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THE THERMODYNAMICS OF THORIUM-OXYGEN AND URANIUM-OXYGEN SYSTEMS

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The calorimetric, spectroscopic, and vapor pressure data for the uranium-oxygen and thorium-oxygen systems have been reviewed. Free energies of formation for the species UO, UO_2, ThO, and ThO_2 have been chosen. Tables of thermodynamic functions for these species are presented.

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THERMODYNAMICS OF THE URANIUM-OXYGEN SYSTEM

The vapor above uranium oxide condensed phases includes U, UO, UO_2, and UO_3. The composition of the vapor is strongly dependent upon the O/U ratio. In the three phase system $U(\ell)/UO_2(s)$ and vapor ($O/U \leq 1.7$) the principal vapor phase species is UO with smaller amounts of U and UO_2 vapors. For UO_2 a congruent evaporation seems to predominate giving mostly UO_2 with about equimolar but much smaller quantities of UO and UO_3. For hyperstoichiometric uranias ($O/U > 2$) UO_3 and UO_2 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 $\Delta H^\circ_{s\ 298} = 126.3 \pm 1.0$ kcal/mole. Pattoret et al (4) give

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

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

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.

$UO_2(s)/U(\ell)$

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

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

where σ_i and ν_i are the cross-section for ionization by electrons of 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 $U(\ell)/UC_2(s)$ system used equal sensitivities for U(v), UO(v) and UO_2(v). A recent work by Blackburn and Danielson (4) has advocated values of 0.66, 1.29, and 0.31 for the product of multiplier yield and partial relative ionization cross-section for U, UO and UO_2 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 $U(\ell)$,UO_2(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 $UO_2(s)/U(\ell)$ is far from ideal. Therefore the activities of the condensed phases cannot be assumed to be unity, for the process

$$U_{(\ell)} + UO_{2(s)} = 2UO\ (g).$$

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

$$U_{(g)} + UO_{2(g)} = 2UO_{(g)}$$

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.

$$K = P^2_{UO}/P_U P_{UO_2}$$

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

They computed ΔG°_f (UO,g)

$$\Delta G^\circ_f (UO,g) = 1/2\ \Delta G^\circ_f (UO_2,g) + 1/2\ \Delta G^\circ_f (U,g) - 1/2\ R'T \log K$$

$$= -7,800 - 13.84T.$$

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 ΔG°_f UO_2(g) and ΔG°_f U(g). As will be seen later in this report an uncertainty in the entropy of formation, ΔS°_f UO_2 (g) is not unlikely. This error would contribute an uncertainty of 1.5 e.u. to the ΔS°_f 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). Pattoret et al (5) determined a D_0° for UO(g) from the isomolecular exchange reaction

$$UC(g) + Si(g) = U(g) + SiC(g) \quad \Delta H \text{ then } D_0^\circ(UO,g) = \Delta H + D_0^\circ SiO =$$
$$= -8.6 + 190.4 = 181.8 \pm 2.2 \text{ kcal/mole}$$

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 UO_2 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 $U(\ell) + 1/2O_2 = UO(g)$ (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 ΔS_f° = 11.78 gives a ground state degeneracy of about 5).

The partial pressures of the U, UO, UO_2 species above the three phase system $U(\ell)/UO_{2-x(s)}$ 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 $\sigma_i \nu_i$ 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 $\sigma_i \nu_i$ given by Pattoret et al (5) and Blackburn and Danielson (4) respectively. The partial pressures computed using the three sets of $\sigma_i \nu_i$ 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(atm)	P_{UO}(atm)	P_{UO_2}(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	UO	UO_2	Ke
PDS (5)	1.15	0.80	0.55	0.988
ARC (3)	1	1	1	1
BD (4)	0.66	1.29	0.31	0.123

for $U_{(g)} + UO_{2(g)} = 2UO_{(g)}$

$$K_p(T) = \left[\frac{I^+_{UO^2}/(\sigma\gamma)_{UO^2}}{I^+_{UO_2}/(\sigma\gamma)_{UO_2} I^+U/(\sigma\gamma)U} \right] K_e$$

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

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

Stoichiometric UO_2

The vapor pressure above stoichiometric UO_2 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 residu s 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 UO_3 is present even at lower temperatures, UO_3 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

$$\Delta G = -RT \ln P_{(U)} = \dot{\Delta H} - T\dot{\Delta S}$$

$$\text{or } \log P(\text{atm}) = \frac{-\dot{\Delta H}}{R'T} + \frac{\dot{\Delta S}}{R'}$$

ΔH	ΔS	method	temp. range	ref.	P_{2200K}
137.1	36.4	mass effusion	1600-2200	AGT(6)	2.17×10^{-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

$$UO_2(g) + Si(g) \rightarrow UO(g) + SiO(g) \quad \Delta H = 18.6 \text{ cal/mole}$$

and from a knowledge of D_0° UO(g) and SiO(g). Pattoret et al (5) computed a D_0° of UO_2 of 353.6 ± 3.2 kcal/mole,

$$D_0^\circ\ UO_2 = \Delta H + D_0^\circ\ SiO + D_0^\circ\ UO$$
$$= 18.6 + 190.4 + 181.8 = 353.6.$$

This value is in good agreement with 353.2 (14.9eV) given by Ackermann Gilles and Thorn (6). These workers used the $UO_2(g)$ equilibria coupled with the data for $UO_2(s)$ 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 $UO_2(s) = UO_2(g)$ using

$$\Delta H^\circ_{f\ 298}\ UO_2(s) = -259.5 \text{ kcal/mole}$$
$$\Delta H^\circ_{s\ 298}\ UO_2 = 125 \text{ kcal/mole}$$

then

$$UO_2(s) = UO_2(g) \quad \Delta H^\circ_f = 152.5$$
$$D_0^\circ(UO_2g) = -\Delta H_f(UO_{2,g}) + \Delta H_s\ U_{(s)} + D_0^\circ\ O_2$$
$$= (259.5 - 152.5) + 129.0 + 117 = 353 \text{ kcal/mole}$$
$$UO_2(g) = U(g) + 2O(g) \quad D_0^\circ\ UO_2$$

Therefore since both gas phase equilibria coupled with assumed previously determined dissociation energies agree well with ΔH for $UO_{2(s)} = UO_{2(g)}$ coupled with $\Delta H_s U$ and $D_0^\circ O_2$ for the determination of $D_0^\circ(UO_2)$ 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, ΔG_f° $UO_2(g)$ can in principle be derived from the vapor pressure measurements above stoichiometric UO_2 assuming the principal reaction is

$$UO_2(s) \rightarrow UO_2(g) \quad \Delta G_s UO_2(s) = -R'T \log P.$$

This quantity coupled with ΔG_f° $UO_2(s)$ then yields ΔG_f° $UO_2(g)$ = ΔG_f $UO_2(s)$ + ΔG_s $UO_2(s)$.

If one inspects table 3 which gives the ΔG_s° $UO_2(s) = \Delta H^\circ_{(s)} - T\Delta S^\circ_{(s)}$ 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 ΔS_f° $UO_2(g)$. Using Ackermann et al (6) vapor pressure data one obtains ΔS_f° = -4.24 e.u, the data of Pattoret et al (5) gives ΔS_f° = -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 $\nu_2 = 81$ cm^{-1} for a linear UO_2 molecule with a r U-O = 1.75 Å a S°_{2000K} = 92.3 cal $mole^{-1}, ^{-1}$ is computed. Small variations of r will not significantly effect the computed functions. Coupling this with S°_{2000} U(ℓ) = 12.53 and S°_{2000} O_2 = 64.18 one obtains a ΔS_f $UO_2(g)$ = -4.41 cal $mole^{-1}K^{-1}$ in excellent agreement with ΔS°_f = -4.24 given by Ackermann et al (6) and in good agreement with ΔS°_f = -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°_{2000K} 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 $UO_2(g)$ 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 ΔH_f UO and ΔH_f UO_2 then can be used to

estimate exothermicities of reactions such as:

Reaction	eV
$U(s) + O_2 \rightarrow UO_2(g)$	-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
$U(g) + \frac{1}{2}O_2 \rightarrow UO^+ + e$	+0.3[illegible]
$U(g) + O_3 \rightarrow UO_2 + O$	-[illegible].71
$U(g) + O_3 \rightarrow UO_2^+ + O + e$	1.21
$U(g) + O_3 \rightarrow UO + O_2$	-4.34
$U(g) + O_3 \rightarrow UO^+ + O_2$	+1.3[illegible]
$U(g) + N_2O \rightarrow UO + N_2$	-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 APPROXIMATED AS 4(BE)**3/(WE)**2 2.93576E-7 STATE 1

T K	CP CAL/K MOL	H-H0 CAL/MOL	S CAL/K MOL	-(G-H0)/T CAL/K MOL
298.15	7.57708	2119.57	57.2717	50.1626
300	7.58519	2133.59	57.3186	50.2066
400	7.96808	2912.23	59.5559	52.2753
500	8.23568	3723.29	61.3646	53.9181
600	8.41637	4556.48	62.8832	55.2891
700	8.54034	5404.69	64.1905	56.4695
800	8.62786	6263.34	65.3369	57.5078
900	8.69151	7129.47	66.357	58.4354
1000	8.7391	8001.11	67.2753	59.2742
1100	8.77559	8876.92	68.11	60.0401
1200	8.8042	9755.97	68.8749	60.7449
1300	8.82707	10637.6	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	13293.4	71.4185	63.1102
1700	8.88497	14181.3	71.9568	63.6149
1800	8.89441	15070.3	72.465	64.0926
1900	8.90262	15960.2	72.9461	64.546
2000	8.90983	16850.8	73.4029	64.9775
2100	8.91622	17742.1	73.8378	65.3891
2200	8.92193	18634.	74.2525	65.7827
2300	8.92707	19526.5	74.6494	66.1596
2400	8.93175	20419.4	75.0294	66.5213
2500	8.93602	21312.8	75.3941	66.869
2600	8.93995	22206.6	75.7447	67.2037
2700	8.94358	23100.8	76.0821	67.5263
2800	8.94697	23995.3	76.4074	67.8377
2900	8.95013	24890.2	76.7215	68.1386
3000	8.9531	25785.3	77.0249	68.4298
3100	8.95591	26680.8	77.3185	68.7118
3200	8.95857	27576.5	77.6029	68.9852
3300	8.9611	28472.5	77.8786	69.2506
3400	8.96352	29368.7	78.1462	69.5083
3500	8.96584	30265.2	78.406	69.7588
3600	8.96806	31161.9	78.6586	70.0025
3700	8.97021	32058.8	78.9044	70.2398
3800	8.97228	32955.9	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	79.8256	71.1308
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	8.98526	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	8.99343	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	8.99806	46434.6	82.1329	73.3716
5400	8.99957	47334.5	82.3011	73.5354
5500	9.00105	48234.6	82.4662	73.6963
5600	9.00253	49134.7	82.6284	73.8543
5700	9.00399	50035.1	82.7877	74.0097
5800	9.00544	50935.5	82.9443	74.1623
5900	9.00687	51836.2	83.0983	74.3125
6000	9.00829	52736.9	83.2497	74.4602

MOLECULAR WEIGHT= 254.07
MOLECULAR CONSTANTS ARE LISTED AS.
LEVEL,WE,WEXE,WEYE,BE,ALPHAE,DE,MULTIPLICITY,[illegible]

0 820 0 0 .3668 0 2.93576E-7 1 0

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

T	(F-H0)/T	(H-H0)/T	S	CP
298.15	-55.0126	10.5306	65.5432	12.2796
300	-55.078	10.5812	65.6592	12.2967
400	-58.1969	11.1133	69.3102	13.0749
500	-60.7964	11.5608	72.3572	13.5907
600	-62.8679	11.9093	74.7772	13.9998
700	-64.7303	12.2024	76.9327	14.1581
800	-66.3996	12.4837	78.8833	14.3171
900	-67.8635	12.6941	80.5575	14.4314
1000	-69.2104	12.8799	82.0904	14.5158
1100	-70.4446	13.0947	83.4693	14.5709
1200	-71.5837	13.1564	84.7401	14.6095
1300	-72.6414	13.2713	85.9127	14.6686
1400	-73.6257	13.3723	87.0009	14.7
1500	-74.5544	13.4617	88.016	14.7256
1600	-75.4255	13.5413	88.9671	14.7467
1700	-76.2459	13.6125	89.8617	14.7647
1800	-77.0255	13.6779	90.706	14.779
1900	-77.7699	13.7355	91.5054	14.7916
2000	-78.4755	13.7886	92.2644	14.8024
2100	-79.1497	13.8371	92.9866	14.8117
2200	-79.7945	13.8816	93.676	14.8197
2300	-80.4125	13.9225	94.335	14.8266
2400	-81.0058	13.9603	94.9661	14.833
2500	-81.5764	13.9953	95.5718	14.8385
2600	-82.126	14.0279	96.1538	14.8434
2700	-82.6559	14.0582	96.7141	14.8478
2800	-83.1677	14.0864	97.2542	14.8517
2900	-83.6625	14.1129	97.7754	14.8552
3000	-84.1414	14.1377	98.2791	14.8583
3100	-84.6053	14.161	98.7663	14.8612
3200	-85.0553	14.1829	99.2382	14.8637
3300	-85.499	14.2036	99.6956	14.8662
3400	-85.9163	14.2231	100.139	14.8683
3500	-86.3259	14.2415	100.57	14.8703
3600	-86.7283	14.259	100.989	14.8721
3700	-87.1243	14.2756	101.397	14.8738
3800	-87.5092	14.2914	101.794	14.8754
3900	-87.8736	14.3064	102.18	14.8769
4000	-88.234	14.3207	102.557	14.8781
4100	-88.5898	14.3343	102.924	14.8794
4200	-88.9359	14.3473	103.283	14.8805
4300	-89.2731	14.3597	103.633	14.8816
4400	-89.6033	14.3716	103.975	14.8826
4500	-89.9264	14.3829	104.309	14.8835
4600	-90.2427	14.3935	104.636	14.8844
4700	-90.552	14.4043	104.957	14.8852
4800	+90.8557	14.4143	105.27	14.8859
4900	-91.152	14.4239	105.577	14.8867
5000	-91.4425	14.4332	105.878	14.8873
5100	-91.7264	14.4421	106.173	14.888
5200	-92.0109	14.4507	106.462	14.8884
5300	-92.2843	14.4589	106.745	14.8891
5400	-92.5566	14.4669	107.024	14.8897
5500	-92.8229	14.4746	107.297	14.8902
5600	-93.083	14.482	107.565	14.8907
5700	-93.3384	14.4892	107.829	14.8911
5800	-93.5915	14.4961	108.088	14.8916
5900	-93.8393	14.5028	108.342	14.892
6000	-94.0831	14.5093	108.592	14.8924

EESC	MULT	EESC	MULT
765.4	1	776.1	1
81	2	0	0

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

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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 $ThO_2(s)$ and the 3 phase system $Th(\ell)/ThO_2(s)$/vapor, or in the lower temperature regimes $Th(s)/ThO_2(s)$/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 $ThO_2(s)$ two processes are important

$$(1)\quad ThO_2(s) \rightarrow ThO_2(g)$$

$$(2)\quad ThO_2(s) \rightarrow ThO(g) + O(g).$$

The assumptions are made that the mass spectrometric peak intensities of the $ThO^+(g)$ and $ThO_2^+(g)$ ions can be related to pressures and vaporization of reaction (2) is congruent. Thermodynamic functions of ThO(g) and $ThO_2(g)$ can be obtained from a knowledge of $\Delta G_f(T)$ of $ThO_2(s)$. (This assumes that $a_{ThO_2(s)} = 1$).

For a study of either the three phase system $ThO_2(s)/Th(\ell)$ or the $ThO_2(s)/Th(s)$ for which the principal vaporization can be represented by

$$\tfrac{1}{2}ThO_2(s) + \tfrac{1}{2}Th(s) \rightarrow ThO(g)$$

$$\tfrac{1}{2}ThO_2(s) + \tfrac{1}{2}Th(\ell) \rightarrow ThO(g)$$

one must know the activity of $ThO_2(s)$ and $Th(s,\ell)$. It has been shown

that prolonged vaporization of ThO from this system at temperature below 2400K does not appreciably alter the stoichiometry of the ThO_2(s) phase (7). This then allows one to assume unit activity for both Th (s,ℓ) and ThO_2(s). Therefore combining the pressures of ThO obtained and the thermal properties of ThO_2(s) and Th(s,ℓ), allows a determination of ΔG_f° of ThO(g). Ackermann and Rauh (3) give $\Delta G_f^\circ ThO(g) = -16{,}500-12.15T$ kcal mol^{-1} [2400-2800 K]. Hildenbrand and Murad (5) give an expression for $\log_{10} P_{ThO} = (8.386 \pm 0.164) - (30{,}480 \pm 306)/T$ which is in experimental agreement with the pressures given by Ackermann and Rauh. These values are also in excellent agreement with the pressure of ThO(g) given in reference 1 for 2369K. (The pressure over ThO_2(g)/Th(ℓ) was only given at this temperature for this system by these workers.)

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

Estimates of the electronic contributions to S°_{2000K} of ThO have been made in the past by equating this entropy with that of S°_{2000K} of Th(III). This method gives an absolute entropy of 80.5 cal/mole °K compared with an S°_{2000K} of 73.9 cal/mole K using molecular constants of the known electronic states of ThO(g). The latter value in good agreement with a second law treatment of the vaporization data for the ThO_2(s)/Th(s,ℓ) system.

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

$$YO(g) + Th(g) \rightarrow ThO(g) + Y(g)$$

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

$\frac{1}{2}Th(s,\ell) + \frac{1}{2}ThO_2$ (s) $\rightarrow$ ThO(g), ΔHs Th(s) and $\frac{1}{2}D_0^\circ$ of O_2 via the cycle

$$Th(s) + \tfrac{1}{2}O_2 \rightarrow ThO \qquad \Delta H_0^\circ$$

$$ThO \rightarrow Th(g) + O(g) \qquad D_0^\circ.$$

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

$$ThO(g) + Si(g) \rightarrow Th(g) + SiO(g)$$

and a study of the Th(s) + ThO_2(s) system. The D_0° recommend 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 ThO_2(s) by these two different laboratories.

From a knowledge of ΔG_f° of $ThO_2(s)$ one can obtain ΔH_f° (ThO_2,g) since

$\log_{10} P(ThO_2,g) = -35,070/T + 7.96$

over $ThO_2(s)$ and ΔG_f° $ThC_2(s) = -292,600 + 43.66\ T$

ΔG_f° $ThO_2(g) = -132,100 + 7.23\ T.$

From a knowledge of ΔS° for this process coupled with frequencies of $ThO_2(g)$ 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 $ThO_2(s) \rightarrow ThO_2(g)$ process.

Using the entropy for $Th(\ell,s)$ derived from the calorimetric data (12) by Rand (8) and the entropy of molecular oxygen (13), one computes and entropy for $ThO_2(g)$ of $S^\circ_{2600} = 92.8$ e.u., (since $\Delta G_f(ThO_2,g) = -132,100 + 7.23\ T$ 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 $\nu_2 = 81\ cm^{-1}$ and 96.7 e.u. for $\nu_2 = 125\ cm^{-1}$. 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 ΔH_0° $ThO_2(g)$ 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 $ThO_2(s)$ 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

$$\tfrac{1}{2}Th(g) + \tfrac{1}{2}ThO_2(g) \rightarrow ThO(g)$$

and

$$ThO_2(g) \rightarrow ThO(g) + O(g)$$

coupled with the known thermodynamic functions for Th(g), ThO(g) and O(g) might be helpful in providing another path to the determination of ΔG_f° (ThO_2,g) from which ΔH_f° could be computed.

The $\Delta H_f^\circ,T$ given by Ackermann and Rauh (1,3) have been reduced to ΔH_{f0}° using the thermodynamic function for $(G-H_0^\circ)/T$ for the species Th(s, *l*), O_2 and $ThO_2(g)$.

This computation gives

ΔH_f° $ThO_2(g)$ = -105.4 kcal/mole

ΔH_f° ThO(g) = -6.15 kcal/mole.

This enables an estimate of D_0° of ThO_2

$D_0^\circ = \Delta H_{s0}^\circ$ (Th,s) + D_0° (O_2) - ΔH_f° (ThO_2,g) = 142.7 + 118 + 105.4

= 366.1 kcal/mole or 15.9 eV/mole.

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:

Reaction	eV
$Th + O \rightarrow ThO^+ + e$	-2.9
$Th + O_2 \rightarrow ThO_2^+ + e$	-2.1
$Th + O_2 \rightarrow ThO + O$	-3.9
$Th + O_3 \rightarrow ThO + O_2$	-7.4
$Th + O_3 \rightarrow ThO^+ + O_2 + e$	-1.3
$Th + O_3 \rightarrow ThO_2^+ + O + e$	-0.5

These quantities were calculated using the following energies:

Reaction	eV
$Th \rightarrow Th^+ + e$	5.9
$Th \rightarrow ThO^+ + e$	6.1
$ThO_2 \rightarrow ThO_2^+ + e$	8.7
$ThO \rightarrow Th + O$	9.0
$ThO_2 \rightarrow Th + 2O$	15.9
$Th(s) + O_2 \rightarrow ThO_2(g)$	-5
$Th(s) + \frac{1}{2}O_2 \rightarrow ThO$	-0.22
$O_2 \rightarrow 2O$	5.1
$O_3 \rightarrow O_2 + O$	1
$Th(s) \rightarrow Th(g)$	6.2

The thermodynamic functions of ThO and ThO_2 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 $6(^3\Delta)$ from a comparison of the levels of TiO, H_fO 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 S°_{2600} of ThO(g) by about 1.13 e.u. Tables 4 and 5 give thermodynamic functions for ThO_2, (g) using both vibrational assignments for ν_2 of 81 and 125 cm^{-1} and $\alpha = 115°$, $r = 1.75$ Å. Small variations of α and r will not significantly effect the computed entropy. The choice of $\nu_2 = 125$ 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 3. THERMODYNAMIC FUNCTIONS FOR ThO(g)

T K	CP CAL/K MOL	H-H0 CAL/MOL	S CAL/K MOL	-(G-H0)/T CAL/K MOL
298.15	7.47295	210[illegible].99	57.3511	50.2775
300	7.4807	2122.22	57.3973	50.3213
400	7.86413	2891.77	59.6039	52.377
500	8.15022	3692.3	61.3913	54.0067
600	8.35275	4518.02	62.8962	55.3662
700	8.50132	5361.06	64.1955	56.5368
800	8.6214	62[illegible].34	65.3387	57.567
900	8.73175	7[illegible]5.02	66.3605	58.4883
1000	8.84455	7[illegible]3.78	67.2863	59.3225
1100	8.96632	8834.24	68.1349	60.0856
1200	9.09925	9757.42	68.9207	60.7895
1300	9.24274	10674.4	69.6546	61.4435
1400	9.39457	11606.2	70.345	62.0549
1500	9.55197	12552.5	70.9985	62.6295
1600	9.71214	13516.7	71.6201	63.1721
1700	9.87268	14496.	72.2137	63.6866
1800	10.0317	15491.2	72.7825	64.1763
1900	10.1878	16502.2	73.329	64.6437
2000	10.3402	17528.7	73.8555	65.0912
2100	10.4884	18570.1	74.3636	65.5206
2200	10.6322	19626.2	74.8548	65.9338
2300	10.7718	[illegible]96.4	75.3305	66.332
2400	10.9071	2[illegible]780.4	75.7918	66.7166
2500	11.0385	22877.7	76.2397	67.0886
2600	11.1663	23988.	76.6751	67.4489
2700	11.2905	25110.8	77.0988	67.7985
2800	11.4113	26246.	77.5115	68.138
2900	11.5289	27393.	77.914	68.4681
3000	11.6431	28551.6	78.3067	68.7895
3100	11.754	29721.5	78.6903	69.1027
3200	11.8614	30902.3	79.0651	69.4082
3300	11.9651	32093.6	79.4317	69.7063
3400	12.065	33295.2	79.7903	69.9976
3500	12.1608	34506.5	80.1414	70.2824
3600	12.2522	35727.2	80.4652	70.561
3700	12.339	36956.7	80.822	70.8337
3800	12.421	38194.8	81.1521	71.1008
3900	12.4981	39440.8	81.4757	71.3627
4000	12.5699	40694.2	81.793	71.6194
4100	12.6363	41954.5	82.1041	71.8713
4200	12.6973	43221.2	82.4093	72.1185
4300	12.7527	44493.7	82.7086	72.3613
4400	12.8026	457[illegible]1.5	83.0023	72.5997
4500	12.8468	47054.	83.2905	72.834
4600	12.8855	48340.7	83.5732	73.0643
4700	12.9187	49630.9	83.8506	73.2908
4800	12.9466	50924.2	84.1228	73.5136
4900	12.9691	52220.	84.3899	73.7327
5000	12.9866	53517.7	84.652	73.9484
5100	12.9991	54817.	84.9092	74.1607
5200	13.0069	561[illegible]7.3	85.1616	74.3698
5300	13.0102	57418.2	85.4093	74.5756
5400	13.0092	58719.1	85.6523	74.7784
5500	13.00[illegible]	60019.8	85.8909	74.9782
5600	12.9954	6131[illegible].7	[illegible]	75.1751
5700	12.98[illegible]	62618.6	86.3548	75.3691
5800	12.9672	63916.1	86.5804	75.5604
5900	12.9483	65211.6	86.8018	75.7489
6000	12.9267	66505.6	87.0191	75.9348

MOLECULAR WEIGHT= 248.0[illegible]
MOLECULAR CONSTANTS ARE LISTED AS:
LEVEL,WE,XEWE,YEWE,BE,ALPHAE,DE,MULTIPLICITY,V00

1	895.77	2.39	0	.332644	.001302	1.83300E-7	1	0
2	864.1	2.31	0	.326413	.00122	1.8[illegible]300E-7	2	5305
3	846.4	2.4	0	.323044	.001294	1.86600E-7	1	10600.8
4	842.8	2.18	0	.324973	.001299	1.94200E-7	2	11129.1
5	835.1	2.39	0	.322455	.0012[illegible]	1.93100E-7	2	14490.
6	839.2	2.5	0	.32155	.0013	1.85000E-7	2	15946.2
7	829.26	2.3	0	.32[illegible]9	.001303	1.29000E-7	1	16320.4
8	816.9	2.26	0	.317172	.00124	1.93400E-7	2	17998
9	816.2	2.26	0	.321397	.00124	1.99339E-7	1	18337.6
10	800.85	1.47	0	.3296	.00124	2.40000E-7	2	19539.1
11	850.57	1.47	0	.32516	.00124	2.05900E-7	2	21[illegible]4.3
12	795.5	1.47	0	.318	.00124	2.00000E-7	2	22635.7

TABLE 4. THERMODYNAMIC FUNCTIONS FOR ThO_2(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	69.182R	11.3625
400	-62.1467	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	11.4203	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	84.4481	13.5331
1100	-73.5895	12.1515	85.741	13.5954
1200	-74.6529	12.2739	86.9261	13.6437
1300	-75.639	12.3806	88.0198	13.6817
1400	-76.56	12.4748	89.0348	13.7123
1500	-77.4236	12.5582	89.9818	13.7371
1600	-78.2065	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	-81.7106	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	13.8715
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	102.468	13.8812
3800	-89.5033	13.3347	102.838	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	13.3986	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	-94.7109	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 $ThO_2(g)$

T	(G-H0)/T	(H-H0)/T	S	CP
298.15	-58.8495	9.7781	68.2677	11.3116
300	-58.55	9.7876	68.3377	11.3209
400	-61.0341	10.2765	71.7105	12.1068
500	-63.7738	10.6973	74.4711	12.6186
600	-65.7561	11.0478	76.8038	12.9534
700	-67.4815	11.3368	78.8183	13.1784
800	-69.0115	11.5773	80.5888	13.3388
900	-70.3971	11.7791	82.1662	13.4471
1000	-71.6379	11.9503	83.5875	13.52
1100	-72.7839	12.0969	84.8801	13.5809
1200	-73.8416	12.2236	86.065	13.6415
1300	-74.8243	12.3342	87.1585	13.6788
1400	-75.749	12.4315	88.1735	13.7107
1500	-76.6026	12.5176	89.1203	13.7358
1600	-77.413	12.5944	90.0078	13.7564
1700	-78.1786	12.6633	90.849	13.7736
1800	-78.9062	12.7254	91.6297	13.7881
1900	-79.5938	12.7817	92.3755	13.8006
2000	-80.2507	12.8329	93.0836	13.811
2100	-80.878	12.8797	93.7577	13.8201
2200	-81.4782	12.9226	94.4 a	13.828
2300	-82.0535	12.9621	95.0156	13.835
2400	-82.6059	12.9986	95.6086	13.841
2500	-83.1373	13.0324	96.1807	13.8464
2600	-83.649	13.0638	96.7139	13.8513
2700	-84.1426	13.0931	97.2357	13.8555
2800	-84.6193	13.1206	97.7307	13.8593
2900	-85.0801	13.1459	98.2061	13.8627
3000	-85.5262	13.1699	98.6961	13.8658
3100	-85.9584	13.1924	99.1528	13.8684
3200	-86.3776	13.2135	99.5911	13.8710
3300	-86.7845	13.2335	100.010	13.8735
3400	-87.1799	13.2524	100.412	13.8756
3500	-87.5643	13.2703	100.796	13.8776
3600	-87.9383	13.2871	101.165	13.8794
3700	-88.3026	13.3031	101.518	13.881
3800	-88.6576	13.3183	101.856	13.8825
3900	-89.0037	13.3328	102.182	13.8838
4000	-89.3415	13.3466	102.498	13.8849
4100	-89.6712	13.3598	102.801	13.8859
4200	-89.9933	13.3723	103.096	13.8867
4300	-90.3081	13.3843	103.382	13.8875
4400	-90.6159	13.3958	103.659	13.8881
4500	-90.9171	13.4068	103.929	13.8886
4600	-91.2119	13.4173	104.192	13.8891
4700	-91.5005	13.4274	104.448	13.8895
4800	-91.7833	13.4371	104.69	13.8899
4900	-92.0605	13.4464	104.927	13.8902
5000	-92.3322	13.4553	105.158	13.8905
5100	-92.5988	13.464	105.383	13.8908
5200	-92.8603	13.4722	105.603	13.8911
5300	-93.117	13.4802	105.817	13.8914
5400	-93.369	13.4878	106.027	13.8916
5500	-93.6166	13.4951	107.113	13.892
5600	-93.8598	13.5021	107.269	13.8923
5700	-94.0989	13.5088	107.42	13.8979
5800	-94.3339	13.5152	107.65	13.8984
5900	-94.5648	13.5214	105.597	13.8976
6000	-94.7923	13.5273	108.321	13.8991

FREQ 787.9 MULT 1
FREQ 735.5 MULT 1
FREQ 125 MULT 1
MOLECULAR WEIGHT 264.037
SYMMETRY 2
MOMENTS 24.863 69.798 94.571
END OF RUN

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