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VAPOR PRESSURES AND VAPOR COMPOSITIONS
IN EQUILIBRIUM WITH
HYPOSTOICHIOMETRIC URANIUM DIOXIDE
AT HIGH TEMPERATURES

by

David W. Green and Leonard Leibowitz



ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

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**ARGONNE NATIONAL LABORATORY
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Argonne, Illinois 60439**

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Chemical Engineering Division

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June 1981

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VAPOR PRESSURES AND VAPOR COMPOSITIONS IN EQUILIBRIUM
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ABSTRACT

Thermodynamic functions of the gaseous species, thermodynamic functions of the condensed phase, and an oxygen-potential model have been combined to calculate the vapor pressures and vapor compositions in equilibrium with condensed-phase UO_{2-x} for $1500 \leq T \leq 6000$ K and $0 \leq x \leq 0.5$. A method for extending the oxygen-potential model of Blackburn to the liquid region has been derived and evaluated. New thermodynamic functions of the UO_2 condensed phase have been derived from the best available data, including the heat capacity recommended by Fink et al. The Gibbs free energies of formation of liquid and solid UO_{2-x} have been calculated as functions of T and x. Results of these calculations show that the oxygen-to-uranium ratio of the vapor is larger than that of the condensed phase with which it is in equilibrium for most of the ranges of T and x of interest. Near 6000 K the vapor is very oxygen-rich so that the composition of the condensed phase would be changed considerably by even a few percent vaporization. In general, the vapor in equilibrium with UO_{2-x} is poorly approximated as $\text{UO}_2(\text{g})$; the species U, UO , UO_3 , O_2 , or O each have higher partial pressures than UO_2 for some conditions. The calculated total pressure at high temperatures is in good agreement with that recommended by the International Working Group on Fast Reactors (IWGFR).

I. INTRODUCTION

Reactor-safety analyses require thermophysical property data on reactor materials from low temperatures up to about 6000 K. One of the most important properties, the vapor pressure of reactor fuel, has been the subject of considerable investigation for many years. A review by Ackermann, Rauh, and Rand¹ of the data on solid UO_2 shows there is reasonably good agreement among many of the reported studies. Some experimental and theoretical investigations of liquid UO_2 have been reported; however, considerable uncertainty about its properties remains. Pressures over liquid UO_2 have been measured by transpiration² as well as by newly devised pulse techniques.³⁻⁵ Calculations of properties using corresponding states theory,^{6,7} significant structures theory,⁸ and oxygen-potential theories⁹ have also been performed. Most of these studies have failed to allow for the fact that the vapor in equilibrium with UO_2 does not consist simply of UO_2 molecules but is, rather, a complex mixture of various species, including the O, O_2 , U, UO , UO_2 , and UO_3 molecules.

We have adopted a different approach to the determination of the vapor pressures and compositions in equilibrium with a UO_{2-x} condensed phase. Our approach involves statistical-mechanical calculation of the thermodynamic functions for individual molecular species, using molecular energy levels obtained from spectroscopic data. The process consists of several steps, as shown in Fig. 1.

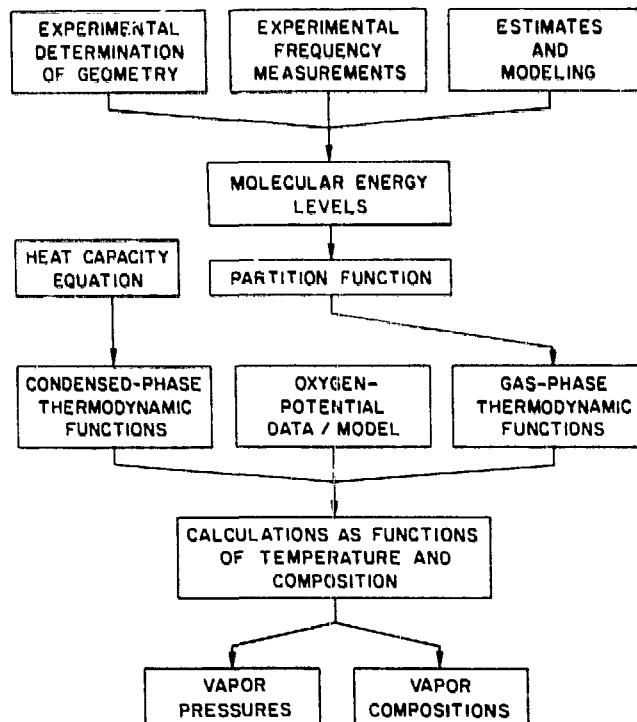


Fig. 1. Scheme for Calculation of Vapor Pressures from Spectroscopic Data

Some experimental data are available for known uranium, plutonium, and thorium oxide vapor species; however, these data are incomplete. When experimental data are not available, estimates and modeling are required for the calculation of thermodynamic functions and vapor pressures. The steps in Fig. 1 leading to gas-phase thermodynamic functions must be followed for each important vapor species. The condensed-phase data and oxygen potentials must be known as functions of composition, and the condensed-phase data, gas-phase data, and oxygen potentials must be known as functions of temperature.

In the following sections we (1) describe the calculational procedures used to obtain the needed information, (2) describe the gas- and condensed-phase thermodynamic functions, (3) extend the oxygen-potential model to the liquid, and (4) give vapor pressures and compositions as functions of temperature and condensed-phase composition. A discussion of the effect of ionization is also given.

II. METHODS

A. General

The total pressure, $p(\text{total})$, in equilibrium with UO_{2-x} condensed phase is the sum of the partial pressures of all vapor species. If we consider the neutral species first (ions are considered in Section II-F) we may write:

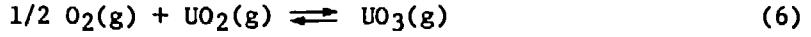
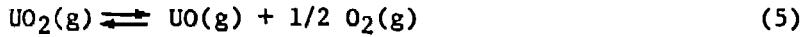
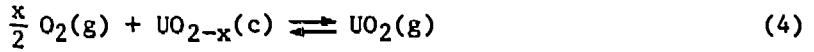
$$p(\text{total}) = p(\text{U}) + p(\text{UO}) + p(\text{UO}_2) + p(\text{UO}_3) + p(\text{O}) + p(\text{O}_2) \quad (1)$$

The oxygen-to-uranium molar ratio in the gas phase, $R(\text{gas})$, is given by:

$$R(\text{gas}) = \frac{p(\text{O}) + 2p(\text{O}_2) + p(\text{UO}) + 2p(\text{UO}_2) + 3p(\text{UO}_3)}{p(\text{U}) + p(\text{UO}) + p(\text{UO}_2) + p(\text{UO}_3)} \quad (2)$$

Thus, to determine both $p(\text{total})$ and $R(\text{gas})$ we need to determine the individual partial pressures as functions of both temperature and condensed-phase composition.

The set of partial pressures given by Eq. (1) must satisfy equilibria among themselves and with the condensed phase. Of the several possible choices of independent equilibria, the following set is a convenient one:



where c represents the condensed phase. Equations (5), (6), and (7) are one set of gaseous equilibria that must be satisfied.

If we know the oxygen pressure, $p(\text{O}_2)$, from the oxygen potential (Section II-E), the required partial pressures may be obtained from Eqs. (3)-(7), in sequence, using the following relationships:

$$\ln p(\text{O}) = 1/2 \ln p(\text{O}_2) - \Delta G_f^\circ(\text{O})/RT \quad (8)$$

$$\ln p(\text{UO}_2) = \frac{x}{2} \ln p(\text{O}_2) + [\Delta G_f^\circ(\text{UO}_{2-x}, \text{c}) - \Delta G_f^\circ(\text{UO}_2, \text{g})]/RT \quad (9)$$

$$\ln p(\text{UO}) = [\Delta G_f^\circ(\text{UO}_2, \text{g}) - \Delta G_f^\circ(\text{UO}, \text{g})]/RT - 1/2 \ln p(\text{O}_2) + \ln p(\text{UO}_2) \quad (10)$$

$$\ln p(\text{UO}_3) = \ln p(\text{UO}_2) + 1/2 \ln p(\text{O}_2) + [\Delta G_f^\circ(\text{UO}_2, \text{g}) - \Delta G_f^\circ(\text{UO}_3, \text{g})]/RT \quad (11)$$

$$\ln p(\text{U}) = [\Delta G_f^\circ(\text{UO}_2, \text{g}) - \Delta G_f^\circ(\text{U}, \text{g})]/RT - \ln p(\text{O}_2) + \ln p(\text{UO}_2) \quad (12)$$

These equations define not only the method to be used, but the data requirements as well.

B. The Phase Boundaries

At this point it is convenient to define qualitatively the nature of the uranium-oxygen phase diagram. Specific quantitative descriptions of the temperature dependence of the phase boundaries will be deferred until the oxygen-potential model is discussed more fully in Section II-E. Figure 2 defines the six regions of the phase diagram that we shall use, namely:

Region I: $\text{UO}_{2-x}(s)$ for $T \leq 2700$ K

Region II: $\text{UO}_{2-x}(s) + \text{U}(l)$

Region III: $\text{UO}_{2-x}(s)$ for $2700 \leq T \leq 3120$ K

Region IV: $\text{UO}_{2-y}(l) + \text{UO}_{2-z}(s)$

Region V: $\text{UO}_{2-x}(l)$, $T \leq 3120$ K

Region VI: $\text{UO}_{2-x}(l)$, $T \geq 3120$ K

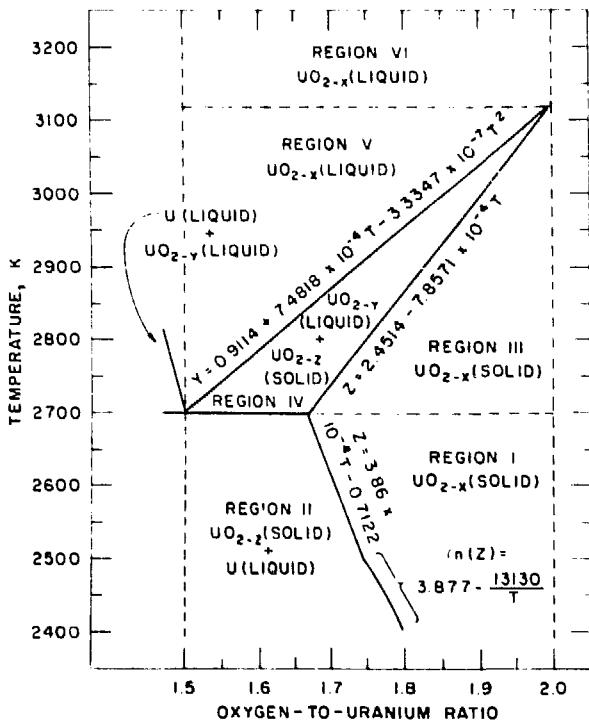


Fig. 2.
Phase Diagram of the
Oxygen-Uranium System

In every case, the overall composition of the system is defined by UO_{2-x} [i.e., the oxygen-to-uranium ratio is $(2 - x)$]; the subscripts y and z are not equal to x .

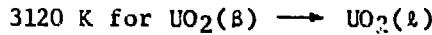
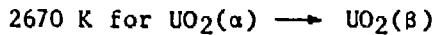
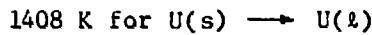
The calculation of vapor pressure is accomplished in slightly different ways, depending upon which of these six regions represents the physical state of the condensed phase.

C. Thermodynamic Functions of the Gases

To apply Eqs. (8)-(12) we require free energies of formation, ΔG_f° , for all gaseous species as functions of T . Tabulated data were used in a least-squares fitting procedure to derive an analytical equation for ΔG_f° of each species. Tabulated data for the uranium oxide vapor species,^{10,11} which were calculated from spectroscopic data, were used; for $\text{O}(g)$ the JANAF data¹² were used; and for $\text{U}(g)$ data from the compilation of Oetting *et al.*¹³ were used. The coefficients of the equations for ΔG_f° of the gaseous species are included in Table 1. Also included in Table 1 is the equation for $\Delta G_f^\circ(\text{UO}_2, c)$ that was derived from the tabulated data in Table 2 by a least-squares fitting procedure. The methods and data used to obtain Table 2 are described in the next section.

D. Thermodynamic Functions of the Condensed Phases

The thermodynamic functions for condensed-phase UO_2 are given in Table 2. The important transition temperatures are:



where the uranium transition temperatures were derived¹¹ from the data of Oetting *et al.*¹³ and those for UO_2 are from Fink *et al.*¹⁴ The $C_p^\circ(\text{UO}_2, c)$ values, column 2 in Table 2, are calculated from the function recommended by Fink *et al.*,¹⁴ namely, Eqs. (13)-(15):

$$C_p^\circ(\text{UO}_2, \alpha) = \frac{C_1 e^{2\theta/T}}{T^2(e^{\theta/T} - 1)^2} + 2C_2 T + C_3 k e^{-E_a/kT} \left[1 + \frac{(T - \bar{\epsilon})E_a}{kT^2} \right] \quad (13)$$

for $298.15 \leq T \leq 2670 \text{ K}$ where

Table 1. Coefficients of the Equations ΔG_f° (in kJ mol⁻¹) = A + BT
 $+ CT^2 + D/T + E \cdot \ln(T) + FT^3$. (\mathbb{T} represents 298.15 K.)

Species	T-range, K	A	B	C	D	E	F
O(g)	298-1400	25236	-6.2747×10^{-2}	-1.3294×10^{-6}	-527.69	--	--
	1400-6000	259.03	-6.7710×10^{-2}	-1.6525×10^{-8}	-3747.4	--	--
U(g)	298-1400	539.11	-1.6007×10^{-1}	1.7321×10^{-5}	-1046.4	--	--
	1400-4435	749.73	-8.3008×10^{-2}	-2.0904×10^{-6}	--	-40.548	--
	4435-6000	0.00	--	--	--	--	--
UO(g)	298-1400	26.863	-1.0515×10^{-1}	1.6100×10^{-5}	-1002.4	--	--
	1400-4435	178.98	-4.2342×10^{-2}	2.0064×10^{-6}	--	-29.432	--
	4435-6000	-521.65	5.8124×10^{-2}	2.4020×10^{-6}	--	--	--
UO ₂ (g)	298-1400	-501.42	-4.2567×10^{-2}	1.4530×10^{-5}	--	7.5475	--
	1400-4435	-367.02	1.4476×10^{-2}	1.7735×10^{-6}	--	-18.571	--
	4435-6000	-989.24	1.1823×10^{-1}	2.0798×10^{-6}	--	--	--
UO ₃ (g)	298-1400	-822.97	2.5295×10^{-2}	1.4770×10^{-5}	--	4.9754	--
	1400-4435	-707.37	8.0256×10^{-2}	1.9058×10^{-6}	--	-18.131	--
	4435-6000	-1321.1	1.8201×10^{-1}	2.4230×10^{-6}	--	--	--
UO ₂ (c)	298-1400	-1131.0	1.4405×10^{-1}	8.1068×10^{-6}	--	9.7445	--
	1400-2670	-1079.8	1.5714×10^{-1}	1.2365×10^{-5}	--	--	-2.6564×10^{-1}
	2670-3120	-1167.1	2.4280×10^{-1}	-1.4569×10^{-5}	--	--	--
	3120-4435	-1002.7	1.6163×10^{-1}	-5.4369×10^{-6}	--	--	--
	4435-6000	-1453.7	2.5458×10^{-1}	-3.4634×10^{-6}	--	--	--

Table 2. Thermodynamic Functions of UO₂ Condensed Phase.
 (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°	- $\left(\frac{G^{\circ}-H^{\circ}}{T}\right)$ - $\left(\frac{G^{\circ}-H_{298}^{\circ}}{T}\right)$	H°-H° ₀	H°-H° ₂₉₈	ΔH° _F	ΔG° _F
0	0.0	0.0	INF	INF	0.0	-11.3	-10d1.1
298.15	63.60	77.0	39.2	77.0	11.3	0.0	-1084.9
300	63.79	77.4	39.4	77.0	11.4	0.1	-1084.9
400	71.30	96.9	51.4	79.6	18.2	6.9	-1083.9
500	75.48	113.3	62.2	84.8	15.5	14.3	-1082.7
600	78.20	127.3	71.2	95.7	12.2	11.2	-1081.5
700	80.17	139.5	80.7	96.9	41.2	29.9	-1080.3
800	81.73	150.4	88.8	102.9	49.3	38.0	-1079.7
900	83.05	160.1	98.2	108.7	57.5	46.2	-1079.2
1000	84.22	168.9	103.0	114.3	65.0	54.6	-1081.0
1100	85.29	176.3	109.4	119.6	74.3	63.1	-1085.5
1200	85.29	184.4	115.3	124.7	82.9	71.6	-1084.3
1300	85.25	191.4	120.7	129.6	91.6	80.3	-1083.0
1400	88.21	197.5	126.2	134.2	100.4	89.1	-1081.7
1408	88.29	198.4	126.6	134.6	101.1	89.6	-1081.6
1408	88.29	198.4	126.6	134.6	101.1	89.6	-1090.7
1500	89.21	204.0	131.1	136.7	109.2	78.6	-1090.4
1600	90.31	209.0	135.9	142.5	115.2	106.9	-1089.9
1700	91.64	215.3	140.4	147.0	127.3	116.0	-1089.4
1800	93.33	220.6	144.7	151.0	136.6	125.3	-1088.7
1900	95.59	225.7	148.8	154.8	146.0	134.7	-1087.9
2000	96.68	230.6	152.3	158.4	155.7	144.4	-1086.8
2100	102.88	235.6	156.5	162.0	165.8	154.5	-1085.4
2200	106.54	240.5	160.3	165.4	174.3	165.0	-1084.5
2300	116.03	245.5	163.9	168.6	187.5	176.3	-1081.0
2400	125.76	250.6	167.4	172.1	199.6	188.3	-1077.7
2500	138.13	256.0	170.9	175.4	212.8	201.5	-1073.3
2600	153.56	261.7	174.2	179.6	227.3	216.1	-1067.5
2670	166.40	265.9	176.6	180.6	238.5	227.2	-1062.4
2670	167.04	266.0	176.6	180.6	238.6	227.5	-1062.1
2700	167.04	267.9	177.5	181.7	244.0	232.7	-1059.6
2800	167.04	273.9	180.5	184.9	260.7	249.4	-1051.8
2900	167.04	279.8	184.2	188.0	277.4	266.1	-1043.9
3000	167.04	285.5	187.4	191.2	294.1	292.8	-1036.0
3100	167.04	290.5	190.7	194.3	310.8	299.5	-1028.2
3120	167.04	292.0	191.3	195.0	314.1	302.6	-1026.6
3120	130.95	316.0	191.3	195.0	388.9	377.6	-451.6
3200	130.95	319.3	194.5	198.0	399.4	366.1	-946.5
3300	130.95	323.3	198.3	201.8	412.5	401.2	-944.3
3400	130.95	327.2	202.1	205.4	425.6	414.3	-940.1
3500	130.95	331.0	205.7	208.9	438.7	427.4	-936.0
3600	130.95	334.7	209.2	212.4	451.8	440.5	-931.8
3700	130.95	338.3	212.7	215.7	464.9	453.6	-927.7
3800	130.95	341.8	216.0	219.0	478.0	466.7	-923.6
3900	130.95	345.2	219.3	222.2	491.1	479.8	-919.5
4000	130.95	348.5	222.5	225.5	504.1	492.9	-915.4
4100	130.95	351.8	225.6	228.4	517.2	506.0	-911.3
4200	130.95	354.9	228.7	231.3	530.3	519.1	-907.1
4300	130.95	358.0	231.6	234.2	543.4	522.2	-903.2
4400	130.95	361.0	234.5	237.1	556.5	545.2	-899.2
4435	130.95	362.1	235.5	238.1	561.1	549.8	-897.8
4435	130.95	362.1	235.5	238.1	561.1	549.8	-1359.3
4500	130.95	364.0	237.4	239.9	569.6	556.3	-1364.8
4600	130.95	366.8	240.2	242.6	582.7	571.4	-1381.2
4700	130.95	369.6	242.9	245.3	595.8	584.5	-1377.6
4800	130.95	372.4	245.6	247.9	608.9	597.6	-1374.0
4900	130.95	375.1	248.2	250.5	622.0	610.7	-1370.4
5000	130.95	377.6	250.7	253.0	635.1	623.8	-1366.8
5100	130.95	380.3	253.2	255.5	648.2	636.9	-1363.2
5200	130.95	382.9	255.7	257.9	661.3	650.0	-1359.5
5300	130.95	385.4	258.1	260.3	674.4	663.1	-1355.8
5400	130.95	387.8	260.5	262.6	687.5	676.2	-1352.1
5500	130.95	390.2	262.9	264.9	700.6	689.3	-1348.4
5600	130.95	392.6	265.2	267.2	713.7	702.4	-1344.6
5700	130.95	394.9	267.4	269.4	726.8	715.5	-1340.8
5800	130.95	397.2	269.6	271.6	739.9	728.6	-1336.9
5900	130.95	399.4	271.8	273.7	753.0	741.7	-1333.1
6000	130.95	401.6	274.0	275.8	766.0	754.8	-1329.1

$$C_1 = 78.212 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_2 = 3.8616 \times 10^{-3} \text{ J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$$

$$C_3 = 3.3993 \times 10^8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{eV}^{-1}$$

$$E_a = 1.8815 \text{ eV}$$

$$\theta = 516.11 \text{ K}$$

$$\mathfrak{T} = 298.15 \text{ K}$$

$$k = 8.5144 \times 10^{-5} \text{ eV}\cdot\text{K}^{-1}$$

$$C_p^\circ(UO_2, \beta) = 167.04 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$2670 \leq T \leq 3120 \text{ K} \quad (14)$$

$$C_p^\circ(UO_2, \alpha) = 130.95 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$3120 \leq T \leq 6000 \text{ K} \quad (15)$$

The absolute entropy, S° , which is column 3 in Table 2, is in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and is given by:

$$S^\circ(UO_2, \alpha) = 77.027 + \int_{\mathfrak{T}}^T \frac{C_p^\circ}{T} dT$$

$$\mathfrak{T} \leq T \leq 2670 \text{ K} \quad (16)$$

where $S^\circ(UO_2, \alpha, \mathfrak{T}) = 77.027 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is from Rand et al.¹⁵ The value $S^\circ(UO_2, \beta) - S^\circ(UO_2, \alpha) = 300/2670 = 0.11 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is from Fink et al.¹⁴ so that:

$$S^\circ(UO_2, \beta) = 266.0 + 167.04 \ln(T/2670)$$

$$2670 \leq T \leq 3120 \text{ K} \quad (17)$$

The entropy change upon melting, $\Delta S^\circ = 74814/3120 = 23.98 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is taken from Fink et al.¹⁴ so that:

$$S^\circ(UO_2, \beta) = 316.0 + 130.95 \ln(T/3120)$$

$$3120 \leq T \leq 6000 \text{ K} \quad (18)$$

The free-energy function, base 0 K, $-[G^\circ - H^\circ(0 \text{ K})]/T$, which is column 4 in Table 2, may be derived from the functions in columns 3 and 6 of Table 2 by the following relationship:

$$\begin{aligned}
 -\frac{[G^\circ - H^\circ(0 K)]}{T} &= -\frac{[G^\circ(T) - H^\circ(T)]}{T} - \frac{[H^\circ(T) - H^\circ(0 K)]}{T} \\
 &= S^\circ - \frac{[H^\circ(T) - H^\circ(0 K)]}{T}
 \end{aligned} \tag{19}$$

Similarly, the free-energy function base 298.15 K = \mathbb{T} , which is column 5 in Table 2, can be derived from columns 3 and 7:

$$-\frac{[G^\circ - H^\circ(\mathbb{T})]}{T} = S^\circ - \frac{[H^\circ - H^\circ(\mathbb{T})]}{T} \tag{20}$$

The enthalpy increment function in column 6 of Table 2 can be derived from column 7 using the value $H^\circ(\mathbb{T}) - H^\circ(0 K) = 11.28 \text{ kJ}\cdot\text{mol}^{-1}$ from Rand et al.¹⁵

$$[H^\circ(T) - H^\circ(0 K)] = [H^\circ(T) - H^\circ(\mathbb{T})] + 11.28 \tag{21}$$

The enthalpy increment function in column 7 of Table 2 is derived by integrating the C_p° function given by Eqs. (14)-(16). The values $\Delta H = 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ at 2670 K and $74.814 \text{ kJ}\cdot\text{mol}^{-1}$ at 3120 K are from Fink et al.¹⁴ In general,

$$[H^\circ(T) - H^\circ(\mathbb{T})] = \int_{\mathbb{T}}^T C_p^\circ(UO_2, c) dT + \sum_{\text{trans}} \Delta H_t \tag{22}$$

where the sum is over all transitions, and the C_p° is the appropriate one for the temperature range.

The enthalpy and free energy of formation of $UO_2(c)$, columns 8 and 9 of Table 2, respectively, depend upon properties of $O_2(g)$ and $U(\text{ref})$ as well as on properties of $UO_2(c)$. The standard enthalpy of formation is given by:

$$\begin{aligned}
 H_f^\circ(UO_2, c, T) &= -1084.9 + \Delta H^\circ(UO_2, c) - \Delta H^\circ(U, \text{ref}) \\
 &\quad - \Delta H^\circ(O_2, g)
 \end{aligned} \tag{23}$$

where the last three terms are the enthalpy increments relative to the standard state at 298.15 K for $UO_2(c)$ [column 7 of Table 2], for U in its reference state,¹³ and for gaseous O_2 ,¹² respectively. The $\Delta H_f^\circ(UO_2, c, \mathbb{T}) = -1084.9 \text{ kJ}\cdot\text{mol}^{-1}$ is from Rand et al.¹⁵ and has been confirmed by Johnson and Steele.¹⁶

One way to obtain $\Delta G_f^\circ(UO_2, c)$ is from:

$$\Delta G_f^\circ(UO_2, c) = \Delta H_f^\circ(UO_2, c, \mathbb{T}) - T[fef'(UO_2, c) - fef'(U, \text{ref}) - fef'(O_2, g)] \tag{24}$$

where $f_{ef}' = - [G^\circ - H^\circ(T)]/T$. Data for U^{13} and O_2^{12} are available in tabulated form and data for $f_{ef}'(UO_2, c)$ are in Table 2; condensed-phase thermodynamic functions for uranium are taken from Oetting et al.¹³ The coefficients of the terms derived from applying a least-squares-fit procedure to $\Delta G_f^\circ(UO_2, c)$ are included in Table 1.

The free energy of formation of UO_{2-x} is related to the partial molal free energies of $U(\text{ref})$ and $O_2(g)$, the activity of U , and pressure of O_2 , as shown in Fig. 3, by

$$\Delta G_f^\circ(UO_{2-x}, c) = \bar{\Delta G}^\circ(U, \text{ref}) + (1 - \frac{x}{2}) \bar{\Delta G}^\circ(O_2, g) \quad (25)$$

where:

$$\bar{\Delta G}^\circ(U, \text{ref}) = RT \ln a(U) \quad (26)$$

$$\bar{\Delta G}^\circ(O_2, g) = RT \ln p(O_2) \quad (27)$$

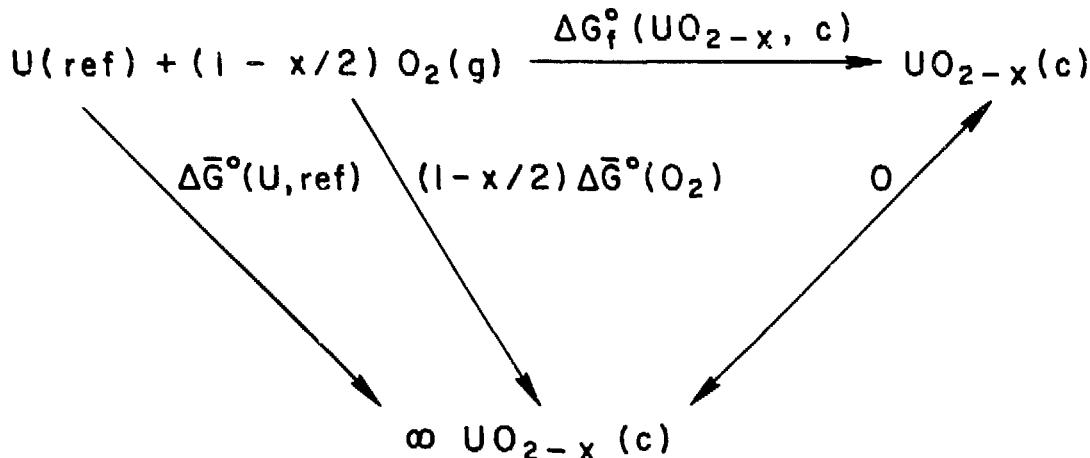


Fig. 3. A Thermodynamic Cycle to Relate the Partial Molal Free Energies of U and O_2 to the Standard Free Energy of Formation of UO_{2-x}

The Gibbs-Duhem equation gives (for n moles):

$$n(O_2) d\bar{\Delta G}^\circ(O_2, g) + n(U) d\bar{\Delta G}^\circ(U, \text{ref}) = 0 \quad (28)$$

so that the variation of $\Delta G_f^\circ(UO_{2-x}, c)$ with x from Eq. (25) becomes:

$$\frac{d}{dx} \Delta G_f^\circ(UO_{2-x}, c) = \frac{-\bar{\Delta G}^\circ(O_2, g)}{2} \quad (29)$$

Equation (29) may be integrated from $x = 0$ (i.e., UO_2) to $x = x'$ (hypostoichiometric UO_2) to give:

$$\Delta G_f^\circ(UO_2, c) - \Delta G_f^\circ(UO_{2-x}, c) = \frac{RT}{2} \int_0^{x'} \ln p(O_2) dz \quad (30)$$

If phase boundaries must be crossed to integrate Eq. (29) or if two phases exist in equilibrium, we must modify Eq. (30). If we consider separately each of the regions defined by Fig. 2, $\Delta G_f^\circ(UO_{2-x}, c)$ at each temperature, T, is given by:

$$\begin{aligned} \Delta G_f^\circ(UO_{2-x}, s) &= \Delta G_f^\circ(UO_2, s) - \Delta(0, x) \\ &\text{for Regions I and III} \end{aligned} \quad (31)$$

$$\begin{aligned} \Delta G_f^\circ(UO_{2-z}, s) &= \Delta G_f^\circ(UO_2, s) - \Delta(0, z) \\ &\text{for Region II with } z < x \end{aligned} \quad (32)$$

$$\begin{aligned} \Delta G_f^\circ(UO_{2-z}, s) &= \Delta G_f^\circ(UO_{2-y}, l) + \phi \\ &= \Delta G_f^\circ(UO_2, s) - \Delta(0, z) \\ &\text{for Region IV with } z < x < y \end{aligned} \quad (33)$$

$$\begin{aligned} \Delta G_f^\circ(UO_{2-y}, l) &= \Delta G_f^\circ(UO_2, s) - \Delta(0, z) - \Delta(y, x) - \phi \\ &\text{for Region V with } z < y < x \end{aligned} \quad (34)$$

and

$$\begin{aligned} \Delta G_f^\circ(UO_{2-x}, l) &= \Delta G_f^\circ(UO_2, l) - \Delta(0, x) \\ &\text{for Region VI} \end{aligned} \quad (35)$$

where

$$\Delta(a, b) \equiv \frac{RT}{2} \int_a^b \ln p(O_2) dx \quad (36a)$$

and

$$\phi = \frac{y - z}{2} RT \ln p(O_2) \quad (36b)$$

and the overall composition of the system is O/U = 2-x in all cases.

Thus, in all cases we must know $p(O_2)$ as a function of x and T for all regions of interest. The oxygen-potential models required to do this are considered in the following section.

E. Oxygen Potentials

1. The Phase Diagram

In Section II-B of this report, the six regions of Fig. 2 were defined qualitatively so that the calculational methods could be discussed. We now wish to define the phase boundary choices in a more quantitative manner. It is not our purpose here to critically review the bases for the phase diagram of Rand *et al.*¹⁵ because we shall demonstrate that the calculated equilibrium vapor pressures and vapor compositions at high temperatures (up to 6000 K) are relatively insensitive to the exact nature of the phase diagram, within the temperature and composition ranges shown in Fig. 2. Thus, we wish to accept the major features of the diagram of Rand *et al.*¹⁵ and intend to find suitable mathematical approximations to the boundary lines.

The following features of Fig. 2 are identical with those of the diagram of Rand *et al.*¹⁵:

1. The lower phase boundary for $1500 \leq T \leq 2500$ K is that of Winslow¹⁷ and is given by the equation shown in Fig. 2.

2. At the monotectic temperature of 2700 K, the values of the O/U ratio are 1.50 ($x = 0.50$) and 1.67 ($x = 0.33$), to the nearest 0.01, at the phase-boundary intersections shown in Fig. 2.

3. The normal melting temperature of UO_2 ($x = 0$) is 3120 K.

We shall limit our concern to the region of Fig. 2 given by $0 \leq x \leq 0.5$ so that the liquid miscibility gap boundary (shown in Fig. 2 as a sloped line¹⁵) is not of interest. The exact nature of the solidus (the boundary line joining the points $T = 2700$, $x = 0.33$ and $T = 3120$, $x = 0$), the liquidus (the boundary line joining the points $T = 2700$, $x = 0.50$ and $T = 3120$, $x = 0$), and the portion of the lower phase boundary between 2500 and 2700 K (corresponding to the values $x = 0.253$ and $x = 0.33$, respectively) are of concern only to the extent that they define the regions of Fig. 2 and, therefore, they define the appropriate method of calculation of the equilibrium vapor pressures and compositions. In this work we make the following choices:

1. The lower phase boundary between 2500 and 2700 K: This phase line must be consistent with $O/U = 1.67$ ($x = 0.33$) at the monotectic temperature of 2700 K. Rand *et al.*¹⁵ appear to recognize that extension of Winslow's equation¹⁷ does not meet the point $x = 0.33$ at 2700 K [$\exp(3.877 - 13130/27000) = 0.373$]; for this reason they have "taken rather smaller values of x between 2500 and 2700 K." Because there appears to be no physical basis for this portion of the lower phase boundary, we choose to separate regions I and II by a straight line that connects the points $T = 2500$, $x = 0.253$ and $T = 2700$, $x = 0.33$.

2. The solidus: The diagram of Rand *et al.*¹⁵ is nearly linear except as $T \rightarrow 3120$ K. We approximate this curve by a straight line that joins the points $T = 2700$, $x = 0.33$ and $T = 3120$, $x = 0$.

3. The liquidus: The diagram of Rand et al.¹⁵ can be approximated by suitable polynomials; however, the solidus and liquidus must be consistent with each other, and we have already defined the solidus. In particular, for each temperature the oxygen pressures obtained from the oxygen-potential models for the solid and liquid at the solidus and liquidus, respectively, must be equal. We use this equality to derive the liquidus from the model and the solidus.

2. Blackburn's Model

An oxygen-potential model for $UO_{2+x}(s)$ has been developed¹⁸ and the parameters in this model have been evaluated and updated to include the most recent empirical data.^{19,20} The most recent evaluation is consistent with the lower phase boundary of Winslow¹⁷ and the ΔG_f° values given in Table 2 of this report. The model can be used to calculate $p(O_2)$ as functions of T and x in regions I and III of Fig. 2. The most recent values²⁰ of $p(O_2)$ obtained from the model are similar to those obtained previously^{18,19} and comparisons with experimental data are similar to those discussed previously.¹⁸ We shall discuss briefly some of the equations and assumptions that comprise this model, so that we may extend it to other regions of Fig. 2 in which a liquid phase is present. In addition, we wish to provide some comparison between Blackburn's model parameter values for UO_2 and other systems to show that there is some physical basis for extension of the model to the liquid regions.

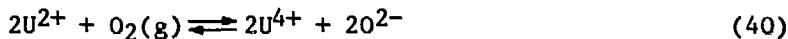
For $UO_{2-x}(s)$, i.e., regions I and III of Fig. 2, the total uranium balance requires:

$$(U^{6+}) + (U^{4+}) + (U^{2+}) = 1 \quad (37)$$

and the charge balance requires:

$$3(U^{6+}) + 2(U^{4+}) + (U^{2+}) = 2 - x \quad (38)$$

Let us consider the following two equilibria:



with respective equilibrium constants:

$$K_1 = \frac{(U^{6+})(U^{2+})}{(U^{4+})^2} \quad (41)$$

$$K_2 = \frac{(U^{4+})^2 (O^{2-})^2}{(U^{2+})^2 p(O_2)} \quad (42)$$

We shall assume that the temperature dependence of each equilibrium constant is:

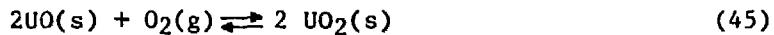
$$\ln K_1 = A_1 + B_1/T \quad (43)$$

$$\ln K_2 = A_2 + B_2/T \quad (44)$$

Blackburn has derived²⁰ values for the four coefficients in Eqs. (43) and (44) based on the most recent empirical data.

Some understanding of the physical basis of these parameter values can be obtained by recognizing that the form of Eqs. (43) and (44) follows from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$. Thus, we may associate A_1 with $\Delta S^\circ/R$ for reaction (39) and A_2 with $\Delta S^\circ/R$ for reaction (40). Furthermore, we may reasonably expect that A_1 is small because of the nature of reaction (39) and we may also expect A_2 to be relatively large and negative at 300 K because reaction (40) involves the loss of one mole of gas. Thus, as a first approximation $A_1 = 0$ and $A_2 = -S^\circ(O_2, 3000 K)/R = -34$ (from JANAF¹²).

To improve these rough estimates, we rewrite reaction (40) as:



so that for reaction (45) we have:

$$\frac{\Delta S^\circ}{R} = A_2 = 2 \left[\frac{S^\circ(UO_2, s) - S^\circ(UO, s)}{R} \right] - \frac{S^\circ(O_2, g)}{R} \quad (46)$$

The second term on the right-hand side of Eq. (46) is available from the JANAF tables,¹² and the first term may be estimated based on the data in Table 3 for other systems. Thus, a better approximation would be:

$$A_2 = 2(5) - 34 = -24 \quad (47)$$

Table 3. Dimensionless Entropy Differences, $\Delta S^\circ/R$, between Solid-Phase Dioxides and Monoxides (Data from JANAF¹²)

M	$[S^\circ(MO_2, s) - S^\circ(MO, s)]/R$		
	T = 298.15	T = 1000	T = 2000
Pb	0.4	3.4	--
Ti	1.9	4.5	4.9
Nb	1.0	4.5	7.9

To improve our estimate of A_1 , we rewrite reaction (39) as:



The data in Table 4 are for reactions of the type:



where $y < x < z$. Because these data in Table 4 support our first approximation, there is no strong reason to revise our estimate of $\Delta S^\circ/R = A_1 \approx 0$. Table 5 compares the estimated values of the constants with the values obtained by Blackburn²⁰ using empirical data, including that of Winslow and the ΔG_f° values in Table 2.

Table 4. Dimensionless Entropy Changes, $\Delta S^\circ/R$, for Solid-Phase Reactions (Data from JANAF¹²)

Reaction	$\Delta S^\circ/R$		
	T = 298.15	T = 1000	T = 2000
$3\text{NbO}_2 \rightarrow 2\text{Nb}_2\text{O}_5 + \text{NbO}$	2.4	1.0	--
$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{FeO}$	0.3	-1.1	--
$\text{Ti}_2\text{O}_3 \rightarrow \text{TiO} + \text{TiO}_2$	0.9	-1.1	-1.3

To solve for $p(O_2)$ at a particular T and x, given the constants in Table 5, we combine Eqs. (37) and (38) to obtain:

$$(U^{2+}) = [1 + x - (U^{4+})]/2 \quad (50)$$

$$(U^{6+}) = [1 - x - (U^{4+})]/2 \quad (51)$$

We may substitute Eqs. (50) and (51) into Eq. (41) and solve for (U^{4+}) in terms of x and K_1 .

$$(U^{4+}) = \frac{-1 + [1 - (x^2 - 1)(4K_1 - 1)]^{1/2}}{4K_1 - 1} \quad (52)$$

Because K_1 is known from Eq. (43) and x is known, we may determine both (U^{4+}) from Eq. (52) and (U^{2+}) from Eq. (50). These values can be substituted into Eqs. (42) and (44) to solve for $p(O_2)$:

$$\ln p(O_2) = 2 \ln \left[\frac{(U^{4+})(2 - x)}{(U^{2+})} \right] - A_2 - B_2/T \quad (53)$$

where we have used $(O^{2-}) = 2 - x$.

Table 5. Various Approximations to the Coefficients
of Eqs. (43) and (44)

Coefficient	First Approx.	Better Approx.	Blackburn ^a
A ₁	0	0	7.680
B ₁	--	--	-60805
A ₂	-34	-24	-28.786
B ₂	--	--	159317

^aRef. 20.

3. Extension of Blackburn's Model to the Liquid

We shall assume that the basic ideas of the oxygen-potential model of Blackburn, as discussed in Section II-E-2, are valid for a UO_{2-x}(l) condensed phase. Thus, we assume there are equilibria among the U²⁺, U⁴⁺, U⁶⁺, and O²⁻ ions in the liquid and O₂(g), so that there are analogs to Eqs. (37)-(44) that are valid for a liquid condensed phase. In particular, for the equilibria with UO_{2-x}(l) the analogs to Eqs. (43) and (44) are:

$$\ln K_{1l} = A_{1l} + B_{1l}/T \quad (54)$$

$$\ln K_{2l} = A_{2l} + B_{2l}/T \quad (55)$$

As a first approximation, we assume A₁ = A_{1l} and A₂ = A_{2l}; this is equivalent to assuming that the entropy changes for reactions (39) and (40) are the same as the corresponding changes in the liquid. The values of the two remaining unknown constants, B_{1l} and B_{2l}, can be derived from the known equality of p(O₂), as calculated by Eq. (53) and the analogous equation for the liquid: (1) at 2700 K for UO_{1.50}(l) and UO_{1.67}(s); and (2) at 3120 K for UO₂(l) and UO₂(s).

At 2700 K we have (U⁶⁺) << (U²⁺) so that, from Eqs. (37) and (38) and the liquid analogs, we get (O²⁻) = 2 - x, (U⁴⁺) = 1 - x, and (U²⁺) = x. Thus, Eq. (53) becomes:

$$\ln p(O_2) = 2 \ln \left[\frac{2 - 3x + x^2}{x} \right] + 28.786 - \frac{159317}{T} \quad (56)$$

for T = 2700, x = 0.33. The analogous equation for the liquid UO_{1.50} becomes:

$$-27.778 = 2 \ln \left[\frac{2 - 3(0.5) + (0.5)^2}{(0.5)} \right] + 28.786 - \frac{B_{2l}}{2700} \quad (57)$$

which can be solved to give B_{2l} = 154913.

At 3120 K, we let $a_s = (U^{6+}) = (U^{2+})$ for the solid UO_2 , $a_l = (U^{6+}) = (U^{2+})$ for the liquid UO_2 and $(O^{2-}) = 2$ for both liquid and solid. Equations (41) and (43) may be combined with these definitions to give:

$$\ln K_1 = 7.680 - \frac{60805}{3120} = 2 \ln \left[\frac{a_s}{1 - 2a_s} \right] \quad (58)$$

and Eq. (53) becomes:

$$\ln p(O_2) = 2 \ln \left[\frac{1 - 2a_s}{a_s} \right] + 2 \ln 2 + 28.786 - \frac{159317}{3120} \quad (59)$$

If we substitute Eq. (58) into Eq. (59), we get $\ln p(O_2) = -9.082$. This $p(O_2)$ is also in equilibrium with $UO_2(l)$ at 3120 K. The analogy to Eq. (58) is:

$$\ln K_{1l} = 7.680 + \frac{B_{1l}}{3120} = 2 \ln \left[\frac{a_l}{1 - 2a_l} \right] \quad (60)$$

and the analog to Eq. (59) is

$$-9.082 = 2 \ln \left[\frac{1 - 2a_l}{a_l} \right] + 2 \ln 2 + 28.786 - \frac{154913}{3120} \quad (61)$$

If we combine Eqs. (60) and (61), we obtain $B_{1l} = 56385$. The constants in this first approximation are given in Table 6.

Table 6. Values^a of the Coefficients of $\ln K = A + B/T$
Equations for the Oxygen-Potential Model of
 UO_{2-x} Solid and Liquid

Constant	First Approx.	Second Approx.
A_1	7.680	7.680
B_1	-60805	-60805
A_2	-28.786	-28.786
B_2	159317	159317
A_{1l}	7.680	7.680
B_{1l}	-56385	-57576
A_{2l}	-28.786	-25.986
B_{2l}	154913	147352

^aValues for A_1 , B_1 , A_2 , and B_2 are from Blackburn;²⁰ values for other constants are from this work.

Before attempting to improve this approximation, it is instructive to examine some of the consequences of doing so. Equations (37) and (38) (and their liquid analogs) are not independent for $x = 0$; both give $(U^{4+})_s = 1 - 2a_s$ [and $(U^{4+})_l = 1 - 2a_l$]. Equations (41)-(44) may be combined for $x = 0$ to give at 3120 K:

$$\ln p(O_2) = -A_1 - A_2 - \frac{B_1}{3120} - \frac{B_2}{3120} + \ln 4 \quad (62)$$

There is an analogous equation for the liquid, so that Eq. (62) and its analog give:

$$B_1 + B_2 = B_{1l} + B_{2l} \quad (63)$$

If we let $R_p = \ln p(O_2)_s - \ln p(O_2)_l$, where the subscripts s and l imply the pressures are calculated from the solid and liquid models, respectively, then from Eq. (62) and its analog, we obtain at any T:

$$\begin{aligned} R_p &= [-A_1 - A_2 - B_1/T - B_2/T + \ln 4] - [-A_{1l} - A_{2l} - B_{1l}/T - B_{2l}/T + \ln 4] \\ &= \frac{B_{1l} + B_{2l}}{T} - \frac{B_1 + B_2}{T} \\ &= 0 \end{aligned} \quad (64)$$

by substitution of Eq. (63). Thus, a consequence of the approximation that $A_1 = A_{1l}$ and $A_2 = A_{2l}$, is that $p(O_2)$ in equilibrium with (real or hypothetical) solid UO_2 is identical with the $p(O_2)$ in equilibrium with (real or hypothetical) liquid UO_2 for all T. We know, in fact, that $R_p = 0$ only at 3120 K, $R_p < 0$ for $T < 3120$ K, and $R_p > 0$ for $T > 3120$ K. Let us examine refinements to our first approximation.

Equation (46) gives $\Delta S^\circ/R$ (which is A_2) for reaction (45). We have the numerical value of A_2 from Blackburn's model, and it is consistent with our expectation of a relatively large negative number as shown in Table 5. We can improve the first approximation of $A_{2l} = A_2$ by comparing $\Delta S_s^\circ/R$ ($= A_2$) to $\Delta S_l^\circ/R$ ($= A_{2l}$) for several known oxides. If we let $\Delta_2 = \Delta S_l^\circ - \Delta S_s^\circ$, then from Eq. (46) and its liquid analog, we obtain:

$$\begin{aligned} \Delta_2 &= \Delta S_l^\circ - \Delta S_s^\circ = R[A_{2l} - A_2] \\ &= 2[S^\circ(UO_2, l) - S^\circ(UO_2, s)] - 2[S^\circ(UO, l) - S^\circ(UO, s)] \\ &= 2[\Delta S_m^\circ(UO_2) - \Delta S_m^\circ(UO)] \end{aligned} \quad (65)$$

where ΔS_m° is the entropy of melting. An estimate of Δ_2 can be obtained from the data¹² in Table 7. The average of all values of R_m [$R_m = \Delta S_m^\circ(T_m)/(R \cdot n)$, where n is the number of atoms per molecule, R is the gas constant, T_m is the melting temperature in K], giving 1/2 weight to

Table 7. Values of $R_m = \Delta S_m^\circ(T_m)/(R \cdot n)$ Where n is the Number of Atoms per Molecule, the Subscript m Refers to Melting, and R is the Gas Constant. (Data are from JANAF¹² and numbers in brackets are estimated.)

Molecule	R_m	Molecule	R_m
Al_2O_3	1.1	SrO	[1.6]
BaO	[1.6]	TiO	[1.3]
BeO	1.9	TiO_2	[1.3]
CaO	1.5	Ti_2O_3	[1.2]
Cr_2O_3	[1.2]	Ti_3O_5	[1.3]
Cu_2O	1.5	Ti_4O_7	[1.3]
FeO	[0.9]	VO	[1.6]
MgO	[1.5]	V_2O_3	[1.2]
MoO_3	[1.4]	V_2O_4	1.9
NbO	2.3	V_2O_5	0.6
NbO_2	1.7	ZrO_2	1.2
PbO	1.3		
SiO_2	0.2		

estimated values, is $R_m = 1.4$. The data in Table 2 give $R_m = 1.0$ for UO_2 . Thus, a reasonable improvement in the approximation for A_{2L} is:

$$\begin{aligned} A_{2L} &= A_2 + \Delta_2/R = A_2 + 2R_m \\ &= A_2 + 2.8 \end{aligned} \quad (66)$$

By a completely analogous procedure, we may use our average R_m to refine our estimate for A_{1L} . If we let ΔS_s° be for reaction (48) and ΔS_L° be for its liquid analog, then

$$\begin{aligned} \Delta_1 &= \Delta S_L^\circ - \Delta S_s^\circ \\ &= 2R_m + 4R_m - 2(3R_m) \\ &= 0 \end{aligned} \quad (67)$$

Now B_{2L} and B_{1L} can be derived in the same manner used in our first approximation, i.e., by Eqs. (56) - (61). The complete set of coefficients for the second approximation is given in Table 6. Calculations using these values do give the expected behavior of R_p as a function of T and, thus, appear to represent an improvement.

This method, which we call the second approximation to Blackburn's extended oxygen-potential model, obtains the four unknown coefficients ($A_{1\ell}$, $B_{1\ell}$, $A_{2\ell}$, and $B_{2\ell}$) from data at two temperatures (2700 and 3120 K) and from a fixed relationship between the solid and liquid entropy changes, (i.e., by fixing the relationship between A_1 and $A_{1\ell}$ and between A_2 and $A_{2\ell}$). Alternatively, we could eliminate the fixed relationships for the A coefficients and use points on the phase diagram of Rand et al.¹⁵ to derive all four unknown coefficients. The success of the latter approach, which we shall call the third approximation, depends, in part, on the reliability of the liquidus curve. The only good criteria for evaluating the coefficients obtained using this third approximation are: (1) the derived set of four coefficients should be independent of the choices of points on the liquidus (within the expected uncertainties); and (2) the A coefficients should be reasonably consistent with the thermodynamic arguments that were used to derive the coefficients in the second approximation.

Several trial calculations were made using the following equation for the liquidus:

$$T = -1197.5 + 3258.6 R - 110.58 R^2 - 219.65 R^3 \quad (68)$$

where R is the oxygen-to-uranium ratio and T is in K. Equation (68) was obtained from a least-squares fit of points read from Rand's diagram (other forms of the equation fit the data almost as well). The set of four unknown coefficients ($A_{1\ell}$, $B_{1\ell}$, $A_{2\ell}$, $B_{2\ell}$) were derived using the points $T = 2700$, $x = 0.50$, $T = 3120$, $x = 0$ and various pairs of points from Eq. (68). The derived values of the coefficients depend upon the choice of the latter two points. Part of the reason for the difficulties with the third approximation is that the O_2 pressure is relatively insensitive to the values of $A_{1\ell}$ and $B_{1\ell}$, provided $K_{1\ell}$ is sufficiently small. The value of $K_{1\ell}$ can vary several orders of magnitude [as long as $(U^{6+}) + (U^{2+}) \approx (U^{2+})$] at points along the liquidus that are not near 3120 K (or near $x = 0$). There is no reason to believe Eq. (68), which is based largely on data of Latta and Fryxell,²¹ is particularly reliable near 3120 K. Therefore, the third approximation was not pursued further because extension of the model to 6000 K requires insensitivity to the details of the phase diagram, and this is not the case.

We conclude that our second approximation and the coefficients given in the last column of Table 6 provide the best means to calculate reliable pressures at high temperatures. Trial calculations indicate that small changes in the relationships between A_1 and $A_{1\ell}$ or between A_2 and $A_{2\ell}$ do not greatly affect the calculated vapor compositions or calculated total pressures at 6000 K provided a consistent set of coefficients is used.

4. Other Models

The model that was developed in the preceding section gives $p(O_2)$ as functions of both x and T . There are some other approaches that have been used previously for part of the range of x and T values of interest.

Winslow's equation:²²

$$\log_{10} p(O_2) = 11.358 - 43078/T - 0.4604 \log_{10} T \quad (69)$$

for p in atm [1 atm = 0.1013 MPa] is valid only for O_2 in equilibrium with UO_2 and is extrapolated to 6000 K. His equations²³ for $p(O_2)$ in equilibrium with UO_{2-x} , which are less easily expressed in analytical form, do not give the same $p(O_2, 6000\text{ K})$ for equilibrium with UO_2 as that given by Eq. (69). Tabulated results for every 250 K have been interpolated to given $p(O_2, 3150\text{ K})$ as a function of condensed-phase composition, and these are given in Table 8.

Table 8. Pressure (in MPa) of O_2 in Equilibrium with $UO_{2-x}(l)$ Calculated from Various Oxygen-Potential Models ($R \equiv$ oxygen/uranium)

T, K	R	This work ^a	Winslow ^b	Winslow ^c	Chapman et al. ^d	Bober et al. ^e
3150	1.90	2.8×10^{-8}	--	2.7×10^{-9}	1.5×10^{-11}	--
3150	1.96	2.0×10^{-7}	--	5.2×10^{-8}	4.5×10^{-9}	--
3150	2.00	1.5×10^{-5}	1.2×10^{-5}	--	2.0×10^{-7}	6.9×10^{-6}
6000	1.90	6.5	--	2.7	--	--
6000	1.96	9.2	--	18	--	--
6000	2.00	11	--	1.1×10^3	--	13

^aCoefficients from last column of Table 6.

^bRef. 22; Eq. (69) in this report.

^cRef. 23.

^dRef. 24.

^eRef. 25; Eq. (71) in this report extrapolated to 6000 K.

The measurements of Chapman et al.,²⁴ were made on samples with a large temperature gradient (about 1000 K), so that some assumptions must be made about the nature of the equilibrium. If the measured $p(O_2)$ values are assumed to be for O_2 in equilibrium with the molten UO_{2-x} interior of the sample, then

$$\log_{10} p(O_2) = 41.1 R - 87.9 \quad (70)$$

where $p(O_2)$ is in atm. Oxygen pressures calculated with this equation are compared in Table 8 to the values of $p(O_2)$ calculated from the models.

The oxygen-potential model used by Bober et al.²⁵ and the resultant equation for $p(O_2)$ in atm:

$$p(O_2) = \exp [11.07 - 411700/T + (43030/T \cdot \ln T)] \quad (71)$$

are valid only between the melting point of UO_2 and 5000 K and are for equilibrium with $\text{UO}_2(\ell)$.

Winslow's $p(\text{O}_2, 6000 \text{ K})$ is high relative to the total pressure recommended by the International Working Group on Fast Reactors (IWGFR);²⁶ a full discussion will be given later. There are large disagreements among the various $p(\text{O}_2, 6000 \text{ K})$ values for O_2 in equilibrium with $\text{UO}_2(\ell)$. The model developed in the previous section appears to be preferable to the alternatives presented in this section because it can be applied for the entire range of parameters of interest and because it gives results more in accord with expectations.²⁶

F. Ions

The ionization potentials of the vapor species in equilibrium with a UO_{2-x} condensed phase are given in Table 9. Karow^{31,32} has considered the ionization of UO_2 , including the effects of thermal population of neutral UO_2 states, and concludes that between 3120 and 5000 K the percent ionization of UO_2 varies between 1 and 5%. Although his calculations could not include the most recent data^{10,11} for the oxides, we shall consider his maximum of 5% ionization of UO_2 to be valid at 5000 K so that we may examine the consequences.

Table 9. Ionization Potentials (IP) of the Molecules and Atoms in Equilibrium with a Uranium Dioxide Condensed Phase.
($1 \text{ eV} \cdot \text{molecule}^{-1} = 23.06 \text{ kcal} \cdot \text{mol}^{-1} = 96.48 \text{ kJ} \cdot \text{mol}^{-1}$)

Species	IP, eV	Reference
U	6.2 ± 0.5	Steinhaus et al. ^a
UO	5.6 ± 0.1	Rauh and Ackermann ^b
UO_2	5.4 ± 0.1	Rauh and Ackermann ^b
UO_3	10.6 ± 0.1	Rauh and Ackermann ^b
O	13.61	Moore ^c
O_2	12.07	Huber and Herzberg ^d

^aRef. 27.

^bRef. 28.

^cRef. 29.

^dRef. 30.

The data in Table 9 can be used to show that ionization is significant only for U, UO , and UO_2 because ionization potentials of other species are much larger. We shall show in the next section that the high-temperature partial pressures of U and UO are relatively small compared to those of other species in equilibrium with a UO_{2-x} condensed phase for $0 \leq x \leq 0.1$.

The fraction of the total vapor that is UO_2 decreases significantly above the melting point as the temperature is increased, so that at 6000 K, for example, the UO_2 partial pressure is only 5 to 7% of the total pressure for the range of x of interest. Thus, ionization of U, UO , or UO_2 will not significantly affect the total pressure or the oxygen-to-uranium ratio of the vapor. However, if other properties of the vapor were found to be sensitive to a small degree of ionization, a more complete calculation would be required. (Some transport properties, for example, could be sensitive to the presence of small numbers of ions.)

III. RESULTS

The partial pressures of O, O_2 , U, UO , UO_2 , and UO_3 were calculated as functions of T ($1500 \leq T \leq 6000$ K) and x ($0 \leq x \leq 0.5$) with particular emphasis on $0 \leq x \leq 0.1$. The ΔG° for the condensed phase and the $p(\text{O}_2)$ from the model (Section II-E-3 of this report) are both consistent with the phase diagram shown in Fig. 2.

The vapor composition in equilibrium with a $\text{UO}_{1.96}$ condensed phase, which is a typical composition for a reactor fuel, is shown in Fig. 4. Although UO_2 is an important vapor constituent for this temperature range, it is not the principal vapor species at temperatures above 3900 K or below 2000 K. Because the principal vapor species for $5000 \leq T \leq 6000$ K are oxygen-rich (O, O_2 , UO_3), the oxygen-to-uranium ratio of the vapor will be higher than 1.96.

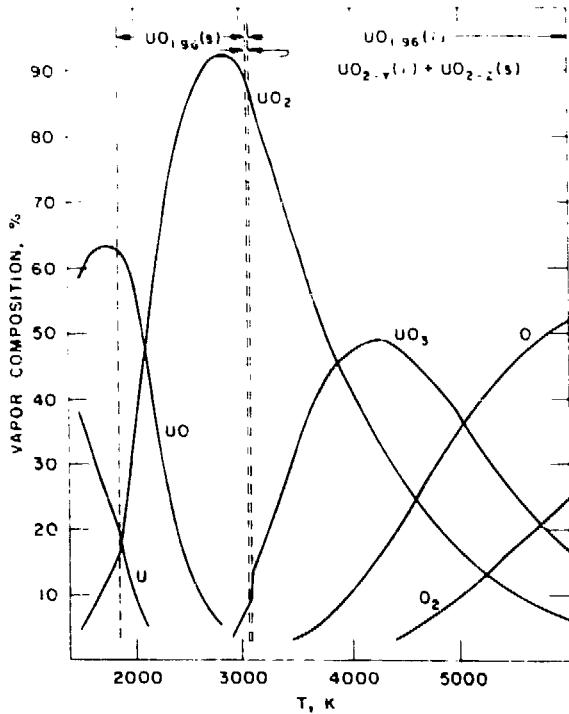


Fig. 4.
Vapor Composition in Equilibrium
with a $\text{UO}_{1.96}$ Condensed Phase

The data in Fig. 5 show that the vapor in equilibrium with a UO_{2-x} condensed phase for $0 \leq x \leq 0.1$ is very oxygen-rich, particularly for $T \geq 4000$ K. One implication of these calculations is that the condensed-phase and vapor-phase compositions will depend upon the extent of vaporization of a sample with an overall composition given by $\text{O}/\text{U} = 2 - x$.

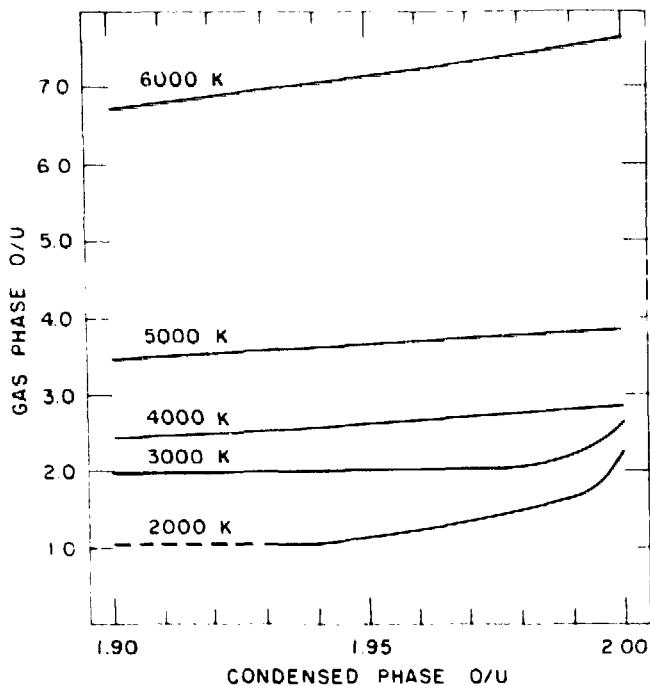


Fig. 5. Oxygen-to-Uranium Ratio of the Vapor in Equilibrium with a UO_{2-x} Condensed Phase for Temperatures between 2000 and 6000 K

The total pressure is relatively insensitive to the condensed-phase composition. Figure 6 shows that as T increases above the melting point, the total pressures in equilibrium with $\text{UO}_{2.00}$ and $\text{UO}_{1.90}$ are converging. This result is somewhat surprising because the individual partial pressures are sensitive to x .

The total pressure in equilibrium with $\text{UO}_2(\text{c})$ can be compared with that recommended²⁶ by the IWGFR. Our preliminary results^{26,33,34} had given a lower total pressure than that recommended by IWGFR, however, the calculations described in this report give a total pressure that is in remarkably good agreement, as shown in Fig. 7.

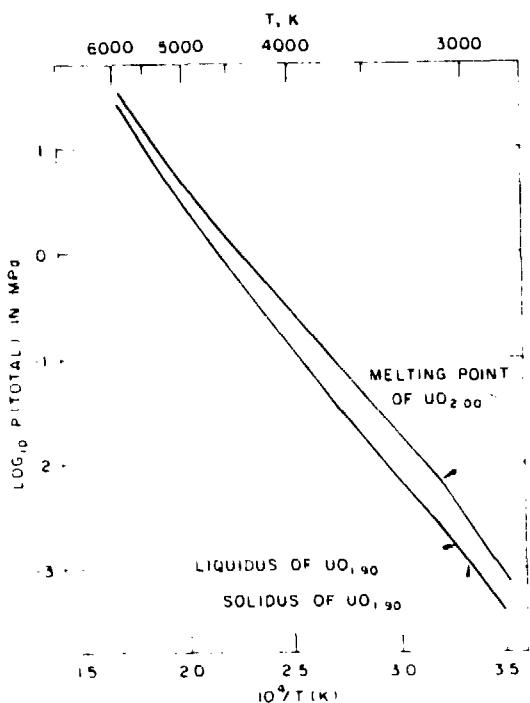


Fig. 6.

Log of Total Pressure (in MPa) in Equilibrium with UO_{2.00} and UO_{1.90}

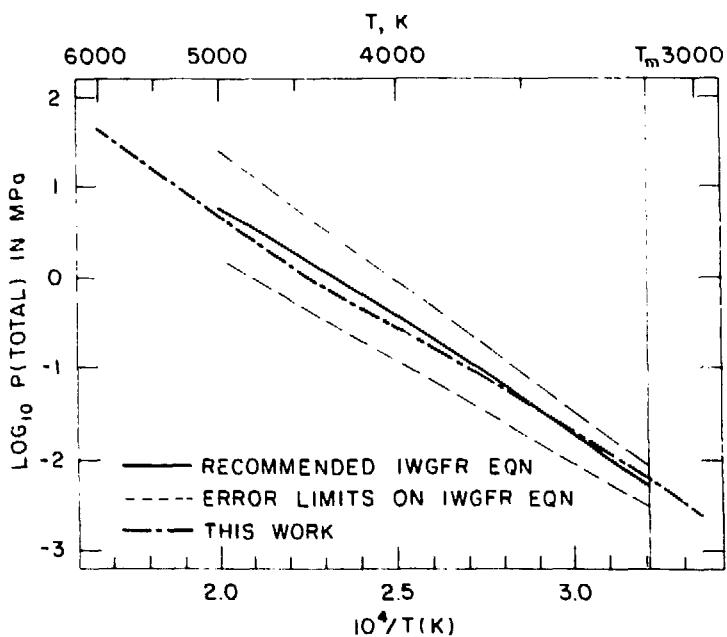


Fig. 7. Comparison of the Total Pressure in Equilibrium with a UO₂ Condensed Phase for this Work with that Recommended by the International Working Group on Fast Reactors

IV. DISCUSSION AND CONCLUSIONS

The results obtained from application of the approach outlined in Fig. 1 contain information about the total pressure of the equilibrium vapor (usually available from other methods) and the composition of the vapor (not always available from alternative methods).

The calculations show that the total pressure in equilibrium with a condensed-phase UO_{2-x} is relatively insensitive to the value of x in the range $0 \leq x \leq 0.1$. This conclusion is important because the process of vaporization itself changes the oxygen-to-uranium ratio of the condensed phase. Thus, the extent of vaporization of a sample (or its reactions with other substances present in the system) may lead to changes in the oxygen-to-uranium ratio of the condensed phase. We have found that there is not a correspondingly large effect on the total pressure.

The thermophysical properties of the vapor that depend on the vapor composition are sensitive to the value of x . Partial pressures of the vapor species, particularly at high temperatures, do depend on the extent of vaporization as well as on the value of x . The results shown in Fig. 4 for a $\text{UO}_{1.96}$ condensed phase may be generalized to other values of x . There will, of course, be quantitative differences, but qualitatively for all x , the vapor will consist of several species whose relative importance changes with both x and T . Thermophysical properties of the vapor in equilibrium with UO_{2-x} are, in general, poorly approximated as those of $\text{UO}_2(\text{g})$. Furthermore, no single mixture of gases is an adequate approximation because the composition of the mixture is sensitive to both x and T . Account should be taken of the complex nature of the vapor in most calculations of vapor properties.

The total pressure in equilibrium with a UO_2 condensed phase has been the subject of numerous investigations and calculations. The IWGFR equation²⁶ has rather large error limits that reflect, in part, the difficulty of obtaining reliable experimental information at temperatures above 3000 K. The agreement of our calculated total pressure with the IWGFR equation, as shown in Fig. 7, is excellent.

The vapor in equilibrium with a UO_{2-x} condensed phase consists of many species of which O, O_2 , U, UO , UO_2 , UO_3 , and their singly-charged positive ions have been considered. It has been implicitly assumed that all other vapor species [e.g., U_2O , U_2 , $\text{U}-\text{O}-\text{O}$, $(\text{UO})_2$] have sufficiently low partial pressures that their presence does not significantly affect the total pressure or O/U ratio of the vapor. It is expected that this assumption is valid or at least that the uncertainty introduced by this assumption is smaller than the uncertainties from other sources. This expectation is based, in part, on the absence of data suggesting that there are other major vapor species below 3000 K.

Our calculations are based on the need to reliably extrapolate from 3000 K, where much of the available data begin to become seriously deficient, to 6000 K, where available data do not exist. Although a 3000 K extrapolation is hardly small, in many ways this factor of two in T is no more difficult or

dangerous than extrapolating from room temperature to 600 K. Many of the thermodynamic properties of interest are dependent primarily on the ratio of a characteristic energy to the value of kT or the exponential of this ratio. Many of the experimental data available for the U-O vapor system are for $2000 < T < 3000$ K, and some data are available for $T > 3000$ K. Thus, we have some guidance for this extrapolation of a factor of two in T .

There is no good way to discuss the uncertainties involved in these calculations without making qualitative judgments. As Fig. 1 shows, there are many pieces that must fit together in order to obtain reliable vapor pressures and compositions. Each component has an uncertainty. The gas-phase thermodynamic functions are relatively well established, but uncertainties remain (and probably will remain for some time) in the electronic contributions to the functions. The condensed-phase thermodynamic functions must be extrapolated and the assumption of a constant heat capacity could be improved. The oxygen-potential model has a sound thermodynamic basis, but there are insufficient data upon which a reliable evaluation of the parameters can be made. The scatter is large in the data points used to determine the oxygen-uranium phase diagram, particularly at temperatures near the melting point. Measurements of properties of the UO_2 system at temperatures above 3120 K (the melting point) would be useful. It would also be useful to measure properties of systems other than the uranium-oxygen system in order to provide an experimental basis for the discussion of the errors expected in the pulse techniques.³⁻⁵

The above discussion suggests the need for continuing experimental and supporting theoretical work to help reduce the uncertainty in the thermo-physical properties of the uranium-oxygen system at high temperatures. The results we have obtained should provide a reasonable standard for comparing experimental measurements and theoretical results. One clear implication of our results for other studies is that the vapor composition is variable, and, to avoid potential problems, this variation must be considered in whatever method is used.

One area of potentially fruitful work is the calculation (or measurement) of the properties of the uranium-oxygen system near the critical point. In many previous discussions of critical phenomena, the complex nature of the vapor phase in equilibrium with UO_{2-x} was not recognized. It would seem reasonable that the oxygen-rich nature of the vapor cannot continue to increase with temperature in the manner suggested in Fig. 6. Perhaps a careful consideration of the expected behavior above 6000 K can help provide some limits on the oxygen-potential model.

Another promising area of work is the determination of the expected deviations from ideal gas behavior for the complex vapor system. Although nonideal equations for UO_2 may be derived, their application to the real system that consists of multiple vapor species is limited.

In summary, our results provide strong support for the IWGFR total-pressure equation and, in our judgment, reduce the uncertainty in that equation at high temperatures. The vapor in equilibrium with a UO_{2-x} condensed phase is poorly approximated as $UO_2(g)$ for most conditions of interest. The vapor, particularly at very high temperatures, is oxygen-rich, relative to the condensed phase with which it is in equilibrium.

ACKNOWLEDGMENTS

We gratefully acknowledge helpful discussions with Dr. J. K. Fink and Dr. P. E. Blackburn.

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APPENDIX

CALCULATED PARTIAL PRESSURES IN EQUILIBRIUM
WITH A UO_{2-x} CONDENSED PHASE

Each of the following tables contains the calculated partial pressures and total pressure (in MPa) in equilibrium with UO_{2-x} as a function of temperature for one value of x . The applicable regions of the phase diagram, as defined in Fig. 2, are given in the tables. These data were calculated using a program called TOTPR, which is based on the methods outlined in Section II-E of this report. Numerical integrations to obtain $\Delta G_f^\circ(\text{UO}_{2-x})$ were done with subroutine SQUANK (J. N. Lyness and K. E. Hillstrom, Argonne National Laboratory, Applied Mathematics Division, July 1970). With the output from TOTPR (or minor modifications of it) the data were obtained for Figs. 4-7.

Table A-1. Partial Pressures and Total Pressure (in MPa) in Equilibrium with a UO_{2.00} Condensed Phase

T K	REG ^a	p(O ₂)	p(O)	p(UO ₂)	p(UO ₃)	p(UO)	p(U)	p(total)
1500	I	0.1786D-19	0.1713D-15	0.7648D-13	0.6314D-14	0.9173D-17	0.5497D-22	0.8297D-13
1600	I	0.1082D-17	0.4766D-14	0.1551D-11	0.1834D-12	0.2604D-15	0.2583D-20	0.1740D-11
1700	I	0.4048D-16	0.8983D-13	0.2190D-10	0.3554D-11	0.4928D-14	0.7645D-19	0.2555D-10
1800	I	0.1013D-14	0.1223D-11	0.2286D-09	0.4915D-10	0.6653D-13	0.1540D-17	0.2790D-09
1900	I	0.1805D-13	0.1266D-10	0.1848D-08	0.5111D-09	0.6755D-12	0.2245D-16	0.2372D-08
2000	I	0.2411D-12	0.1038D-09	0.1202D-07	0.4169D-08	0.5383D-11	0.2484D-15	0.1630D-07
2100	I	0.2517D-11	0.6970D-09	0.6482D-07	0.2760D-07	0.3483D-10	0.2169D-14	0.9315D-07
2200	I	0.2123D-10	0.3938D-08	0.2973D-06	0.1525D-06	0.1881D-09	0.1544D-13	0.4539D-06
2300	I	0.1488D-09	0.1915D-07	0.1183D-05	0.7191D-06	0.8684D-09	0.9197D-13	0.1922D-05
2400	I	0.8862D-09	0.8162D-07	0.4157D-05	0.2952D-05	0.3491D-00	0.4685D-12	0.7195D-05
2500	I	0.4577D-08	0.3099D-06	0.1308D-04	0.1072D-04	0.1242D-07	0.2378D-11	0.2413D-04
2600	I	0.2084D-07	0.1062D-05	0.3731D-04	0.3489D-04	0.3963D-07	0.8157D-11	0.7333D-04
2700	III	0.8477D-07	0.3324D-05	0.9713D-04	0.1026D-03	0.1143D-06	0.2859D-10	0.2033D-03
2800	III	0.3120D-06	0.9590D-05	0.2323D-03	0.2749D-03	0.3006D-06	0.9028D-10	0.5174D-03
2900	III	0.1050D-05	0.2572D-04	0.5155D-03	0.6778D-03	0.7282D-06	0.2601D-09	0.1221D-02
3000	III	0.3257D-05	0.6464D-04	0.1070D-02	0.1552D-02	0.1639D-05	0.6902D-09	0.2691D-02
3100	III	0.9394D-05	0.1529D-03	0.2090D-02	0.3323D-02	0.3450D-05	0.1700D-08	0.5579D-02
3200	VI	0.2364D-04	0.3312D-03	0.3607D-02	0.6036D-02	0.6612D-05	0.3919D-08	0.1000D-01
3300	VI	0.5533D-04	0.6789D-03	0.5872D-02	0.1022D-01	0.1197D-04	0.8534D-08	0.1684D-01
3400	VI	0.1232D-03	0.1334D-02	0.9238D-02	0.1669D-01	0.2081D-04	0.1769D-07	0.2740D-01
3500	VI	0.2619D-03	0.2523D-02	0.1408D-01	0.2634D-01	0.3482D-04	0.3504D-07	0.4324D-01
3600	VI	0.5340D-03	0.4604D-02	0.2086D-01	0.4031D-01	0.5631D-04	0.6662D-07	0.6637D-01
3700	VI	0.1048D-02	0.8135D-02	0.3009D-01	0.5999D-01	0.6824D-04	0.1219D-06	0.9935D-01
3800	VI	0.1984D-02	0.1395D-01	0.4373D-01	0.8697D-01	0.1343D-03	0.2155D-06	0.1454D+00
3900	VI	0.3636D-02	0.2327D-01	0.5834D-01	0.1231D+00	0.1990D-03	0.3688D-06	0.2086D+00
4000	VI	0.6465D-02	0.3784D-01	0.7869D-01	0.1704D+00	0.2877D-03	0.6129D-06	0.2937D+00
4100	VI	0.1118D-01	0.6010D-01	0.1041D+00	0.2312D+00	0.4065D-03	0.9907D-06	0.4070D+00
4200	VI	0.1882D-01	0.9336D-01	0.1353D+00	0.3077D+00	0.5623D-03	0.1561D-05	0.5557D+00
4300	VI	0.3095D-01	0.1421D+00	0.1730D+00	0.4023D+00	0.7627D-03	0.2403D-05	0.7491D+00
4400	VI	0.4974D-01	0.2122D+00	0.2178D+00	0.5174D+00	0.1016D-02	0.3617D-05	0.9982D+00
4500	VI	0.7827D-01	0.3113D+00	0.2713D+00	0.6568D+00	0.1336D-02	0.5337D-05	0.1319D+01
4600	VI	0.1208D+00	0.4492D+00	0.3325D+00	0.8210D+00	0.1722D-02	0.7721D-05	0.1725D+01
4700	VI	0.1829D+00	0.6381D+00	0.4028D+00	0.1013D+01	0.2190D-02	0.1098D-04	0.2239D+01
4800	VI	0.2723D+00	0.8933D+00	0.4826D+00	0.1236D+01	0.2750D-02	0.1535D-04	0.2887D+01
4900	VI	0.3989D+00	0.1234D+01	0.5726D+00	0.1492D+01	0.3410D-02	0.2114D-04	0.3700D+01
5000	VI	0.5755D+00	0.1582D+01	0.6728D+00	0.1782D+01	0.4181D-02	0.2870D-04	0.4716D+01
5100	VI	0.8183D+00	0.2650D+01	0.7836D+00	0.2107D+01	0.5071D-02	0.3843D-04	0.5979D+01
5200	VI	0.1148D+01	0.3015D+01	0.9049D+00	0.2469D+01	0.6089D-02	0.5080D-04	0.7544D+01
5300	VI	0.1590D+01	0.3972D+01	0.1037D+01	0.2869D+01	0.7241D-02	0.6635D-04	0.9475D+01
5400	VI	0.2176D+01	0.5178D+01	0.1179D+01	0.3306D+01	0.8534D-02	0.8567D-04	0.1185D+02
5500	VI	0.2944D+01	0.6687D+01	0.1331D+01	0.3780D+01	0.9973D-02	0.1094D-03	0.1475D+02
5600	VI	0.3940D+01	0.8557D+01	0.1493D+01	0.4291D+01	0.1156D-01	0.1383D-03	0.1829D+02
5700	VI	0.5220D+01	0.1086D+02	0.1664D+01	0.4837D+01	0.1330D-01	0.1732D-03	0.2259D+02
5800	VI	0.6848D+01	0.1366D+02	0.1847D+01	0.5417D+01	0.1519D-01	0.2149D-03	0.2778D+02
5900	VI	0.8903D+01	0.1705D+02	0.2070D+01	0.6028D+01	0.1722D-01	0.2643D-03	0.3403D+02
6000	VI	0.1147D+02	0.2114D+02	0.2223D+01	0.6669D+01	0.1941D-01	0.3224D-03	0.4152D+02

^aRegion defined in Fig. 2.

Table A-2. Partial Pressures and Total Pressure (in MPa)
in Equilibrium with a UO_{1.98} Condensed Phase

T, K	REG ^a	p(U ₂)	p(O)	p(UO ₂)	p(UO ₃)	p(UO)	p(U)	p(total)
1500	II	0.1614D-29	0.1628D-20	0.7589D-13	0.5956D-19	0.9578D-12	0.6038D-12	0.1637D-11
1600	II	0.4058D-27	0.9229D-19	0.1531D-11	0.3504D-17	0.1327D-10	0.6799D-11	0.2160D-10
1700	I	0.6035D-25	0.3468D-17	0.2146D-10	0.1345D-15	0.1251D-09	0.5026D-10	0.1968D-09
1800	I	0.1101D-22	0.1275D-15	0.2240D-09	0.5022D-14	0.6252D-09	0.1388D-09	0.9880D-09
1900	I	0.1161D-20	0.3211D-14	0.1811D-08	0.1270D-12	0.2610D-08	0.3419D-09	0.4762D-08
2000	I	0.7686D-19	0.5861D-13	0.1178D-07	0.2306D-11	0.9343D-08	0.7636D-09	0.2189D-07
2100	I	0.3413D-17	0.8116D-12	0.6352D-07	0.3149D-10	0.2931D-07	0.1568D-08	0.9443D-07
2200	I	0.1073D-15	0.8854D-11	0.2913D-06	0.3359D-09	0.8201D-07	0.2994D-08	0.3766D-06
2300	I	0.2501D-14	0.7850D-10	0.1160D-05	0.2890D-08	0.2076D-06	0.5362D-08	0.1375D-05
2400	I	0.4482D-13	0.5805D-09	0.4075D-05	0.2058D-07	0.4811D-06	0.9079D-08	0.4586D-05
2500	I	0.6377D-12	0.3658D-08	0.1282D-04	0.1240D-06	0.1031D-05	0.1463D-07	0.1400D-04
2600	I	0.7394D-11	0.2001D-07	0.3659D-04	0.6446D-06	0.2063D-05	0.2254D-07	0.3934D-04
2700	III	0.7146D-10	0.9651D-07	0.9529D-04	0.2923D-05	0.3064D-05	0.3327D-07	0.1022D-03
2800	III	0.5866D-09	0.4158D-06	0.2280D-03	0.1170D-04	0.6806D-05	0.4714D-07	0.2470D-03
2900	III	0.4154D-08	0.1618D-05	0.5064D-03	0.4189D-04	0.1137D-04	0.6457D-07	0.5613D-01
3000	III	0.2571D-07	0.5740D-05	0.1052D-02	0.1356D-03	0.1813D-04	0.8596D-07	0.1211D-02
3100	IV	0.2266D-06	0.2375D-04	0.2066D-02	0.5101D-03	0.2196D-04	0.6967D-07	0.2622D-02
3200	VI	0.1593D-05	0.8598D-04	0.3564D-02	0.1548D-02	0.2517D-04	0.5748D-07	0.5225D-02
3300	VI	0.5873D-05	0.2212D-03	0.5812D-02	0.3296D-02	0.3637D-04	0.7958D-07	0.9372D-02
3400	VI	0.1928D-04	0.5279D-03	0.9157D-02	0.6545D-02	0.5213D-04	0.1120D-06	0.1630D-01
3500	VI	0.5673D-04	0.1174D-02	0.1398D-01	0.1217D-01	0.7427D-04	0.1606D-06	0.2745D-01
3600	VI	0.1509D-03	0.2448D-02	0.2073D-01	0.2130D-01	0.1053D-03	0.2343D-06	0.4474D-01
3700	VI	0.3672D-03	0.4816D-02	0.2994D-01	0.3533D-01	0.1483D-03	0.3461D-06	0.7060D-01
3800	VI	0.8263D-03	0.9003D-02	0.4219D-01	0.5589D-01	0.2072D-03	0.5152D-06	0.1081D+03
3900	VI	0.1739D-02	0.1609D-01	0.5813D-01	0.8483D-01	0.2867D-03	0.7684D-06	0.1611D+00
4000	VI	0.3455D-02	0.2766D-01	0.7844D-01	0.1242D+00	0.3923D-03	0.1143D-05	0.2342D+00
4100	VI	0.6531D-02	0.4594D-01	0.1038D+00	0.1763D+00	0.5304D-03	0.1691D-05	0.3331D+00
4200	VI	0.1183D-01	0.7400D-01	0.1350D+00	0.2433D+00	0.7078D-03	0.2479D-05	0.4648D+00
4300	VI	0.2062D-01	0.1160D+00	0.1726D+00	0.3277D+00	0.9324D-03	0.3598D-05	0.6379D+00
4400	VI	0.3479D-01	0.1775D+00	0.2174D+00	0.4319D+00	0.1212D-02	0.5162D-05	0.8628D+00
4500	VI	0.5698D-01	0.2656D+00	0.2709D+00	0.5595D+00	0.1563D-02	0.7320D-05	0.1155D+01
4600	VI	0.9089D-01	0.3897D+00	0.3320D+00	0.7112D+00	0.1983D-02	0.1025D-04	0.1526D+01
4700	VI	0.1416D+00	0.5613D+00	0.4022D+00	0.8904D+00	0.2487D-02	0.1417D-04	0.1998D+01
4800	VI	0.2158D+00	0.7951D+00	0.4821D+00	0.1099D+01	0.3086D-02	0.1936D-04	0.2595D+01
4900	VI	0.3224D+00	0.1109D+01	0.5719D+00	0.1340D+01	0.3789D-02	0.2613D-04	0.3347D+01
5000	VI	0.4730D+00	0.1524D+01	0.6721D+00	0.1614D+01	0.4607D-02	0.3488D-04	0.4288D+01
5100	VI	0.6824D+00	0.2068D+01	0.7829D+00	0.1923D+01	0.5548D-02	0.4604D-04	0.5461D+01
5200	VI	0.9694D+00	0.2771D+01	0.9041D+00	0.2267D+01	0.6621D-02	0.6011D-04	0.6918D+01
5300	VI	0.1357D+01	0.3669D+01	0.1036D+01	0.2648D+01	0.7832D-02	0.7767D-04	0.8719D+01
5400	VI	0.1875D+01	0.4807D+01	0.1178D+01	0.3066D+01	0.9187D-02	0.9935D-04	0.1094D+02
5500	VI	0.2557D+01	0.6233D+01	0.1330D+01	0.3521D+01	0.1069D-01	0.1259D-03	0.1365D+02
5600	VI	0.3448D+01	0.8004D+01	0.1492D+01	0.4011D+01	0.1235D-01	0.1580D-03	0.1697D+02
5700	VI	0.4596D+01	0.1019D+02	0.1663D+01	0.4536D+01	0.1416D-01	0.1966D-03	0.2100D+02
5800	VI	0.6064D+01	0.1285D+02	0.1842D+01	0.5094D+01	0.1613D-01	0.2426D-03	0.2587D+02
5900	VI	0.7922D+01	0.1609D+02	0.2029D+01	0.5683D+01	0.1825D-01	0.2969D-03	0.3174D+02
6000	VI	0.1025D+02	0.1998D+02	0.2222D+01	0.6302D+01	0.2051D-01	0.3605D-03	0.3878D+02

^aRegion defined in Fig. 2.

Table A-3. Partial Pressures and Total Pressure (in MPa)
in Equilibrium with a UO_{1.96} Condensed Phase

T, K	REG ^a	p(O ₂)	p(O)	p(UO ₂)	p(UO ₁)	p(UO)	p(U)	p(total)
1500	II	0.16140D-29	0.16280D-20	0.75890D-13	0.59560D-19	0.95780D-12	0.60380D-12	0.1637D-11
1600	II	0.40580D-27	0.92290D-19	0.1531D-11	0.35040D-17	0.13270D-10	0.67990D-11	0.2160D-10
1700	II	0.52720D-25	0.3242D-17	0.2143D-10	0.1255D-15	0.13360D-09	0.5745D-10	0.2125D-09
1800	II	0.39370D-23	0.7626D-16	0.2210D-09	0.2963D-14	0.1032D-08	0.3831D-09	0.1636D-08
1900	I	0.27300D-21	0.1557D-14	0.1773D-08	0.6031D-13	0.5271D-08	0.1424D-08	0.8469D-08
2000	I	0.18070D-19	0.2842D-13	0.1153D-07	0.1095D-11	0.1867D-07	0.3181D-08	0.3359D-07
2100	I	0.8022D-18	0.3935D-12	0.6220D-07	0.1495D-10	0.5921D-07	0.6532D-08	0.1280D-06
2200	I	0.2523D-16	0.4293D-11	0.2853D-06	0.1545D-09	0.1656D-06	0.1247D-07	0.4635D-06
2300	I	0.5879D-15	0.3806D-10	0.1135D-05	0.1372D-08	0.4193D-06	0.2234D-07	0.1579D-05
2400	I	0.1054D-13	0.2815D-09	0.3990D-05	0.9772D-08	0.9717D-06	0.3782D-07	0.5010D-05
2500	I	0.1499D-12	0.1774D-08	0.1256D-04	0.5890D-07	0.2083D-05	0.6092D-07	0.1476D-04
2600	I	0.1739D-11	0.9705D-08	0.3584D-04	0.3061D-06	0.4166D-05	0.9115D-07	0.4041D-04
2700	III	0.1682D-10	0.4683D-07	0.4332D-04	0.1384D-05	0.7799D-05	0.1384D-06	0.1027D-03
2800	III	0.1383D-09	0.2019D-06	0.2213D-03	0.5563D-05	0.1373L-04	0.1958D-06	0.2430D-03
2900	III	0.9827D-09	0.7870D-06	0.4960D-03	0.1499D-04	0.2289D-04	0.2673D-06	0.5399D-03
3000	III	0.6121D-08	0.2801D-05	0.1010D-02	0.6479D-04	0.3640D-04	0.3537D-06	0.1135D-02
3100	V	0.9615D-07	0.1547D-04	0.2046D-02	0.3292D-03	0.3339D-04	0.1626D-06	0.2424D-02
3200	VI	0.4173D-06	0.4400D-04	0.3496D-02	0.7772D-03	0.4824D-04	0.2152D-06	0.4366D-02
3300	VI	0.1638D-05	0.1168D-03	0.5705D-02	0.1709D-02	0.6763D-04	0.2800D-06	0.7601D-02
3400	VI	0.5842D-05	0.2906D-03	0.8999D-02	0.3540D-02	0.9306D-04	0.3633D-06	0.1293D-01
3500	VI	0.1897D-04	0.6789D-03	0.1376D-01	0.6924D-02	0.1264D-03	0.4726D-06	0.2151D-01
3600	VI	0.5625D-04	0.1494D-02	0.2043D-01	0.1282D-01	0.1700E-03	0.6195D-06	0.3497D-01
3700	VI	0.1528D-03	0.3107D-02	0.2955D-01	0.2250D-01	0.2264D-03	0.3208D-06	0.5554D-01
3800	VI	0.3825D-03	0.6125D-02	0.4171D-01	0.3759D-01	0.3011D-03	0.1103D-05	0.8611D-01
3900	VI	0.8869D-03	0.1149D-01	0.5755D-01	0.5998D-01	0.3975D-03	0.1492D-05	0.1303D-03
4000	VI	0.1920D-02	0.2062D-01	0.7776D-01	0.9174D-01	0.5170D-03	0.3039D-05	0.1926D-03
4100	VI	0.3909D-02	0.3554D-01	0.1030D+00	0.1353D+00	0.6803D-03	0.2404D-05	0.2785D+00
4200	VI	0.7539D-02	0.5909D-01	0.1341D+00	0.1930D+00	0.8805D-03	0.3863D-05	0.3946D+00
4300	VI	0.1387D-01	0.9513D-01	0.1716D+00	0.2672D+00	0.1133D-02	0.5311D-05	0.5889D+00
4400	VI	0.2447D-01	0.1489D+00	0.2163D+00	0.3604L+00	0.1438D-02	0.7299D-05	0.7514D+00
4500	VI	0.4163D-01	0.2271D+00	0.2696D+00	0.4750D+00	0.1820D-02	0.9972D-05	0.1016D+01
4600	VI	0.6856D-01	0.3384D+00	0.3306D+00	0.6151D+00	0.1273D-02	0.1352D-04	0.1355D+01
4700	VI	0.1097D+00	0.4941D+00	0.4007D+00	0.7808D+00	0.2814D-02	0.1821D-04	0.1788D+01
4800	VI	0.1711D+00	0.7080D+00	0.4804D+00	0.9754D+00	0.3453D-02	0.2433D-04	0.2338D+01
4900	VI	0.2606D+00	0.9970D+00	0.5761D+00	0.1201D+01	0.4201D-02	0.3222D-04	0.3033D+01
5000	VI	0.3888D+00	0.1382D+01	0.6702D+00	0.1459D+01	0.5066D-02	0.4231D-04	0.3905D+01
5100	VI	0.5691D+00	0.1889D+01	0.7807D+00	0.1751D+C1	0.6059D-02	0.5505D-04	0.4995D+01
5200	VI	0.8185D+00	0.2546D+01	0.9018D+C0	0.2078D+01	0.7187D-02	0.7101D-04	0.6352D+01
5300	VI	0.1158D+01	0.3390D+01	0.1033D+01	0.2441D+01	0.8457D-02	0.9078D-04	0.8031D+01
5400	VI	0.1615D+01	0.4461D+C1	0.1175D+01	0.2840D+01	0.9876D-02	0.1151D-03	0.1010D+02
5500	VI	0.2222D+01	0.5808D+C1	0.1327D+01	0.3274D+01	0.1145D-01	0.1446D-03	0.1264D+02
5600	VI	0.3016D+01	0.7486D+01	0.1489D+01	0.3744D+01	0.1318D-01	0.1803D-03	0.1575D+02
5700	VI	0.4046D+01	0.9557D+01	0.1660D+01	0.4248D+01	0.1506D-01	0.2229D-03	0.1953D+02
5800	VI	0.5368D+01	0.1209D+02	0.1838D+01	0.4784D+01	0.1711D-01	0.2735D-03	0.2410D+02
5900	VI	0.7048D+01	0.1517D+02	0.2025D+01	0.5351D+01	0.1931D-01	0.3331D-03	0.2962D+02
6000	VI	0.9163D+01	0.1889D+02	0.2219D+01	0.5947D+01	0.2166D-01	0.4028D-03	0.3624D+02

^aRegion defined in Fig. 2

Table A-4. Partial Pressures and Total Pressure (in MPa)
in Equilibrium with a UC_{1.94} Condensed Phase

<i>T</i> , K	REG ^a	<i>p</i> (O ₂)	<i>p</i> (N ₂)	<i>p</i> (CO ₂)	<i>p</i> (NO _x)	<i>p</i> (NO)	<i>p</i> (U)	<i>p</i> (total)
1500	II	0.1614D-29	0.1628D-20	0.7539D-13	0.5956D-19	0.9578D-12	0.6038D-12	0.1637D-11
1600	II	0.4058D-27	0.9129D-19	0.1531D-11	0.3504D-17	0.1327D-10	0.6799D-11	0.2160D-10
1700	II	0.5272D-25	0.3242D-17	0.2143D-10	0.1255D-15	0.1336D-09	0.5745D-10	0.2125D-09
1800	II	0.3937D-23	0.7626D-16	0.2210D-09	0.2963D-14	0.1032D-08	0.3831D-09	0.1636D-08
1900	II	0.1837D-21	0.1277D-14	0.1758D-08	0.4905D-13	0.6370D-08	0.2098D-08	0.1024D-07
2000	I	0.7543D-20	0.1936D-13	0.1123D-07	0.6924D-12	0.2858D-07	0.7457D-08	0.4733D-07
2100	I	0.3349D-19	0.2542D-12	0.6087D-07	0.9454D-11	0.8968D-07	0.1531D-07	0.1659D-06
2200	I	0.1053D-16	0.2774E-11	0.2792D-06	0.1009D-09	0.2509D-06	0.2924D-07	0.5594D-06
2300	I	0.2454D-15	0.2455D-10	0.1111D-05	0.8676D-09	0.6351D-06	0.5236D-07	0.1800D-05
2400	I	0.4399D-14	0.1819D-09	0.1905D-05	0.6179D-08	0.1472D-05	0.8866D-07	0.5472D-05
2500	I	0.6260D-13	0.1146D-08	0.1229D-04	0.3725D-07	0.3155D-05	0.1428D-06	0.1563D-04
2600	I	0.7261D-12	0.6271D-08	0.3507D-04	0.1936D-06	0.6309D-05	0.2200D-06	0.4180D-04
2700	III	0.7024D-11	0.3026D-07	0.9133D-04	0.8783D-06	0.1181D-04	0.3244D-06	0.1044D-03
2800	III	0.5777D-10	0.1305D-06	0.2185D-03	0.3519D-05	0.2079D-04	0.4588D-06	0.2434D-03
2900	III	0.4107D-09	0.5088D-06	0.4854D-03	0.1262D-04	0.3466D-04	0.6259D-06	0.5334D-03
3000	III	0.2561D-08	0.1814D-05	0.1008D-02	0.4102D-04	0.5507D-04	0.8272D-06	0.1107D-02
3100	V	0.4065D-07	0.1006D-04	0.2012D-02	0.2105D-03	0.5050D-04	0.3783D-06	0.2283D-02
3200	VI	0.1781D-06	0.2875D-04	0.3423D-02	0.4972D-03	0.7230D-04	0.4937D-06	0.4022D-02
3300	VI	0.7098D-06	0.7689D-04	0.5568D-02	0.1102D-02	0.1006D-03	0.6331D-06	0.5869D-02
3400	VI	0.2587D-05	0.1934D-03	0.8819D-02	0.2309D-02	0.1371D-03	0.3040D-06	0.1146D-01
3500	VI	0.8661D-05	0.4588D-03	0.1349D-01	0.4589D-02	0.1835D-03	0.1615D-05	0.1873D-01
3600	VI	0.2672D-04	0.1030D-02	0.2006D-01	0.6872D-02	0.2424D-03	0.1280D-05	0.3030D-01
3700	VI	0.7618D-04	0.2144D-02	0.2405D-01	0.1561D-01	0.3158D-03	0.1619D-05	0.4725D-01
3800	VI	0.2012D-03	0.4443D-02	0.4105D-01	0.2083D-01	0.4086D-03	0.2059D-05	0.7294D-01
3900	VI	0.4919D-03	0.8577D-02	0.5572D-01	0.4411D-01	0.5249D-03	0.2644D-05	0.1104D+00
4000	VI	0.1132D-02	0.1583D-01	0.7674D-01	0.6955D-01	0.6707D-03	0.1415D-05	0.1639D+00
4100	VI	0.2432D-02	0.2803D-01	0.1018D+00	0.1055D+00	0.8923D-03	0.4451D-05	0.2386D+00
4200	VI	0.4930D-02	0.4778D-01	0.1327D+00	0.1544D+00	0.1077D-02	0.5845D-05	0.3409D+00
4300	VI	0.9482D-02	0.7866D-01	0.1700D+00	0.2188D+00	0.1354D-02	0.7706D-05	0.4783D+00
4400	VI	0.1740D-01	0.1455D+00	0.2144D+00	0.3013D+00	0.1690D-02	0.1018D-04	0.6604D+00
4500	VI	0.3063D-01	0.1947D+00	0.2676D+00	0.4052D+00	0.2105D-02	0.1345D-04	0.9003D+00
4600	VI	0.5195D-01	0.2946D+00	0.3283D+00	0.5317D+00	0.2594D-02	0.1773D-04	0.1209D+01
4700	VI	0.8525D-01	0.4356D+00	0.3982D+00	0.6840D+00	0.3172D-02	0.2329D-04	0.1606D+01
4800	VI	0.1359D+00	0.6310D+00	0.4776D+00	0.8643D+00	0.3853D-02	0.3045D-04	0.2113D+01
4900	VI	0.2110D+00	0.8970D+00	0.5671D+00	0.1075D+01	0.4645D-02	0.3960D-04	0.2754D+01
5000	VI	0.3199D+00	0.1254D+01	0.6669D+00	0.1317D+01	0.5559D-02	0.5118D-04	0.3563D+01
5100	VI	0.4748D+00	0.1725D+01	0.7772D+00	0.1592D+01	0.6604D-02	0.6569D-04	0.4576D+01
5200	VI	0.6912D+00	0.2340D+01	0.8980D+00	0.1902D+01	0.7778D-02	0.8373D-04	0.5838D+01
5300	VI	0.9886D+00	0.3132D+01	0.1029D+01	0.2246D+01	0.9118D-02	0.1060D-03	0.7405D+01
5400	VI	0.1391D+01	0.4141D+01	0.1171D+01	0.2626D+01	0.1060D-01	0.1331D-03	0.9339D+01
5500	VI	0.1929D+01	0.5413D+01	0.1323D+01	0.3040D+01	0.1224D-01	0.1659D-03	0.1172D+02
5600	VI	0.2638D+01	0.7001D+01	0.1484D+01	0.3490D+01	0.1404D-01	0.2054D-03	0.1463D+02
5700	VI	0.3561D+01	0.8966D+01	0.1654D+01	0.3972D+01	0.1601D-01	0.2525D-03	0.1817D+02
5800	VI	0.4751D+01	0.1138D+02	0.1833D+01	0.4487D+01	0.1813D-01	0.3081D-03	0.2247D+02
5900	VI	0.6269D+01	0.1431D+02	0.2019D+01	0.5032D+01	0.2042D-01	0.3734D-03	0.2765D+02
6000	VI	0.8186D+01	0.1785D+02	0.2212D+01	0.5605D+01	0.2286D-01	0.4496D-03	0.3388D+02

^aRegion defined in Fig. 2.

Table A-5. Partial Pressures and Total Pressure (in MPa) in Equilibrium with a UO_{1.92} Condensed Phase

T, K	REG ^a	p (O ₂)	p (O)	p (UO ₂)	p (UO ₃)	p (UO)	p (U)	p (total)
1500	II	0.1614D-29	0.1628D-20	0.7589D-13	0.5956D-19	0.9578D-12	0.6038D-12	0.1637D-11
1600	II	0.4058D-27	0.9229D-19	0.1531D-11	0.3504D-17	0.1327D-10	0.6799D-11	0.2160D-10
1700	II	0.5272D-25	0.3242D-17	0.2143D-10	0.1255D-15	0.1336D-09	0.5745D-10	0.2125D-09
1800	II	0.3937D-23	0.7626D-16	0.2210D-09	0.2963D-14	0.1032D-08	0.3831D-09	0.1636D-08
1900	II	0.1837D-21	0.1277D-14	0.1758D-08	0.4905D-13	0.6370D-08	0.2098D-08	0.1023D-07
2000	II	0.5722D-20	0.1599D-13	0.1119D-07	0.5978D-12	0.3253D-07	0.9743D-08	0.5346D-07
2100	I	0.1767D-18	0.1847D-12	0.5954D-07	0.6717D-11	0.1207D-06	0.2838D-07	0.2086D-06
2200	I	0.5559D-17	0.2015D-11	0.2730D-06	0.7166D-10	0.3378D-06	0.5417D-07	0.6651D-06
2300	I	0.1295D-15	0.1787D-10	0.1087D-05	0.6165D-09	0.8549D-06	0.9703D-07	0.2039D-05
2400	I	0.2322D-14	0.1321D-09	0.3819D-05	0.4390D-08	0.1981D-05	0.1643D-06	0.5970D-05
2500	I	0.3304D-13	0.8326D-09	0.1202D-04	0.2646D-07	0.4248D-05	0.2646D-06	0.1656D-04
2600	I	0.3832D-12	0.4556D-08	0.3430D-04	0.1375D-06	0.8494D-05	0.4076D-06	0.4334D-04
2700	III	0.3707D-11	0.2198D-07	0.8932D-04	0.6241D-06	0.1590D-04	0.6011D-06	0.1065D-03
2800	III	0.3049D-10	0.9481D-07	0.2137D-03	0.2500D-05	0.2798D-04	0.8500D-06	0.2452D-03
2900	III	0.2169D-09	0.3697D-06	0.4747D-03	0.8972D-05	0.4665D-04	0.1159D-05	0.5319D-03
3000	III	0.1353D-08	0.1317D-05	0.9862D-03	0.2916D-04	0.7411D-04	0.1532D-05	0.1092D-02
3100	V	0.2155D-07	0.7324D-05	0.1975D-02	0.1504D-03	0.6806D-04	0.7002D-06	0.2201D-02
3200	VI	0.9475D-07	0.2097D-04	0.3348D-02	0.3547D-03	0.9697D-04	0.9079D-06	0.3822D-02
3300	VI	0.3797D-06	0.5624D-04	0.5468D-02	0.7885D-03	0.1346D-03	0.1158D-05	0.6449D-02
3400	VI	0.1396D-05	0.1420D-03	0.8632D-02	0.1660D-02	0.1826D-03	0.1459D-05	0.1062D-01
3500	VI	0.4731D-05	0.3390D-03	0.1321D-01	0.3321D-02	0.2431D-03	0.1820D-05	0.1712D-01
3600	VI	0.1485D-04	0.7678D-03	0.1965D-01	0.6334D-02	0.3181D-03	0.2257D-05	0.2709D-01
3700	VI	0.4330D-04	0.1654D-02	0.2848D-01	0.1154D-01	0.4108D-03	0.2792D-05	0.4213D-01
3800	VI	0.1176D-03	0.3397D-02	0.4029D-01	0.2013D-01	0.5245D-03	0.3457D-05	0.6446D-01
3900	VI	0.2982D-03	0.6665D-02	0.5573D-01	0.3368D-01	0.6637D-03	0.4295D-05	0.9704D-01
4000	VI	0.7081D-03	0.1252D-01	0.7549D-01	0.5412D-01	0.8340D-03	0.5368D-05	0.1437D+00
4100	VI	0.1579D-02	0.2259D-01	0.1003D+00	0.8373D-01	0.1042D-02	0.6754D-05	0.2093D+00
4200	VI	0.3322D-02	0.3922D-01	0.1309D+00	0.1250D+00	0.1295D-02	0.8556D-05	0.2997D+00
4300	VI	0.6617D-02	0.6571D-01	0.1679D+00	0.1805D+00	0.1601D-02	0.1090D-04	0.4223D+00
4400	VI	0.1254D-01	0.1086D+00	0.2120D+00	0.2529D+00	0.1968D-02	0.1396D-04	0.5860D+00
4500	VI	0.2274D-01	0.1678D+00	0.2648D+00	0.3455D+00	0.2419D-02	0.1793D-04	0.8033D+00
4600	VI	0.3960D-01	0.2572D+00	0.3252D+00	0.4599D+00	0.2942D-02	0.2303D-04	0.1085D+01
4700	VI	0.6653D-01	0.3848D+00	0.3947D+00	0.5990D+00	0.3560D-02	0.2958D-04	0.1449D+01
4800	VI	0.1082D+00	0.5631D+00	0.4739D+00	0.7652D+00	0.4283D-02	0.3793D-04	0.1915D+01
4900	VI	0.1710D+00	0.8077D+00	0.5630D+00	0.9605D+00	0.5121D-02	0.4849D-04	0.2507D+01
5000	VI	0.2634D+00	0.1138D+01	0.6624D+00	0.1187D+01	0.6084D-02	0.6173D-04	0.3256D+01
5100	VI	0.3963D+00	0.1576D+01	0.7723D+00	0.1445D+01	0.7182D-02	0.7821D-04	0.4197D+01
5200	VI	0.5838D+00	0.2150D+01	0.8927D+00	0.1737D+01	0.8424D-02	0.9855D-04	0.5373D+01
5300	VI	0.8437D+00	0.2893D+01	0.1024D+01	0.2063D+01	0.9816D-02	0.1235D-03	0.6834D+01
5400	VI	0.1198D+01	0.3843D+01	0.1165D+01	0.2424D+01	0.1136D-01	0.1537D-03	0.8641D+01
5500	VI	0.1675D+01	0.5043D+01	0.1316D+01	0.2819D+01	0.1307D-01	0.1902D-03	0.1087D+02
5600	VI	0.2306D+01	0.6546D+01	0.1477D+01	0.3248D+01	0.1495D-01	0.2338D-03	0.1359D+02
5700	VI	0.3133D+01	0.8410D+01	0.1647D+01	0.3709D+01	0.1699D-01	0.2857D-03	0.1692D+02
5800	VI	0.4203D+01	0.1070D+02	0.1825D+01	0.4202D+01	0.1920D-01	0.3468D-03	0.2095D+02
5900	VI	0.5573D+01	0.1349D+02	0.2011D+01	0.4725D+01	0.2156D-01	0.4183D-03	0.2582D+02
6000	VI	0.7309D+01	0.1687D+02	0.2204D+01	0.5275D+01	0.2409D-01	0.5015D-03	0.3168D+02

^aRegion defined in Fig. 2.

Table A-6. Partial Pressures and Total Pressure (in MPa)
in Equilibrium with a $\text{UO}_{1.90}$ Condensed Phase

T	Region ^a	$p(\text{O}_2)$	$p(\text{CO})$	$p(\text{H}_2\text{O})$	$p(\text{UO}_3)$	$p(\text{UO}_4)$	$p(\text{U})$	$p(\text{total})$
1500	II	0.1614D-29	0.1e28D-20	0.7589D-13	0.5956D-19	0.9578D-12	0.6038D-12	0.1637D-11
1600	II	0.4058D-27	0.9229D-19	0.1531D-11	0.3504D-17	0.1327D-10	0.6799D-11	0.2160D-10
1700	II	0.5272D-25	0.3442D-17	0.2143D-10	0.1255D-15	0.1336D-09	0.5745D-10	0.2125D-09
1800	II	0.3937D-23	0.7626D-16	0.2210D-09	0.2963D-14	0.1032D-08	0.3831D-09	0.1636D-08
1900	II	0.1837D-21	0.1277D-14	0.1758D-08	0.4905D-13	0.6370D-08	0.2098D-08	0.1023D-07
2000	II	0.5722D-20	0.1599D-13	0.1119D-07	0.5978D-12	0.3253D-07	0.9743D-08	0.5346D-07
2100	II	0.1255D-18	0.1556D-12	0.5866D-07	0.5576D-11	0.1412D-06	0.3939D-07	0.2392D-06
2200	I	0.3334D-17	0.1561D-11	0.2669D-06	0.5424D-10	0.4262D-06	0.8828D-07	0.7814D-06
2300	I	0.7769D-16	0.1384D-10	0.1062D-05	0.4666D-09	0.1079D-05	0.1581D-06	0.2300D-05
2400	I	0.1393D-14	0.1023D-09	0.3733D-05	0.3323D-08	0.2501D-05	0.2677D-06	0.6505D-05
2500	I	0.1912D-13	0.6448D-09	0.1175D-04	0.2003D-07	0.5360D-05	0.4312D-06	0.1755D-04
2600	I	0.2299D-12	0.3528D-08	0.3352D-04	0.1041D-06	0.1072D-04	0.6642D-06	0.4461D-04
2700	III	0.2224D-11	0.1703D-07	0.8730D-04	0.4724D-06	0.2007D-04	0.9744D-06	0.1688D-03
2800	III	0.1829D-10	0.7343D-07	0.2089D-03	0.1893D-05	0.3531D-04	0.1389D-05	0.2475D-03
2900	III	0.1301D-09	0.2863D-06	0.4644D-03	0.6791D-05	0.5887D-04	0.1389D-05	0.5314D-03
3000	IV	0.9306D-09	0.1092D-05	0.9703D-03	0.2379D-04	0.8791D-04	0.2191D-05	0.1085D-02
3100	V	0.1295D-07	0.5678D-05	0.1935D-02	0.1143D-03	0.8604D-04	0.1142D-05	0.2142D-02
3200	VI	0.5704D-07	0.1627D-04	0.3273D-02	0.2e90D-03	0.1222D-03	0.1474D-05	0.3682D-02
3300	VI	0.2292D-06	0.4369D-04	0.5346D-02	0.5989D-03	0.1694D-03	0.1876D-05	0.6160D-02
3400	VI	0.8458D-06	0.1106D-03	0.8440D-02	0.1263D-02	0.2294D-03	0.2353D-05	0.1050D-01
3500	VI	0.2885D-05	0.2648D-03	0.1292D-01	0.2536D-02	0.3044D-01	0.2919D-05	0.1803D-01
3600	VI	0.9134D-05	0.6022D-03	0.1923D-01	0.4860D-02	0.3969D-03	0.3590D-05	0.2511D-01
3700	VI	0.2696D-04	0.1305D-02	0.2788D-01	0.8915D-02	0.5097D-03	0.4394D-05	0.3H64D-01
3800	VI	0.7436D-04	0.2701D-02	0.3947D-01	0.1568D-01	0.6461D-03	0.5355D-05	0.5858D-01
3900	VI	0.1923D-03	0.5351D-02	0.5464D-01	0.2651D-01	0.8106D-03	0.6533D-05	0.8751D-01
4000	VI	0.4669D-03	0.1017D-01	0.7410D-01	0.4113D-01	0.1008D-01	0.7891D-05	0.1e99D+01
4100	VI	0.1068D-02	0.1858D-01	0.9855D-01	0.6755D-01	0.1245D-02	0.8160D-05	0.1871D+00
4200	VI	0.2306D-02	0.3768D-01	0.1297D+00	0.1025D+00	0.1528D-02	0.1212D-04	0.2677D+00
4300	VI	0.4719D-02	0.5550D-01	0.1653D+00	0.1502D+00	0.1867D-02	0.1506D-04	0.3776D+00
4400	VI	0.9185D-02	0.9120D-01	0.2090D+00	0.2134D+00	0.2258D-02	0.1880D-04	0.5251D+00
4500	VI	0.1707D-01	0.1454D+00	0.2614D+00	0.2955D+00	0.2756D-02	0.2358D-04	0.7222D+00
4600	VI	0.3041D-01	0.2254D+00	0.3214D+00	0.3983D+00	0.1518D-04	0.2964D-04	0.9788D+00
4700	VI	0.5217D-01	0.3408D+00	0.3905D+00	0.5247D+00	0.3976D-02	0.3732D-04	0.1312D+01
4800	VI	0.8644D-01	0.5033D+00	0.4691D+00	0.6771D+00	0.4743D-02	0.4700D-04	0.1741D+01
4900	VI	0.1390D+00	0.7280D+00	0.5577D+00	0.8577D+00	0.5628D-02	0.5912D-04	0.2288D+01
5000	VI	0.2172D+00	0.1033D+01	0.6567D+00	0.1068D+01	0.6642D-02	0.7422D-04	0.2982D+01
5100	VI	0.3310D+00	0.1440D+01	0.7661D+00	0.1310D+01	0.7795D-02	0.9287D-04	0.3856D+01
5200	VI	0.4933D+00	0.1977D+01	0.8860D+00	0.1585D+01	0.9095D-02	0.1157D-03	0.4950D+01
5300	VI	0.7201D+00	0.2673D+01	0.1016D+01	0.1893D+01	0.1055D-01	0.1436D-03	0.6313D+01
5400	VI	0.1032D+01	0.3566D+01	0.1157D+01	0.2234D+01	0.1216D-01	0.1773D-03	0.8002D+01
5500	VI	0.1454D+01	0.4699D+01	0.1308D+01	0.2610D+01	0.1394D-01	0.2177D-03	0.1008D+02
5600	VI	0.2016D+01	0.6120D+01	0.1468D+01	0.3018D+01	0.1589D-01	0.2659D-03	0.1264D+02
5700	VI	0.2755D+01	0.7887D+01	0.1637D+01	0.3458D+01	0.1801D-01	0.3229D-03	0.1576D+02
5800	VI	0.3717D+01	0.1006D+02	0.1815D+01	0.3930D+01	0.2030D-01	0.3900D-03	0.1954D+02
5900	VI	0.4952D+01	0.1272D+02	0.2000D+01	0.4431D+01	0.2277D-01	0.4682D-03	0.2413D+02
6000	VI	0.6524D+01	0.1594D+02	0.2192D+01	0.4959D+01	0.2537D-01	0.5590D-03	0.2964D+02

^aRegion defined in Fig. 2.