2
900.00	43.49	284.3	247.5	257.5	33.2	24.2	13.1	-56.0
1000.00	43.94	288.9	251.4	260.4	37.5	28.5	8.5	-63.4
1100.00	44.30	293.2	255.0	263.2	42.0	33.0	2.4	-70.3
1200.00	44.58	297.0	258.4	265.9	46.4	37.4	1.2	-76.8
1300.00	44.81	300.6	261.5	268.4	50.9	41.9	0.0	-83.3
1400.00	44.99	303.9	264.4	270.8	55.4	46.4	-1.1	-89.7
1500.00	45.15	307.0	267.1	273.1	59.9	50.9	-12.3	-95.3
1600.00	45.29	310.0	269.7	275.3	64.4	55.4	-14.5	-100.8
1700.00	45.41	312.7	272.2	277.5	68.9	59.9	-16.7	-106.1
1800.00	45.52	315.3	274.5	279.5	73.5	64.5	-18.9	-111.3
1900.00	45.62	317.8	276.7	281.4	78.0	69.0	-21.0	-116.4
2000.00	45.70	320.1	278.8	283.3	82.6	73.6	-23.2	-121.4
2100.00	45.78	322.3	280.8	285.1	87.2	78.2	-25.4	-126.2
2200.00	45.85	324.5	282.8	286.9	91.8	82.8	-27.6	-131.0
2300.00	45.92	326.5	284.6	288.5	96.4	87.4	-29.8	-135.6
2400.00	45.99	328.5	286.4	290.2	101.0	92.0	-32.0	-140.2
2500.00	46.04	330.4	288.1	291.7	105.6	96.6	-34.2	-144.6
2600.00	46.10	332.2	289.8	293.3	110.2	101.2	-36.4	-149.0
2700.00	46.16	333.9	291.4	294.7	114.8	105.8	-38.6	-153.3
2800.00	46.21	335.6	292.9	296.2	119.4	110.4	-40.8	-157.5
2900.00	46.27	337.2	294.4	297.5	124.0	115.0	-43.1	-161.6
3000.00	46.32	338.8	295.9	298.9	128.7	119.7	-45.3	-165.6
3100.00	46.36	340.3	297.3	300.2	133.3	124.3	-47.5	-169.6
3200.00	46.42	341.8	298.7	301.5	137.9	128.9	-49.8	-173.5
3300.00	46.47	343.2	300.0	302.7	142.6	133.6	-52.0	-177.4
3400.00	46.52	344.6	301.3	303.9	147.2	138.2	-54.2	-181.1
3500.00	46.57	345.9	302.5	305.1	151.9	142.9	-56.5	-184.8
3600.00	46.62	347.3	303.8	306.3	156.6	147.6	-58.7	-188.5
3700.00	46.67	348.5	305.0	307.4	161.2	152.2	-61.0	-192.0
3800.00	46.71	349.8	306.1	308.5	165.9	156.9	-63.2	-195.5
3900.00	46.76	351.0	307.3	309.6	170.6	161.6	-65.5	-199.0
4000.00	46.81	352.2	308.4	310.6	175.2	166.2	-67.8	-202.4
4100.00	46.87	353.3	309.5	311.6	179.9	170.9	-70.0	-205.7
4200.00	46.92	354.5	310.5	312.7	184.6	175.6	-72.3	-209.0
4300.00	46.97	355.6	311.5	313.6	189.3	180.3	-74.5	-212.3
4400.00	47.03	356.7	312.6	314.6	194.0	185.0	-76.8	-215.4
4500.00	47.08	357.7	313.5	315.5	198.7	189.7	-568.6	-211.4
4600.00	47.14	358.8	314.5	316.5	203.5	194.5	-571.3	-203.5
4700.00	47.20	359.8	315.5	317.4	208.2	199.2	-574.0	-195.4
4800.00	47.26	360.8	316.4	318.3	212.9	203.9	-576.7	-187.3
4900.00	47.32	361.7	317.3	319.2	217.6	208.6	-579.3	-179.2
5000.00	47.38	362.7	318.2	320.0	222.4	213.4	-582.0	-171.0
5100.00	47.46	363.6	319.1	320.9	227.1	218.1	-584.5	-162.8
5200.00	47.53	364.6	320.0	321.7	231.9	222.9	-587.1	-154.5
5300.00	47.60	365.5	320.8	322.5	236.6	227.6	-589.6	-146.1
5400.00	47.66	366.4	321.7	323.3	241.4	232.4	-592.1	-137.7
5500.00	47.72	367.2	322.5	324.1	246.2	237.2	-594.5	-129.3
5600.00	47.79	368.1	323.3	324.9	250.9	242.0	-596.9	-120.8
5700.00	47.85	368.9	324.1	325.7	255.7	246.7	-599.3	-112.3
5800.00	47.91	369.8	324.9	326.4	260.5	251.5	-601.6	-103.7
5900.00	47.98	370.6	325.6	327.1	265.3	256.3	-603.9	-95.1
6000.00	48.04	371.4	326.4	327.9	270.1	261.1	-606.1	-86.5

TABLE B.11. Thermodynamic Functions for $\text{UO}_2(\text{g})$: Units for Columns 2-5 are $\text{J K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kJ mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-13.2	-464.7	-464.7
298.15	57.61	266.3	221.9	266.3	13.2	0.0	-466.5	-469.8
300.00	57.71	266.7	222.2	266.3	13.3	0.1	-466.5	-469.8
400.00	61.87	283.9	235.6	268.7	19.3	6.1	-466.3	-471.0
500.00	64.49	298.0	246.7	273.2	25.7	12.4	-466.2	-472.2
600.00	66.16	310.0	256.3	278.3	32.2	19.0	-466.1	-473.4
700.00	67.29	320.2	264.7	283.6	38.9	25.6	-466.3	-474.5
800.00	68.07	329.3	272.2	288.8	45.7	32.4	-466.9	-475.7
900.00	68.64	337.3	279.0	293.7	52.5	39.3	-467.8	-476.7
1000.00	69.06	344.6	285.2	298.4	59.4	46.1	-471.7	-477.5
1100.00	69.39	351.2	290.9	303.0	66.3	53.1	-477.1	-477.8
1200.00	69.65	357.3	296.2	307.2	73.3	60.0	-477.5	-477.9
1300.00	69.86	362.8	301.1	311.3	80.2	67.0	-477.9	-477.9
1400.00	70.02	368.0	305.7	315.2	87.2	74.0	-478.4	-477.9
1500.00	70.17	372.9	310.0	318.8	94.3	81.0	-488.9	-477.2
1600.00	70.30	377.4	314.1	322.4	101.3	88.0	-490.4	-476.3
1700.00	70.41	381.7	317.9	325.7	108.3	95.1	-492.0	-475.4
1800.00	70.50	385.7	321.6	329.0	115.4	102.1	-493.5	-474.4
1900.00	70.59	389.5	325.1	332.0	122.4	109.2	-495.0	-473.3
2000.00	70.67	393.1	328.4	335.0	129.5	116.3	-496.6	-472.1
2100.00	70.74	396.6	331.6	337.9	136.6	123.3	-498.2	-470.9
2200.00	70.81	399.9	334.6	340.6	143.7	130.4	-499.8	-469.5
2300.00	70.87	403.0	337.5	343.2	150.7	137.5	-501.4	-468.1
2400.00	70.93	406.1	340.3	345.8	157.8	144.6	-503.0	-466.6
2500.00	70.99	409.0	343.0	348.3	164.9	151.7	-504.7	-465.1
2600.00	71.04	411.7	345.6	350.7	172.0	158.8	-506.3	-463.4
2700.00	71.09	414.4	348.1	353.0	179.2	165.9	-508.0	-461.8
2800.00	71.14	417.0	350.5	355.2	186.3	173.0	-509.7	-460.0
2900.00	71.19	419.5	352.8	357.4	193.4	180.2	-511.4	-458.2
3000.00	71.24	421.9	355.1	359.5	200.5	187.3	-513.1	-456.3
3100.00	71.29	424.3	357.3	361.6	207.7	194.4	-514.9	-454.4
3200.00	71.33	426.5	359.4	363.5	214.8	201.6	-516.6	-452.4
3300.00	71.38	428.7	361.5	365.5	221.9	208.7	-518.4	-450.4
3400.00	71.43	430.9	363.5	367.4	229.1	215.8	-520.2	-448.3
3500.00	71.47	432.9	365.4	369.2	236.2	223.0	-522.0	-446.2
3600.00	71.52	435.0	367.3	371.0	243.4	230.2	-523.8	-444.0
3700.00	71.57	436.9	369.2	372.8	250.6	237.3	-525.6	-441.8
3800.00	71.62	438.8	371.0	374.5	257.7	244.5	-527.4	-439.5
3900.00	71.66	440.7	372.8	376.2	264.9	251.7	-529.2	-437.1
4000.00	71.71	442.5	374.5	377.8	272.1	258.8	-531.1	-434.8
4100.00	71.76	444.3	376.2	379.4	279.3	266.0	-532.9	-432.3
4200.00	71.81	446.0	377.8	381.0	286.4	273.2	-534.8	-429.9
4300.00	71.86	447.7	379.4	382.5	293.6	280.4	-536.6	-427.4
4400.00	71.91	449.4	381.0	384.0	300.8	287.6	-538.5	-424.8
4500.00	71.96	451.0	382.5	385.5	308.0	294.8	-1029.9	-416.1
4600.00	72.02	452.6	384.0	386.9	315.2	302.0	-1032.2	-401.4
4700.00	72.07	454.1	385.5	388.3	322.5	309.2	-1034.5	-387.6
4800.00	72.13	455.6	387.0	389.7	329.7	316.4	-1036.8	-373.9
4900.00	72.19	457.1	388.4	391.1	336.9	323.7	-1039.1	-360.0
5000.00	72.24	458.6	389.8	392.4	344.1	330.9	-1041.3	-346.1
5100.00	72.31	460.0	391.1	393.7	351.4	338.1	-1043.6	-332.2
5200.00	72.37	461.4	392.5	395.0	358.6	345.4	-1045.8	-318.2
5300.00	72.44	462.8	393.8	396.3	365.9	352.6	-1047.9	-304.2
5400.00	72.51	464.2	395.1	397.5	373.1	359.9	-1050.0	-290.2
5500.00	72.58	465.5	396.3	398.7	380.4	367.2	-1052.1	-276.1
5600.00	72.66	466.8	397.6	400.0	387.7	374.5	-1054.2	-261.9
5700.00	72.73	468.1	398.8	401.1	395.0	381.7	-1056.1	-247.8
5800.00	72.82	469.4	400.0	402.3	402.3	389.0	-1058.1	-233.6
5900.00	72.93	470.6	401.2	403.5	409.6	396.4	-1060.0	-219.3
6000.00	73.05	471.9	402.4	404.6	416.9	403.7	-1061.8	-205.0

TABLE B.12. Thermodynamic Functions for $\text{UO}_3(\text{g})$: Units for Columns 2-5 are $\text{J K}^{-1} \text{mol}^{-1}$ and for Columns 6-9 are kJ mol^{-1}

T(K)	C_p°	S°	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$	$-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°
0.0	0.0	0.0	INF	INF	0.0	-15.1	-795.9	-795.9
298.15	64.55	309.6	258.8	309.6	15.1	0.0	-800.1	-785.7
300.00	64.67	310.0	259.1	309.6	15.3	0.1	-800.1	-785.7
400.00	70.23	329.4	274.3	312.2	22.0	6.9	-800.7	-780.8
500.00	74.21	345.5	287.0	317.3	29.3	14.1	-801.1	-775.7
600.00	77.17	359.3	297.9	323.2	36.8	21.7	-801.6	-770.6
700.00	79.46	371.4	307.6	329.2	44.7	29.5	-802.3	-765.3
800.00	81.29	382.1	316.2	335.2	52.7	37.6	-803.2	-760.0
900.00	82.78	391.8	324.1	340.9	60.9	45.8	-804.5	-754.5
1000.00	84.00	400.6	331.3	346.5	69.3	54.1	-808.6	-748.7
1100.00	85.00	408.6	338.0	351.8	77.7	62.6	-814.3	-742.5
1200.00	85.84	416.1	344.2	356.8	86.3	71.1	-814.9	-735.9
1300.00	86.54	423.0	350.0	361.6	94.9	79.7	-815.5	-729.3
1400.00	87.13	429.4	355.4	366.3	103.6	88.4	-816.0	-722.7
1500.00	87.64	435.4	360.6	370.7	112.3	97.2	-826.7	-715.3
1600.00	88.07	441.1	365.4	374.9	121.1	105.9	-828.3	-707.9
1700.00	88.44	446.5	370.0	379.0	129.9	114.8	-829.8	-700.3
1800.00	88.77	451.5	374.4	382.8	138.8	123.6	-831.4	-692.6
1900.00	89.05	456.3	378.6	386.6	147.7	132.5	-833.0	-684.9
2000.00	89.29	460.9	382.6	390.2	156.6	141.4	-834.6	-677.0
2100.00	89.51	465.3	386.5	393.7	165.5	150.4	-836.2	-669.1
2200.00	89.71	469.4	390.1	397.0	174.5	159.3	-837.8	-661.1
2300.00	89.87	473.4	393.7	400.3	183.5	168.3	-839.5	-653.1
2400.00	90.04	477.3	397.1	403.4	192.5	177.3	-841.1	-644.9
2500.00	90.18	480.9	400.4	406.4	201.5	186.3	-842.8	-636.7
2600.00	90.30	484.5	403.5	409.3	210.5	195.4	-844.5	-628.4
2700.00	90.42	487.9	406.6	412.2	219.5	204.4	-846.2	-620.1
2800.00	90.53	491.2	409.5	415.0	228.6	213.4	-848.0	-611.6
2900.00	90.62	494.4	412.4	417.6	237.6	222.5	-849.7	-603.2
3000.00	90.72	497.4	415.2	420.2	246.7	231.6	-851.5	-594.6
3100.00	90.80	500.4	417.9	422.8	255.8	240.6	-853.3	-586.0
3200.00	90.87	503.3	420.5	425.3	264.9	249.7	-855.1	-577.4
3300.00	90.95	506.1	423.1	427.7	274.0	258.8	-857.0	-568.7
3400.00	91.01	508.8	425.6	430.0	283.1	267.9	-858.8	-559.9
3500.00	91.08	511.5	428.0	432.3	292.2	277.0	-860.7	-551.1
3600.00	91.14	514.0	430.3	434.5	301.3	286.1	-862.6	-542.2
3700.00	91.19	516.5	432.6	436.7	310.4	295.3	-864.5	-533.3
3800.00	91.25	519.0	434.9	438.9	319.5	304.4	-866.4	-524.3
3900.00	91.30	521.3	437.1	440.9	328.7	313.5	-868.3	-515.3
4000.00	91.35	523.6	439.2	443.0	337.8	322.6	-870.3	-506.2
4100.00	91.40	525.9	441.3	445.0	346.9	331.8	-872.3	-497.1
4200.00	91.44	528.1	443.3	446.9	356.1	340.9	-874.2	-488.0
4300.00	91.48	530.3	445.3	448.8	365.2	350.1	-876.2	-478.7
4400.00	91.53	532.4	447.3	450.7	374.4	359.2	-878.3	-469.5
4500.00	91.57	534.4	449.2	452.5	383.5	368.4	-1369.8	-453.0
4600.00	91.60	536.4	451.1	454.3	392.7	377.5	-1372.3	-432.6
4700.00	91.64	538.4	452.9	456.1	401.8	386.7	-1374.8	-412.2
4800.00	91.68	540.3	454.7	457.8	411.0	395.9	-1377.2	-391.7
4900.00	91.71	542.2	456.5	459.6	420.2	405.0	-1379.7	-371.1
5000.00	91.75	544.1	458.2	461.2	429.4	414.2	-1382.1	-350.5
5100.00	91.78	545.9	459.9	462.9	438.5	423.4	-1384.5	-329.9
5200.00	91.81	547.7	461.6	464.5	447.7	432.6	-1386.9	-309.2
5300.00	91.85	549.4	463.2	466.1	456.9	441.8	-1389.3	-288.4
5400.00	91.88	551.1	464.8	467.6	466.1	450.9	-1391.6	-267.6
5500.00	91.90	552.8	466.4	469.2	475.3	460.1	-1393.9	-246.8
5600.00	91.94	554.5	468.0	470.7	484.5	469.3	-1396.2	-225.9
5700.00	91.97	556.1	469.5	472.2	493.7	478.5	-1398.4	-204.9
5800.00	91.99	557.7	471.0	473.6	502.9	487.7	-1400.6	-184.0
5900.00	92.03	559.3	472.5	475.1	512.1	496.9	-1402.7	-162.9
6000.00	92.06	560.8	473.9	476.5	521.3	506.1	-1404.8	-141.9

TABLE B.13. Thermodynamic Functions for PuO(g); Units for Columns 2-5 are J K⁻¹ mol⁻¹ and for Columns 6-9 are kJ mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-10.1	-89.6	-89.6
298.15	39.03	247.4	213.4	247.4	10.1	0.0	-91.0	-117.4
300.00	39.07	247.6	213.6	247.4	10.2	0.1	-91.0	-117.6
400.00	41.11	259.1	223.6	248.9	14.2	4.1	-95.5	-126.3
500.00	42.45	268.5	231.7	251.9	18.4	8.3	-96.9	-133.9
600.00	43.34	276.3	238.5	255.4	22.7	12.6	-98.4	-141.2
700.00	43.95	283.0	244.4	258.8	27.0	16.9	-99.4	-148.2
800.00	44.37	288.9	249.6	262.2	31.5	21.4	-100.4	-155.0
900.00	44.69	294.2	254.3	265.5	35.9	25.8	-101.3	-161.6
1000.00	44.94	298.9	258.5	268.6	40.4	30.3	-107.0	-167.8
1100.00	45.12	303.2	262.4	271.6	44.9	34.8	-108.5	-173.8
1200.00	45.27	307.1	265.9	274.4	49.4	39.3	-110.0	-179.6
1300.00	45.39	310.8	269.2	277.0	54.0	43.9	-111.5	-185.4
1400.00	45.50	314.1	272.3	279.6	58.5	48.4	-112.0	-191.0
1500.00	45.59	317.3	275.2	282.0	63.1	53.0	-114.4	-196.5
1600.00	45.67	320.2	277.9	284.3	67.6	57.5	-115.9	-201.9
1700.00	45.75	323.1	280.5	286.5	72.2	62.1	-117.4	-207.3
1800.00	45.81	325.6	283.0	288.6	76.8	66.7	-118.9	-212.5
1900.00	45.87	328.1	285.3	290.6	81.4	71.3	-120.4	-217.7
2000.00	45.92	330.5	287.5	292.5	86.0	75.9	-122.0	-222.8
2100.00	45.97	332.7	289.6	294.4	90.6	80.5	-123.5	-227.8
2200.00	46.02	334.8	291.6	296.2	95.2	85.1	-125.0	-232.7
2300.00	46.07	336.9	293.5	297.9	99.8	89.7	-126.5	-237.5
2400.00	46.11	338.9	295.4	299.6	104.4	94.3	-128.1	-242.3
2500.00	46.15	340.7	297.1	301.2	109.0	98.9	-129.6	-247.1
2600.00	46.19	342.6	298.8	302.7	113.6	103.5	-131.2	-251.7
2700.00	46.24	344.3	300.5	304.2	118.3	108.2	-132.8	-256.3
2800.00	46.27	346.0	302.1	305.7	122.9	112.8	-134.3	-260.9
2900.00	46.32	347.6	303.6	307.1	127.5	117.4	-135.9	-265.4
3000.00	46.35	349.2	305.1	308.5	132.2	122.1	-137.5	-269.8
3100.00	46.40	350.7	306.6	309.8	136.8	126.7	-139.1	-274.2
3200.00	46.43	352.2	308.0	311.1	141.5	131.3	-140.7	-278.5
3300.00	46.47	353.6	309.3	312.4	146.1	136.0	-142.3	-282.8
3400.00	46.51	355.0	310.7	313.6	150.8	140.7	-143.9	-287.1
3500.00	46.55	356.4	311.9	314.8	155.4	145.3	-145.5	-291.3
3600.00	46.60	357.7	313.2	316.0	160.1	150.0	-147.1	-295.4
3700.00	46.63	358.9	314.4	317.1	164.8	154.6	-148.6	-299.3
3800.00	46.68	360.2	315.6	318.3	169.4	159.3	-150.2	-303.7
3900.00	46.71	361.4	316.8	319.4	174.1	164.0	-151.5	-307.9
4000.00	46.76	362.6	317.9	320.4	178.8	168.7	-152.9	-312.1
4100.00	46.80	363.8	319.0	321.5	183.5	173.4	-154.2	-316.1
4200.00	46.84	364.9	320.1	322.5	188.2	178.1	-155.6	-320.1
4300.00	46.89	366.0	321.1	323.5	192.9	182.7	-156.9	-324.0
4400.00	46.94	367.1	322.2	324.5	197.6	187.5	-158.3	-327.9
4500.00	46.90	368.1	323.2	325.4	202.3	192.2	-159.6	-331.8
4600.00	47.03	369.2	324.2	326.4	207.0	196.9	-160.9	-335.7
4700.00	47.08	370.2	325.1	327.3	211.7	201.6	-162.2	-339.6
4800.00	47.13	371.2	326.1	328.2	216.4	206.3	-163.5	-343.5
4900.00	47.18	372.1	327.0	329.1	221.1	211.0	-164.8	-347.4
5000.00	47.23	373.1	327.9	329.9	225.9	215.8	-166.1	-351.3
5100.00	47.28	374.0	328.8	330.8	230.6	220.5	-167.4	-355.2
5200.00	47.34	375.0	329.7	331.6	235.3	225.2	-168.7	-359.1
5300.00	47.40	375.9	330.6	332.5	240.1	230.0	-169.9	-363.0
5400.00	47.46	376.8	331.4	333.3	244.9	234.7	-171.2	-366.9
5500.00	47.52	377.6	332.2	334.1	249.6	239.5	-172.5	-370.8
5600.00	47.58	378.5	333.1	334.9	254.4	244.3	-173.8	-374.7
5700.00	47.65	379.3	333.9	335.6	259.2	249.0	-175.1	-378.6
5800.00	47.72	380.2	334.7	336.4	263.9	253.8	-176.4	-382.5
5900.00	47.80	381.0	335.4	337.1	268.7	258.6	-177.7	-386.4
6000.00	47.88	381.8	336.2	337.9	273.5	263.4	-179.0	-390.3

TABLE B.14. Thermodynamic Functions for PuO₂(g); Units for Columns 2-5 are J K⁻¹ mol⁻¹ and for Columns 6-9 are kJ mol⁻¹

T(K)	C _p ^o	S ^o	$-\left(\frac{G^o-H_0^o}{T}\right)$	$-\left(\frac{G^o-H_{298}^o}{T}\right)$	H ^o -H ₀ ^o	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o
0.0	0.0	0.0	INF	INF	0.0	-12.2	-465.5	-465.5
298.15	53.73	259.6	218.8	259.6	12.2	0.0	-469.2	-468.7
300.00	53.85	260.0	219.0	259.6	12.3	0.1	-469.2	-468.7
400.00	59.18	276.2	231.4	261.8	17.9	5.8	-473.5	-468.4
500.00	62.56	289.8	241.7	266.1	24.0	11.9	-474.5	-467.0
600.00	64.73	301.5	250.8	271.0	30.4	18.2	-475.6	-465.5
700.00	66.17	311.5	258.7	276.1	37.0	24.8	-476.0	-463.8
800.00	67.18	320.5	265.9	281.1	43.6	31.5	-476.4	-461.9
900.00	67.89	328.4	272.4	285.9	50.4	38.2	-476.7	-459.9
1000.00	68.43	335.6	278.4	290.5	57.2	45.0	-481.8	-457.5
1100.00	68.83	342.1	283.9	294.9	64.1	51.9	-482.7	-455.0
1200.00	69.15	348.1	289.0	299.1	71.0	58.8	-483.6	-452.5
1300.00	69.40	353.7	293.8	303.1	77.9	65.7	-484.5	-449.9
1400.00	69.61	358.8	298.2	306.9	84.9	72.7	-485.3	-447.2
1500.00	69.78	363.6	302.4	310.5	91.8	79.7	-486.3	-444.4
1600.00	69.93	368.2	306.4	314.0	98.8	86.6	-487.2	-441.6
1700.00	70.05	372.4	310.2	317.3	105.8	93.6	-488.1	-438.7
1800.00	70.16	376.4	313.7	320.5	112.8	100.7	-489.0	-435.8
1900.00	70.25	380.2	317.1	323.5	119.9	107.7	-489.9	-432.8
2000.00	70.33	383.8	320.4	326.5	126.9	114.7	-490.9	-429.8
2100.00	70.40	387.2	323.5	329.3	133.9	121.8	-491.9	-426.7
2200.00	70.47	390.5	326.4	332.0	141.0	128.8	-492.9	-423.6
2300.00	70.52	393.7	329.3	334.6	148.0	135.8	-493.9	-420.4
2400.00	70.58	396.7	332.0	337.1	155.1	142.9	-494.9	-417.2
2500.00	70.63	399.5	334.7	339.6	162.1	150.0	-496.0	-413.9
2600.00	70.67	402.3	337.2	341.9	169.2	157.0	-497.0	-410.6
2700.00	70.71	405.0	339.7	344.2	176.3	164.1	-498.1	-407.2
2800.00	70.75	407.6	342.1	346.4	183.4	171.2	-499.2	-403.9
2900.00	70.79	410.0	344.4	348.6	190.4	178.3	-500.3	-400.4
3000.00	70.83	412.4	346.6	350.7	197.5	185.3	-501.4	-397.0
3100.00	70.86	414.8	348.8	352.7	204.6	192.4	-502.6	-393.5
3200.00	70.89	417.0	350.9	354.7	211.7	199.5	-503.7	-389.9
3300.00	70.92	419.2	352.9	356.6	218.8	206.6	-504.9	-386.3
3400.00	70.96	421.3	354.9	358.5	225.9	213.7	-506.1	-382.7
3500.00	70.98	423.4	356.8	360.3	233.0	220.8	-507.3	-379.1
3600.00	71.01	425.4	358.7	362.1	240.1	227.9	-508.5	-375.4
3700.00	71.04	427.3	360.5	363.8	247.2	235.0	-509.7	-362.5
3800.00	71.07	429.2	362.3	365.5	254.3	242.1	-510.9	-349.1
3900.00	71.10	431.1	364.0	367.2	261.4	249.2	-512.1	-335.5
4000.00	71.13	432.9	365.7	368.8	268.5	256.4	-513.3	-321.9
4100.00	71.16	434.6	367.4	370.4	275.6	263.5	-514.5	-308.2
4200.00	71.18	436.3	369.0	371.9	282.8	270.6	-515.7	-294.4
4300.00	71.21	438.0	370.6	373.4	289.9	277.7	-516.9	-280.5
4400.00	71.23	439.7	372.2	374.9	297.0	284.8	-518.1	-266.6
4500.00	71.26	441.3	373.7	376.4	304.1	292.0	-519.3	-252.6
4600.00	71.28	442.8	375.2	377.8	311.3	299.1	-520.5	-238.5
4700.00	71.31	444.4	376.6	379.2	318.4	306.2	-521.7	-224.3
4800.00	71.33	445.9	378.0	380.6	325.5	313.4	-522.9	-210.1
4900.00	71.36	447.3	379.4	381.9	332.7	320.5	-524.1	-195.8
5000.00	71.38	448.8	380.8	383.2	339.8	327.6	-525.3	-181.4
5100.00	71.40	450.2	382.2	384.5	347.0	334.8	-526.5	-167.0
5200.00	71.43	451.6	383.5	385.8	354.1	341.9	-527.7	-152.5
5300.00	71.45	452.9	384.8	387.1	361.3	349.1	-528.9	-137.9
5400.00	71.48	454.3	386.1	388.3	368.4	356.2	-530.1	-123.3
5500.00	71.50	455.6	387.3	389.5	375.6	363.4	-531.3	-108.7
5600.00	71.53	456.9	388.5	390.7	382.7	370.5	-532.5	-93.9
5700.00	71.55	458.2	389.7	391.9	389.9	377.7	-533.7	-79.2
5800.00	71.58	459.4	390.9	393.0	397.0	384.9	-534.9	-64.3
5900.00	71.60	460.6	392.1	394.2	404.2	392.0	-536.1	-49.4
6000.00	71.63	461.8	393.3	395.3	411.4	399.2	-537.3	-34.5

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