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**THE THERMODYNAMICS OF THORIUM-OXYGEN AND URANIUM-
OXYGEN SYSTEMS**

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SECTION I

THERMODYNAMICS OF THE URANIUM-OXYGEN SYSTEM

The vapor above uranium oxide condensed phases includes U, UO, UO₂, and UO₃. The composition of the vapor is strongly dependent upon the O/U ratio. In the three phase system U(l)/UO₂(s) and vapor (O/U ≤ 1.7) the principal vapor phase species is UO with smaller amounts of U and UO₂ vapors. For UO₂ a congruent evaporation seems to predominate giving mostly UO₂ with about equimolar but much smaller quantities of UO and UO₃. For hyperstoichiometric urania (O/U > 2) UO₃ and UO₂ are the principal vapor phase species.

Uranium (s)

The vapor pressure of uranium has been studied over a wide temperature range most recently by Ackermann and Rauh (2) and Pattoret, Drowart and Smoes (2). Ackermann and Rauh have shown that the activity of the condensed phase varies from 1.0 downward as the electronegativity of the dissolved component increases. They give an expression for the vapor pressure of uranium

$$\log P_U (\text{atm}) = (5.71 \pm 0.17) - (25,230 \pm 370)/T.$$

This yields a $\Delta H_s^\circ_{298} = 126.3 \pm 1.0$ kcal/mole. Pattoret et al (4) give

$$\log P_U (\text{atm}) = (5.920 \pm 0.135) - (26,210 \pm 270)/T \text{ and}$$

$$\Delta H_s^\circ_{298} = 129.0 \pm 2.0 \text{ kcal/mole.}$$

These authors also summarize all the previous work on these systems by their laboratories and others. It is perhaps most significant that the vapor pressures that one will observe in these systems are a strong function of the container material or the dissolved components.

UO₂(s)/U(l)

The partial pressures of the species are determined by mass spectroscopic measurements, while the total pressures have been measured by both effusion and transpiration techniques. The total mass spectroscopic instrument sensitivity to a particular gas phase species has to be known in order to compute the partial pressures

$$P_i = I^+_{(i)} T / \sigma_i v_i = I^+ T / k_i$$

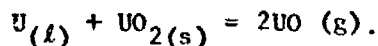
where σ_i and v_i are the cross-section for ionization by electrons at a given energy and the detector sensitivity to the species of interest. Various assumptions have been made concerning these k_i quantities. Ackermann et al (3) in their work on the U(l)/UC₂(s) system used equal sensitivities for U(v), UO(v) and UO₂(v). A recent work by Blackburn and Danielson (4) has advocated values of 0.66, 1.25, and 0.31 for the product of multiplier yield and partial relative ionization cross-section for U, UO and UO₂ using a 10 eV ionizing electron beam. (For this energy beam these partial relative ionization cross-sections are equal to the total relative ionization cross-sections).

The pressure of uranium species above of U(l), UO₂(s) is given by

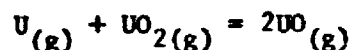
$$\log P_e = (7.25 \pm 0.15) - (27.020 \pm 250)/T \text{ (for 1580-2400°K)}$$

by Ackermann et al (1). Pattoret et al (3) report a pressure of UO given by $\log P = 8.19 - 28,020/T$ in the temperature interval of 1700 - 2150°K.

There is considerable evidence that the system UO₂(s)/U(l) is far from ideal. Therefore the activities of the condensed phases cannot be assumed to be unity, for the process



Consequently the measurement of thermal functions for this system has to be done using gas phase equilibria where activity coefficients can be assumed to be unity. Ackermann et al (3) measured the gas phase equilibria



and from the known free energy functions of $UO_2(g)$ (this will be discussed later) and $U(g)$ and the measured equilibrium constant as a function of temperature.

$$K = \frac{P_{UO}^2}{P_U P_{UO_2}}$$

where, $\log K = (1.268 \pm 0.05) + (2091 \pm 117)/T$

They computed $\Delta G_f^\circ (UO, g)$

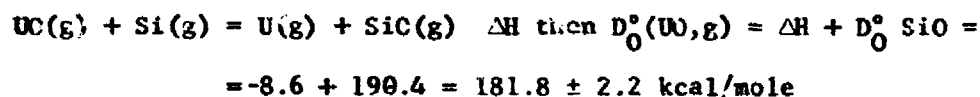
$$\begin{aligned} \Delta G_f^\circ (UO, g) &= 1/2 \Delta G_f^\circ (UO_2, g) + 1/2 \Delta G_f^\circ (U, g) - 1/2 R'T \log K \\ &= -7,800 - 13.84T. \end{aligned}$$

It should be, of course, noted that this measurement of K required a knowledge of the k_i 's. Ackermann et al (3) assumed that k_i of the various species were equal to each other. Incorporation of Blackburn and Danielson's data (4) for partial relative ionization cross-sections would change the measured equilibrium constant by almost a factor of 1/8. This would have the effect of decreasing the ΔS_f° of $UO(g)$ from 13.84 e.u. to about 11.78 e.u. without affecting the ΔH° term. Other potential sources of error are the $\Delta G_f^\circ UO_2(g)$ and $\Delta G_f^\circ U(g)$. As will be seen later in this report an uncertainty in the entropy of formation, $\Delta S_f^\circ UO_2(g)$ is not unlikely. This error would contribute an uncertainty of 1.5 e.u. to the $\Delta S_f^\circ UO(g)$.

The D_0° computed from the ΔH_f° of UO determined by Ackermann et al (3) is

$$D_0^\circ = \Delta H_s(U, g) + 1/2 D_0^\circ O_2 - \Delta H_f(UO) \\ = 115.4_3 + 59.0 + 7.8 = 182.2 \pm 3 \text{ kcal/mole.}$$

(It should of course be noted that a correction for ΔH_s and $\Delta H_f UO$ to 0 K has not been made, however these corrections should go in the same direction and tend to cancel each other). Pattovet et al (5) determined a D_0° for UO(g) from the isomolecular exchange reaction



which is in excellent agreement. Unfortunately no relative ionization cross-sections were quoted in this work. Although in a later work (2) the authors give k_i 's of 1.15, 0.80, and 0.55 for U, UO and UO₂ respectively. These numbers would give an overall correction of 0.99 to the equilibrium constants given by Ackermann et al (3).

A computation of ΔS_f° of UO from spectroscopic data requires a knowledge of the electronic levels of UO. No spectroscopic assignment for the electronic energy levels of UO is available in the literature. The infrared spectrum of matrix isolated UO has been observed by several workers. Using this vibrational frequency and the estimated bond distance of about 1.75Å one can compute the S_{2000K}° for UO without electronic contribution of 73.4 e.u. From this value and those of liquid uranium and molecular oxygen an entropy of formation of UO (defined by the equation $U(l) + 1/2 O_2 = UO(g) (2000K)$) of 8.9 e.u. mole⁻¹ is computed. This value is considerably less than the 13.84 e.u. quoted by Ackermann (or for that

matter the 11.78 obtained by using Blackburn and Danielson's k_i 's). Unfortunately there exists no easy way to remedy this situation without the necessary spectroscopic data. The ΔS_f° of 13.84 can be rationalized to the observed data of 8.1 e.u. if one has a ground state with a degeneracy of about 13. (The $\Delta S_f^\circ = 11.78$ gives a ground state degeneracy of about 5).

The partial pressures of the U, UO, UO₂ species above the three phase system U(l)/UO_{2-x}(s) have been given by Ackermann et al (3) as

$$\log P_U = (5.21 \pm 0.14) - (25,640 \pm 300)/T$$

$$\log P_{UO} = (7.11 \pm 0.14) - (26,880 \pm 300)/T$$

$$\log P_{UO_2} = (7.74 \pm 0.14) - (30,180 \pm 300)/T.$$

These equations were derived from their measurements in the temperature range of 1820 - 2490 K assuming equal $\sigma_i v_i$ for the three species.

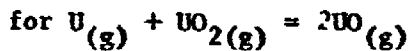
Pattoret et al (5) have also observed that the $I_{UO}^+ / I_U^+ / I_{UO_2}^+$ is about 10/1/1 for this system. Pressure ratios of about 10/1/1 are obtained from Ackermann et al whereas ratios of about 12.5/0.87/1.82 and about 7.75/1.52/3.23 are obtained using the $\sigma_i v_i$ given by Pattoret et al (5) and Blackburn and Danielson (4) respectively. The partial pressures computed using the three sets of $\sigma_i v_i$ are given in the following table. (The data for P_e of Ackermann (3) at 2000 K are used in order to facilitate a direct comparison.)

	$P_U(\text{atm})$	$P_{UO}(\text{atm})$	$P_{UO_2}(\text{atm})$	$P_U/P_{UO}/P_{UO_2}$
ARC(3)	2.45×10^{-8}	4.68×10^{-7}	4.47×10^{-8}	1/18.9/1.82
PDS(5)	2.13×10^{-8}	5.79×10^{-7}	8.13×10^{-8}	1/27.2/3.82
BD (4)	3.72×10^{-8}	3.59×10^{-7}	1.44×10^{-7}	1/9.65/3.87

It should be noted that the partial pressure ratios are significantly different from the three sets of $\sigma_i \gamma_i$ used.

The measurements of Pattoret et al (5) give a pressure of UO about 2.4 times greater than those of Ackermann et al (3). The $\sigma_i \gamma_i$ used by the three workers are given below together with the K_P computed.

relative $\sigma_i \gamma_i$	<u>U</u>	<u>UO</u>	<u>UO₂</u>	<u>Ke</u>
<u>PDS</u> (5)	1.15	0.80	0.55	0.988
<u>ARC</u> (3)	1	1	1	1
<u>BD</u> (4)	0.66	1.29	0.31	0.123



$$K_P(T) = \left[\frac{I^+_{UO_2}/(\sigma\gamma)_{UO_2}}{I^+_{UO_2}/(\sigma\gamma)_{UO_2} I^+_{U}/(\sigma\gamma)_U} \right]^{K_e}$$

At 2000K the pressures given by Ackermann et al (3) and Pattoret et al (5) are

$$\begin{aligned} \text{ARC(3)} P_{UO} &= 4.68 \times 10^{-7} \\ P_{UO_2} &= 4.47 \times 10^{-8} \\ P_U &= 2.45 \times 10^{-8} \\ \text{PDS(5)} P_{UO} &= 1.12 \times 10^{-6} \end{aligned} \quad P_e = 5.495 \times 10^{-7}$$

Stoichiometric UO₂

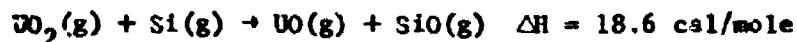
The vapor pressure above stoichiometric UO₂ has been measured by several workers (6-10) using both mass transpiration and effusion techniques. The congruently evaporating compositions of urania have also been systematically measured as a function of temperature by analysis of the residues after appreciable Knudsen effusion loss. These residues become increasingly hypostoichiometric with temperature varying from UO_{2.000} to UO_{1.940} in the 1940 - 2386 K temperature interval (9). It has also been suggested that a significant partial pressure of UO and UO₃ is present even at lower temperatures, UO₃ becoming predominant to the UO as the temperature increases (9).

The results of some of the more recent experiments are given below. The vapor pressure of the uranium bearing species is represented by the equation

$$\Delta G = -RT \ln P_{(U)} = \Delta H - T\Delta S$$
$$\text{or } \log P_{(\text{atm})} = \frac{-\Delta H}{R'T} + \frac{\Delta S}{R'}$$

<u>ΔH</u>	<u>ΔS</u>	<u>method</u>	<u>temp. range</u>	<u>ref.</u>	<u>P_{2200K}</u>
137.1	36.4	mass effusion	1600-2200	AGT(6)	2.17 x 10 ⁻⁶
147.1	42.2	" "	1920-2220	Ivanov(10)	4.08
147.8	42.0	" "	2200-2800	Ohse(8)	3.14
141.2	39.4	mass spect.	1890-2420	PDS '67(5)	3.84
143.1	39.4	transpiration	2085-2705	TH (7)	2.49
134.1	34.5	" "	2000-2940	Alexander (11)	1.66

By observing the equilibrium ion currents for the reaction



and from a knowledge of $D_0^\circ \text{UO}(\text{g})$ and $\text{SiO}(\text{g})$. Pattoret et al (5) computed a D_0° of UO_2 of 353.6 ± 3.2 kcal/mole,

$$\begin{aligned} D_0^\circ \text{UO}_2 &= \Delta H + D_0^\circ \text{SiO} + D_0^\circ \text{UO} \\ &= 18.6 + 190.4 + 181.8 = 353.6. \end{aligned}$$

This value is in good agreement with 353.2 (14.9eV) given by Ackermann Gilles and Thorn (6). These workers used the $\text{UO}_2(\text{g})$ equilibria coupled with the data for $\text{UO}_2(\text{s})$ given by Kelley (Bur. Mines Bull. 476, 1909) and estimated thermodynamic data for the vapor. Pattoret et al (5) obtained a value of 352.5 kcal/mole from the $\text{UO}_2(\text{s}) = \text{UO}_2(\text{g})$ using

$$\Delta H_{f, 298}^\circ \text{UO}_2(\text{s}) = -259.5 \text{ kcal/mole}$$

$$\Delta H_{s, 298}^\circ \text{UO}_2 = 125 \text{ kcal/mole}$$

then

$$\text{UO}_2(\text{s}) = \text{UO}_2(\text{g}) \quad \Delta H_f^\circ = 152.5$$

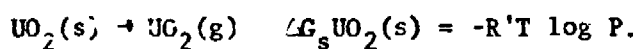
$$\begin{aligned} D_0^\circ(\text{UO}_2\text{g}) &= -\Delta H_f(\text{UO}_2, \text{g}) + \Delta H_s \text{U}(\text{s}) + D_0^\circ \text{O}_2 \\ &= (259.5 - 152.5) + 129.0 + 117 = 353 \text{ kcal/mole} \end{aligned}$$

$$\text{UO}_2(\text{g}) = \text{U}(\text{g}) + 2\text{O}(\text{g}) \quad D_0^\circ \text{UO}_2$$

Therefore since both gas phase equilibria coupled with assumed previously determined dissociation energies agree well with ΔH for $\text{UO}_2(\text{s}) = \text{UO}_2(\text{g})$ coupled with $\Delta H_s \text{U}$ and $D_0^\circ \text{O}_2$ for the determination of $D_0^\circ(\text{UO}_2)$ one can have a degree of confidence of the thermal functions for UO_2 determined by the congruent vaporization of stoichiometric urania.

It has been noted by Tetenbaum and Hunt (7) that the pressures derived from effusion measurements on stoichiometric urania by Ackermann et al (6) and Ohse (8) are higher at temperatures above 2350C than those obtainable using the transpiration methods. The original proposal by Ackermann et al of a UO_2 dimer is not consistent with the pressure measurements of Tetenbaum and Hunt. Mass spectroscopic measurements have not been successful in finding a UO_2 dimer. Rather the positive curvature in the vapor pressure with temperature above 2350 C is probably caused by a departure from molecular flow in the Knudsen cell. Edwards et al (9) have suggested increased pressures of UO_3 in order to reach the proper UO_{2-x} for the higher temperatures. This explanation has also been rejected by Tetenbaum and Hunt since $\ln P$ vs $1/T$ is a straight line over the range of 2080-2705 K for various UO_{2-x} specimens.

The free energy of formation, $\Delta G_f^\circ UO_2(g)$ can in principle be derived from the vapor pressure measurements above stoichiometric UO_2 assuming the principal reaction is



This quantity coupled with $\Delta G_f^\circ UO_2(s)$ then yields $\Delta G_f^\circ UO_2(g) = \Delta G_f^\circ UO_2(s) + \Delta G_s UO_2(s)$.

If one inspects table 3 which gives the $\Delta G_s^\circ UO_2(s) = \Delta H^\circ(s) - T\Delta S^\circ(s)$ one finds the ΔS terms vary from 42.4 to 34.5 cal/mole K. with an average deviation of about 2.4 cal/mole K. The uncertainty in the entropy of this process will be reflected in the computation of $\Delta S_f^\circ UO_2(g)$. Using Ackermann et al (6) vapor pressure data one obtains $\Delta S_f^\circ = -4.24$ e.u., the data of Pattoret et al (5) gives $\Delta S_f^\circ = -1.24$

as does the data of Tetenbaum and Hunt (7). Perhaps this latter value is expected to be more reliable since the method of mass transpiration over a long temperature range is in agreement with mass spectroscopic observations over a smaller and to an extent overlapping temperature range.

Using the vibrational assignment for UO_2 given by Gabelnik et al (12) and Abramowitz et al (13) namely $\nu_1 = 765.9$, $\nu_3 = 776.1$ and $\nu_2 = 81 \text{ cm}^{-1}$ for a linear UO_2 molecule with a $r \text{ U-O} = 1.75 \text{ \AA}$ a $S_{2000\text{K}}^\circ = 92.3 \text{ cal mole}^{-1} \text{ }^{-1}$ as computed. Small variations of r will not significantly effect the computed functions. Coupling this with $S_{2000}^\circ \text{U}(l) = 32.53$ and $S_{2000}^\circ \text{O}_2 = 64.18$ one obtains a $\Delta S_f \text{UO}_2(\text{g}) = -4.41 \text{ cal mole}^{-1} \text{K}^{-1}$ in excellent agreement with $\Delta S_f^\circ = -4.24$ given by Ackermann et al (6) and in good agreement with $\Delta S_f^\circ = -1.24$ given by Tetenbaum and Hunt (7) and Pattoret et al (5). It should of course be noted that for the purposes of this computation of $S_{2000\text{K}}^\circ$ of UO_2 a singlet ground state was assumed and any contribution to the entropy from low lying electronic states has been neglected. (There have not been any electronic spectra of $\text{UO}_2(\text{g})$ or matrix isolated UO_2 observed and analyzed).

The ionization potential of U, UO and UO_2 have been measured using the RPD (retarding potential difference) method by Mann (14). He has given values of 6.1, 5.7, and 5.5 eV for the ionization potentials of U, UO , UO_2 respectively. These values which are probably good to about 0.1 eV have been accepted by other workers in the field. These ionization potentials coupled with the $\Delta H_f \text{UO}$ and $\Delta H_f \text{UO}_2$ then can be used to

estimate exothermicities of reactions such as:

<u>Reaction</u>	<u>eV</u>
$U(s) + O_2 \rightarrow UO_2(g)$	-5.27
$U(s) + \frac{1}{2}O_2 \rightarrow UO(g)$	-0.34
$U(s) \rightarrow U(g)$	+5.00
$U(g) + O_2 \rightarrow UO_2(g)$	-10.27
$U(g) + O_2 \rightarrow UO_2^+ + e$	-4.77
$U(g) + \frac{1}{2}O_2 \rightarrow UO(g)$	-5.34
$U(g) + O \rightarrow UO(g)$	-7.90
$U(g) + O \rightarrow UO^+(g) + e$	-2.20
$U(g) + \frac{1}{2}O_2 \rightarrow UO^+ + e$	+0.36
$U(g) + O_3 \rightarrow UO_2 + O$	-7.71
$U(g) + O_3 \rightarrow UO_2^+ + O + e$	1.21
$U(g) + O_3 \rightarrow UO + O_2$	-4.34
$U(g) + O_3 \rightarrow UO^+ + O_2$	+1.36
$U(g) + N_2O \rightarrow UO + N_2$	-4.49
$U(g) + N_2O \rightarrow UO^+ + N_2 + e$	+1.21

The thermodynamic functions for UO and $UO_2(g)$ are given in Tables 1 and 2. These computations are done assuming singlet ground states for both species and no allowance is made for any possible contribution to these functions from any excited electronic states. This was done in this manner since there are no experimental determinations for the electronically excited levels of UO and UO_2 .

TABLE 1. THERMODYNAMIC FUNCTIONS FOR UO(g)

DE APPROXIMATE AS (DE) 127(1) 2.93574E-7 STATE 1

T K	CP CAL/K MOL	H-HC CAL/MOL	S CAL/K MOL	-(G-HC)/T CAL/K MOL
300.15	7.57709	2119.57	57.2717	50.1626
300	7.58519	2133.59	57.2186	50.2066
400	7.96908	2912.23	59.5559	52.2753
500	8.23568	3723.29	61.2646	53.9181
600	8.41637	4556.48	62.5832	55.2891
700	8.54034	5401.69	64.1905	56.4695
800	8.62796	6263.38	65.2369	57.5078
900	8.69151	7129.47	66.257	58.4354
1000	8.7391	8001.11	67.2753	59.2702
1100	8.77559	8876.92	68.11	60.0001
1200	8.8042	9755.97	68.8709	60.7449
1300	8.82707	10637.7	69.5805	61.3978
1400	8.84569	11521.2	70.2354	62.0059
1500	8.86108	12406.6	70.8462	62.5752
1600	8.874	13293.8	71.4155	63.1102
1700	8.88497	14181.3	71.9518	63.6149
1800	8.89441	15070.3	72.4665	64.0926
1900	8.90262	15960.2	72.9441	64.544
2000	8.90983	16850.8	73.4009	64.9775
2100	8.91622	17742.1	73.8378	65.3891
2200	8.92193	18634.	74.2523	65.7827
2300	8.92707	19526.5	74.6442	66.1596
2400	8.93175	20419.4	75.0294	66.5213
2500	8.93602	21312.6	75.3991	66.869
2600	8.93995	22206.1	75.7447	67.2037
2700	8.94358	23100.8	76.0691	67.5263
2800	8.94697	23995.3	76.3774	67.8377
2900	8.95013	24890.2	76.6715	68.1387
3000	8.9531	25785.3	77.0049	68.4298
3100	8.95591	26680.2	77.3185	68.7118
3200	8.95857	27576.5	77.6099	68.9852
3300	8.96111	28472.5	77.8784	69.2506
3400	8.96352	29369.7	78.1442	69.5089
3500	8.96584	30265.2	78.4086	69.7592
3600	8.96806	31161.9	78.6586	70.0025
3700	8.97021	32058.8	78.9044	70.2398
3800	8.97228	32955.8	79.1436	70.471
3900	8.97428	33853.3	79.3767	70.6963
4000	8.97623	34750.8	79.6039	70.9162
4100	8.97812	35648.5	79.8254	71.1309
4200	8.97997	36546.4	80.0419	71.3404
4300	8.98177	37444.5	80.2532	71.5452
4400	8.98353	38342.8	80.4597	71.7455
4500	8.98524	39241.2	80.6616	71.9414
4600	8.98695	40139.8	80.8591	72.1331
4700	8.98861	41038.6	81.0524	72.3208
4800	8.99024	41937.5	81.2417	72.5047
4900	8.99185	42836.7	81.4271	72.6849
5000	8.99342	43735.9	81.6087	72.8615
5100	8.995	44635.3	81.7868	73.0348
5200	8.99654	45534.9	81.9615	73.2048
5300	8.99804	46434.6	82.1329	73.3714
5400	8.99957	47334.5	82.3011	73.5354
5500	9.00105	48234.6	82.4662	73.6963
5600	9.00257	49134.7	82.6284	73.8543
5700	9.00409	50035.1	82.7877	74.0097
5800	9.00564	50935.5	82.9443	74.1623
5900	9.00717	51836.2	83.0983	74.3125
6000	9.00879	52736.9	83.2497	74.4602

MOLECULAR WEIGHT= 254.07
 MOLECULAR CONSTANTS ARE LISTED AS
 LEVEL=1, E2=AL, Y2=1, E3=1, E4=1, E5=1, MULTIPLICITY=100

1 820 0 0 .3668 0 2.93574E-7 1 0

TABLE 2. THERMODYNAMIC FUNCTIONS FOR $UO_2(g)$

T	(F-HR)/T	(H-HC)/T	S	CP
298.15	-55.0126	10.5006	65.5032	12.2796
300	-55.078	10.5812	65.6592	12.2967
400	-58.1969	11.1133	69.3102	13.0742
500	-60.7262	11.5608	72.2572	13.5907
600	-62.8679	11.9293	74.7472	13.9997
700	-64.7303	12.2324	76.9627	14.1581
800	-66.3926	12.4837	78.8663	14.3171
900	-67.8635	12.6941	80.5575	14.4316
1000	-69.2104	12.8722	82.0824	14.5158
1100	-70.4646	13.0247	83.4693	14.5799
1200	-71.6517	13.1564	84.7401	14.6295
1300	-72.7814	13.2713	85.9127	14.6686
1400	-73.8727	13.3723	87.0009	14.7
1500	-74.9347	13.4617	88.016	14.7256
1600	-75.9755	13.5413	88.9671	14.7467
1700	-76.9959	13.6125	89.8617	14.7642
1800	-77.9957	13.6772	90.706	14.779
1900	-77.9769	13.7355	91.5054	14.7916
2000	-78.9455	13.7886	92.2642	14.8024
2100	-79.9127	13.8371	92.9866	14.8117
2200	-79.8795	13.8816	93.676	14.8197
2300	-80.8425	13.9225	94.335	14.8266
2400	-81.8025	13.9603	94.9661	14.833
2500	-81.7574	13.9953	95.5718	14.8385
2600	-82.7126	14.0279	96.1538	14.8434
2700	-82.6559	14.0582	96.7141	14.8478
2800	-83.6177	14.0864	97.2542	14.8517
2900	-83.5625	14.1129	97.7754	14.8552
3000	-84.5144	14.1377	98.2791	14.8593
3100	-84.4652	14.161	98.7663	14.8612
3200	-85.4252	14.1829	99.2382	14.8632
3300	-85.382	14.2036	99.6956	14.8662
3400	-86.3463	14.2231	100.139	14.8692
3500	-86.3059	14.2415	100.57	14.8722
3600	-87.2733	14.259	100.989	14.8751
3700	-87.2313	14.2754	101.397	14.8775
3800	-88.1922	14.2914	101.794	14.8795
3900	-88.1536	14.3064	102.18	14.8812
4000	-89.1126	14.3207	102.557	14.8828
4100	-89.0725	14.3343	102.924	14.8842
4200	-89.0333	14.3473	103.283	14.8855
4300	-89.9933	14.3597	103.633	14.8866
4400	-89.9533	14.3716	103.975	14.8874
4500	-90.9126	14.3829	104.309	14.8885
4600	-90.8727	14.3935	104.636	14.8894
4700	-91.8326	14.4033	104.957	14.8902
4800	-91.7927	14.4123	105.27	14.8909
4900	-92.7526	14.4209	105.577	14.8917
5000	-92.7127	14.4292	105.878	14.8923
5100	-93.6726	14.4371	106.173	14.8928
5200	-93.6327	14.4452	106.462	14.8934
5300	-94.5926	14.4529	106.745	14.8939
5400	-94.5527	14.4609	107.024	14.8947
5500	-95.5126	14.4686	107.297	14.8952
5600	-95.4727	14.4762	107.565	14.8957
5700	-96.4326	14.4832	107.829	14.8961
5800	-96.3927	14.4901	108.089	14.8964
5900	-97.3526	14.4961	108.342	14.8967
6000	-97.3127	14.5023	108.592	14.8969

FREQ
765.4
81

MULT
1
5

FREQ
776.1
0

MULT
1
0

MOLECULAR WEIGHT 270.08
SYMMETRY 0
MOMENT OF INERTIA 98
TYPE 0
END OF RUN

REFERENCES-SECTION 1

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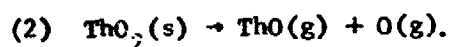
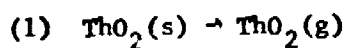
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SECTION 2

THERMODYNAMICS OF THE THORIUM-OXYGEN SYSTEM

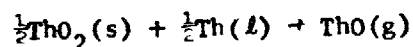
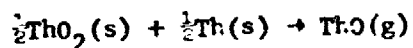
The thorium-oxygen system has been studied by mass spectroscopic techniques by several workers (1-5). A summary and review of some of the older works not referenced in this report are also available (6). The method used in studying these systems is to measure the vapor pressure of the thorium species effusing from a Knudsen cell by weight gain of a circular disc target. The pressures are measured over $\text{ThO}_2(\text{s})$ and the 3 phase system $\text{Th}(\ell)/\text{ThO}_2(\text{s})/\text{vapor}$, or in the lower temperature regimes $\text{Th}(\text{s})/\text{ThO}_2(\text{s})/\text{vapor}$. Partial pressures of the species are determined mass spectrometrically. This requires assumptions of cross sections and detector sensitivities for the various species.

In the case of vaporization from $\text{ThO}_2(\text{s})$ two processes are important



The assumptions are made that the mass spectrometric peak intensities of the $\text{ThO}^+(\text{g})$ and $\text{ThO}_2^+(\text{g})$ ions can be related to pressures and vaporization of reaction (2) is congruent. Thermodynamic functions of $\text{ThO}(\text{g})$ and $\text{ThO}_2(\text{g})$ can be obtained from a knowledge of $\Delta G_f(T)$ of $\text{ThO}_2(\text{s})$. (This assumes that $a_{\text{ThO}_2(\text{s})} = 1$).

For a study of either the three phase system $\text{ThO}_2(\text{s})/\text{Th}(\ell)$ or the $\text{ThO}_2(\text{s})/\text{Th}(\text{s})$ for which the principal vaporization can be represented by



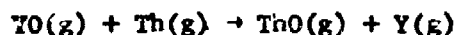
one must know the activity of $\text{ThO}_2(\text{s})$ and $\text{Th}(\text{s}, \ell)$. It has been shown

that prolonged vaporization of ThO from this system at temperature below 2400K does not appreciably alter the stoichiometry of the $\text{ThO}_2(\text{s})$ phase (7). This then allows one to assume unit activity for both Th (s, l) and $\text{ThO}_2(\text{s})$. Therefore combining the pressures of ThO obtained and the thermal properties of $\text{ThO}_2(\text{s})$ and $\text{Th}(\text{s}, \text{l})$, allows a determination of ΔG_f° of $\text{ThO}(\text{g})$. Ackermann and Rauh (3) give $\Delta G_f^\circ \text{ThO}(\text{g}) = -16,500 - 12.15T$ kcal mol⁻¹ [2400-2800 K]. Hildenbrand and Murad (5) give an expression for $\log_{10} P_{\text{ThO}} = (8.386 \pm 0.164) - (30,480 \pm 306)/T$ which is in experimental agreement with the pressures given by Ackermann and Rauh. These values are also in excellent agreement with the pressure of $\text{ThO}(\text{g})$ given in reference 1 for 2369K. (The pressure over $\text{ThO}_2(\text{g})/\text{Th}(\text{l})$ was only given at this temperature for this system by these workers.)

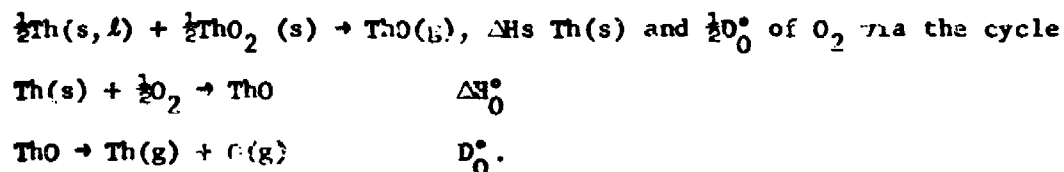
This indicates a ΔS_f° of $\text{ThO}(\text{g})$ of 12.15 entropy units. This value is in agreement with the entropy computed for $\text{ThO}(\text{g})$ using the known spectroscopic states and the measured entropy for $\text{Th}(\text{l})$.

Estimates of the electronic contributions to $S_{2000\text{K}}^\circ$ of ThO have been made in the past by equating this entropy with that of $S_{2000\text{K}}^\circ$ of Th(III). This method gives an absolute entropy of 80.5 cal/mole °K compared with an $S_{2000\text{K}}^\circ$ of 73.9 cal/mole K using molecular constants of the known electronic states of $\text{ThO}(\text{g})$. The latter value in good agreement with a second law treatment of the vaporization data for the $\text{ThO}_2(\text{s})/\text{Th}(\text{s}, \text{l})$ system.

The dissociation energy of ThO may be obtained via several cycles. Ackermann and Rauh (3) considered the isomolecular exchange



and from the known thermodynamic functions of YO(g), Th(g) and Y(g) were able to obtain D_0° of ThO. They also obtained D_0° ThO(g) and ΔH_0° of ThO obtained from the study of the reaction



The ΔH_0° for ThO(g) obtained by the second and third law methods are in rather good agreement. The thermal functions for ThO(g) were generated using the known spectroscopic data for ThO. The values for Th(s, l) were taken from Rand's evaluation (8) as given by Ackermann and Rauh (3).

Hildbenbrand and Murad (5) also obtained D_0° of ThO via an isomolecular exchange reaction



and a study of the Th(s) + ThO₂(s) system. The D_0° recommended by these two groups are within experimental error. A value of 8.78 ± 0.13 eV is given in (4) while 9.0 ± 0.1 eV is recommended in (3). Even this small difference represents to some extent the different choice of thermal functions for ThO₂(s) by these two different laboratories.

From a knowledge of ΔG_f° of $\text{ThO}_2(\text{s})$ one can obtain ΔH_f° (ThO_2, g)

since

$$\log_{10} P(\text{ThO}_2, \text{g}) = -35,070/T + 7.96$$

$$\text{over } \text{ThO}_2(\text{s}) \text{ and } \Delta G_f^\circ \text{ThO}_2(\text{s}) = -292,600 + 43.66 T$$

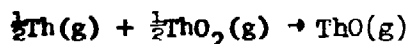
$$\Delta G_f^\circ \text{ThO}_2(\text{g}) = -132,100 + 7.23 T.$$

From a knowledge of ΔS° for this process coupled with frequencies of $\text{ThO}_2(\text{g})$ determined by several workers (assuming a value of ν_2), and the ThO_2 angle and bond distances one can compute S° for ThO_2 which can be compared with values obtained experimentally for the $\text{ThO}_2(\text{s}) \rightarrow \text{ThO}_2(\text{g})$ process.

Using the entropy for $\text{Th}(\text{l}, \text{s})$ derived from the calorimetric data (12) by Rand (8) and the entropy of molecular oxygen (13), one computes and entropy for $\text{ThO}_2(\text{g})$ of $S_{2600}^\circ = 92.8$ e.u., (since $\Delta G_f^\circ(\text{ThO}_2, \text{g}) = -132,100 + 7.23 T$ for the temperature interval of 2400-2800 K). A computation of the entropy of ThO_2 using either of the recently observed vibrational spectra for the stretching modes of ThO_2 coupled with the molecular geometry determined by isotopic shifts for Th^{16}O_2 and Th^{18}O_2 (14, 15) yield values of 97.5 eu. for $\nu_2 = 81 \text{ cm}^{-1}$ and 96.7 e.u. for $\nu_2 = 125 \text{ cm}^{-1}$. The former value was chosen from a determination of 81 cm^{-1} for the bending mode of UO_2 . Lirevsky estimated 125 cm^{-1} for ν_2 from a weak combination band observed in the infrared spectrum. Repeated efforts by the author have not yielded an experimental determination of ν_2 even though the spectrum could be observed down to about 60 cm^{-1} . In any event this difference (4 to 5 eu) between the calculated entropy and the thermodynamically derived entropy is not easily explainable.

To reduce the calculated entropy by 4 would require a change of the bending frequency to a very high value, hence the derived entropy probably is too low by at least 2 entropy units, or more likely 3 units.

A discrepancy of about 12 kcal/mole exists between the determination of the $\Delta H_0^\circ \text{ThO}_2(\text{g})$ using the second and third law methods. There is no apparent problem in any of the experiments used to generate the vapor pressure, heat capacity of the solid phase, and spectroscopic data used for these determinations. Examination of $\text{ThO}_2(\text{s})$ after prolonged vaporization indicated very little departure from stoichiometry. Therefore assumptions of unit activity seem to be justified. An investigation of the temperature variation in the equilibrium constants of the reactions



and



coupled with the known thermodynamic functions for $\text{Th}(\text{g})$, $\text{ThO}(\text{g})$ and $\text{O}(\text{g})$ might be helpful in providing another path to the determination of $\Delta G_f^\circ(\text{ThO}_2, \text{g})$ from which ΔH_f° could be computed.

The $\Delta H_{f, T}^\circ$ given by Ackermann and Rauh (1,3) have been reduced to ΔH_{f0}° using the thermodynamic function for $(G-H_0)/T$ for the species $\text{Th}(\text{s}, l)$, O_2 and $\text{ThO}_2(\text{g})$.

This computation gives

$$\Delta H_f^\circ \text{ThO}_2(\text{g}) = -105.4 \text{ kcal/mole}$$

$$\Delta H_f^\circ \text{ThO}(\text{g}) = -6.15 \text{ kcal/mole.}$$

This enables an estimate of D_0° of ThO_2

$$\begin{aligned} D_0^\circ &= \Delta H_{s0}^\circ (\text{Th}, \text{s}) + D_0^\circ (\text{O}_2) - \Delta H_f^\circ (\text{ThO}_2, \text{g}) = 142.7 + 118 + 105.4 \\ &= 366.1 \text{ kcal/mole or } 15.9 \text{ eV/mole.} \end{aligned}$$

The I.P. Th, I.P. ThO, and I.P. ThO_2 have been given as 5.9, 6.1 and 8.7 eV, respectively in (3). These values which have estimated uncertainties of ± 0.2 eV are in agreement with the recent results given by reference 4 of 6.0 and 8.0 ± 1 eV for ThO and ThO_2 and some yet unpublished results on the optical spectra of Th respectively. (It should of course be noted that thermal population of electronic states may contribute some error to these values.) These ionization potentials coupled with ΔH_f° of ThO and ThO_2 then can be used to estimate exothermicities of reactions such as:

<u>Reaction</u>	<u>eV</u>
$\text{Th} + \text{O} \rightarrow \text{ThO}^+ + \text{e}$	-2.9
$\text{Th} + \text{O}_2 \rightarrow \text{ThO}_2^+ + \text{e}$	-2.1
$\text{Th} + \text{O}_2 \rightarrow \text{ThO} + \text{O}$	-3.9
$\text{Th} + \text{O}_3 \rightarrow \text{ThO} + \text{O}_2$	-7.4
$\text{Th} + \text{O}_3 \rightarrow \text{ThO}^+ + \text{O}_2 + \text{e}$	-1.3
$\text{Th} + \text{O}_3 \rightarrow \text{ThO}_2^+ + \text{O} + \text{e}$	-0.5

These quantities were calculated using the following energies:

<u>Reaction</u>	<u>eV</u>
$\text{Th} \rightarrow \text{Th}^+ + e$	5.9
$\text{Th} \rightarrow \text{ThO}^+ + e$	6.1
$\text{ThO}_2 \rightarrow \text{ThO}_2^+ + e$	8.7
$\text{ThO} \rightarrow \text{Th} + \text{O}$	9.0
$\text{ThO}_2 \rightarrow \text{Th} + 2\text{O}$	15.9
$\text{Th(s)} + \text{O}_2 \rightarrow \text{ThO}_2(\text{g})$	-5
$\text{Th(s)} + \frac{1}{2}\text{O}_2 \rightarrow \text{ThO}$	-0.22
$\text{O}_2 \rightarrow 2\text{O}$	5.1
$\text{O}_3 \rightarrow \text{O}_2 + \text{O}$	1
$\text{Th(s)} \rightarrow \text{Th(g)}$	6.2

The thermodynamic functions of ThO and ThO₂ are appended in tables 3, 4, and 5. It should be noted that all twelve known electronic states of ThO have been included in this calculation. The multiplicity of the lowest excited state has been taken as 2 in this computation. Wentink et. al. (11) have suggested that this state might have a degeneracy of 6(³Δ) from a comparison of the levels of TiO, HfO and ThO. This suggestion has apparently been accepted in reference 3 and those thermal functions reflect this assignment. This has the effect of increasing the S₂₉₀₀^o of ThO(g) by about 1.13 e.u. Tables 4 and 5 give thermodynamic functions for ThO₂, (g) using both vibrational assignments for ν₂ of 81 and 125 cm⁻¹ and α = 115°, r = 1.75 Å. Small variations of α and r will not significantly effect the computed entropy. The choice of ν₂ = 125 cm⁻¹ is probably to be preferred at this point since it reduces the discrepancy between a second and third law treatment of the available data.

TABLE 4. THERMODYNAMIC FUNCTIONS FOR ThO₂(g)

T	(G-H0)/T	(H-H0)/T	S	CP
298.15	-59.1581	9.9545	69.1126	11.3457
300	-59.2197	9.96313	69.1828	11.3625
400	-62.1487	10.4144	72.563	12.1255
500	-64.5163	10.8108	75.3271	12.6309
600	-66.5177	11.1436	77.6613	12.962
700	-68.2569	11.4207	79.6772	13.1847
800	-69.7974	11.6511	81.4485	13.3396
900	-71.1813	11.8452	83.0265	13.4509
1000	-72.438	12.0101	84.4461	13.5331
1100	-73.5895	12.1515	85.741	13.5954
1200	-74.6522	12.2739	86.9261	13.6437
1300	-75.639	12.3801	88.0198	13.6817
1400	-76.56	12.4748	89.0348	13.7123
1500	-77.4236	12.5582	89.9818	13.7371
1600	-78.2265	12.6325	90.869	13.7576
1700	-79.0044	12.6992	91.7036	13.7747
1800	-79.732	12.7594	92.4914	13.7891
1900	-80.4233	12.8139	93.2372	13.8013
2000	-81.0819	12.8636	93.9454	13.8118
2100	-81.7126	12.9089	94.6195	13.8208
2200	-82.3121	12.9506	95.2626	13.8287
2300	-82.8886	12.9889	95.8775	13.8355
2400	-83.4422	13.0243	96.4665	13.8416
2500	-83.9745	13.0571	97.0316	13.8469
2600	-84.4872	13.0876	97.5748	13.8517
2700	-84.9817	13.116	98.0977	13.8559
2800	-85.4592	13.1424	98.6016	13.8597
2900	-85.9208	13.1672	99.088	13.8631
3000	-86.3676	13.1905	99.5581	13.8662
3100	-86.8005	13.2123	100.013	13.869
3200	-87.2203	13.2329	100.453	13.8718
3300	-87.6278	13.2523	100.88	13.8738
3400	-88.0237	13.2706	101.294	13.8759
3500	-88.4086	13.2879	101.697	13.8778
3600	-88.7832	13.3043	102.087	13.8796
3700	-89.1479	13.3199	102.462	13.8812
3800	-89.5033	13.3347	102.832	13.8827
3900	-89.8499	13.3488	103.199	13.8841
4000	-90.188	13.3622	103.55	13.8854
4100	-90.5181	13.3749	103.893	13.8866
4200	-90.8406	13.3871	104.228	13.8877
4300	-91.1557	13.3988	104.554	13.8888
4400	-91.4639	13.4099	104.874	13.8897
4500	-91.7653	13.4206	105.186	13.8906
4600	-92.0604	13.4308	105.491	13.8915
4700	-92.3494	13.4406	105.79	13.8923
4800	-92.6324	13.4501	106.082	13.893
4900	-92.9099	13.4591	106.369	13.8937
5000	-93.1819	13.4678	106.65	13.8944
5100	-93.4486	13.4762	106.925	13.895
5200	-93.7104	13.4842	107.195	13.8956
5300	-93.9673	13.492	107.459	13.8961
5400	-94.2196	13.4995	107.719	13.8966
5500	-94.4674	13.5067	107.974	13.8971
5600	-94.7102	13.5137	108.224	13.8976
5700	-94.95	13.5204	108.47	13.898
5800	-95.1852	13.5269	108.712	13.8985
5900	-95.4165	13.5332	108.95	13.8989
6000	-95.644	13.5393	109.183	13.8992

FREQ 787.2 MULT 1
 FREQ 735.5 MULT 1
 FREQ 81 MULT 1
 MOLECULAR WEIGHT 264.037
 SYMMETRY 2
 MOMENTS 24.863 69.708 94.571
 END OF RUN

TABLE 5. THERMODYNAMIC FUNCTIONS FOR ThO₂(g)

T	(G-H ₀)/T	(H-H ₀)/T	S	CP
298.15	-58.8895	0.77818	68.2677	11.7116
300	-58.55	0.78769	68.3377	11.7200
400	-61.4341	10.2765	71.7195	12.1260
500	-63.7738	10.6973	74.6711	12.6186
600	-65.7561	11.0670	76.8730	12.0530
700	-67.4815	11.3368	78.8100	12.1780
800	-69.0115	11.5773	80.5880	12.2780
900	-70.3871	11.7701	82.1660	12.3670
1000	-71.6770	11.9503	83.5875	12.57
1100	-72.7930	12.0969	84.8801	12.5000
1200	-73.8414	12.2236	86.065	12.6015
1300	-74.8243	12.3302	87.1595	12.6700
1400	-75.740	12.4315	88.1735	12.7107
1500	-76.6026	12.5176	89.1903	12.7350
1600	-77.413	12.5944	90.2270	12.7560
1700	-78.1786	12.6633	91.280	12.7736
1800	-78.9000	12.7254	92.3407	12.7881
1900	-79.5930	12.7817	93.4075	12.8000
2000	-80.2597	12.8329	94.4806	12.811
2100	-80.898	12.8797	95.5597	12.8201
2200	-81.5080	12.9226	96.644	12.828
2300	-82.0895	12.9621	97.7256	12.835
2400	-82.6429	12.9986	98.8036	12.841
2500	-83.1777	13.0324	99.8787	12.846
2600	-83.694	13.0630	100.950	12.850
2700	-84.1926	13.0911	102.019	12.853
2800	-84.673	13.1162	103.086	12.856
2900	-85.1361	13.1389	104.150	12.859
3000	-85.5820	13.1599	105.211	12.862
3100	-85.9580	13.1790	106.269	12.865
3200	-86.3716	13.1955	107.324	12.868
3300	-86.7285	13.2095	108.376	12.871
3400	-87.1200	13.2210	109.426	12.874
3500	-87.5463	13.2300	110.473	12.877
3600	-87.9983	13.2371	111.518	12.880
3700	-88.4766	13.2423	112.561	12.883
3800	-88.9800	13.2457	113.602	12.886
3900	-89.5087	13.2473	114.641	12.889
4000	-90.0615	13.2476	115.678	12.892
4100	-90.6379	13.2466	116.713	12.895
4200	-91.2370	13.2443	117.746	12.898
4300	-91.8581	13.2407	118.777	12.901
4400	-92.5015	13.2358	119.806	12.904
4500	-93.1671	13.2296	120.833	12.907
4600	-93.8549	13.2221	121.858	12.910
4700	-94.5640	13.2134	122.881	12.913
4800	-95.2945	13.2035	123.902	12.916
4900	-96.0465	13.1924	124.921	12.919
5000	-96.8200	13.1801	125.938	12.922
5100	-97.6150	13.1666	126.953	12.925
5200	-98.4310	13.1519	127.966	12.928
5300	-99.2680	13.1360	128.977	12.931
5400	-100.1260	13.1189	129.986	12.934
5500	-101.0050	13.1006	130.993	12.937
5600	-101.9060	13.0811	131.998	12.940
5700	-102.8290	13.0604	132.999	12.943
5800	-103.7740	13.0386	133.998	12.946
5900	-104.7410	13.0156	134.994	12.949
6000	-105.7300	13.0000	135.987	12.952

FREQ 787.2 MULT 1
 FREQ 735.5 MULT 1
 FREQ 125 MULT 1
 MOLECULAR WEIGHT 260.037
 SYMMETRY 2
 MOMENTS 24.863 69.700 94.571
 END OF RUN

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