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A THERMODYNAMIC STUDY OF THE URANIA-URANIUM SYSTEM

by

R. J. Ackermann, E. G. Rauh,
and M. S. Chandrasekharaiah

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OF THE URANIA-URANIUM SYSTEM

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I. INTRODUCTION

It is now generally recognized that most so-called chemical compounds can exist as phases of variable composition.¹ Uranium dioxide is certainly no exception and, in fact, the experimental evidence suggests that its composition can vary within wide limits. The crystallographic and thermodynamic properties of the hyperstoichiometric phase which extends up to a composition given approximately by the oxygen-to-uranium ratio $O/U \cong 2.2$ have been most extensively investigated in recent years.² Early evidence which suggests the existence of a hypostoichiometric urania phase which may extend down to $O/U = 1.75$ was compiled by Brewer,³ but only recently have Anderson *et al.*,⁴ Rothwell,⁵ and Aitken *et al.*,⁶ demonstrated the stability of the hypostoichiometric phase at high temperatures. The mass spectrometric observations of DeMaria *et al.*,⁷ indicate that the total vapor pressure (predominantly UO) of the urania phase saturated with liquid uranium is greater by a factor of approximately ten at $2000^\circ K$ than that (predominantly UO_2) measured by Ackermann *et al.*⁸ for nearly stoichiometric urania. In view of these observations a comprehensive investigation of the evaporation behavior of the urania phase and its dependence on composition has been initiated. The experimental approach to the present investigation has been the following:

1. the determination of the lower boundary of the urania phase from 1860 to $2500^\circ K$ by an isopiestic method;
2. the measurement of the total effusion rate of various mixtures of urania-liquid uranium from 1540 to $2315^\circ K$;
3. the mass spectrometric determination of the vapor species in equilibrium with urania-liquid uranium mixtures and with the urania phase alone, and the temperature dependence of their partial pressures over the range from 1820 to $2330^\circ K$;
4. the combination of the total effusion data with the mass-spectrometric data to yield partial pressures of U , UO , UO_2 , and UO_3 above various compositions of the urania phase;
5. the reevaluation of the standard free energy of formation of $UO(g)$;

6. the examination of the standard free energies of formation of UO(g) , $\text{UO}_2\text{(g)}$, and $\text{UO}_3\text{(g)}$ for thermodynamic consistency.

II. EXPERIMENTAL METHODS AND RESULTS

A. Measurement of the Composition of the Urania Phase in Equilibrium with Liquid Uranium

The phase diagram of uranium-oxygen system in the region between uranium metal and uranium dioxide has been little investigated. Gray and Thompson⁹ reported a very small solubility of urania in liquid uranium; recently Blum *et al.*,¹⁰ reported a complete solubility between liquid uranium and uranium dioxide. Martin and Edwards¹¹ of this Laboratory, in another study, confirmed Gray and Thompson's observations, determined the lower boundary of the urania phase, and proposed a phase diagram for the uranium-oxygen system in this composition region. In the present investigation the composition of the urania phase in equilibrium with liquid uranium was determined by an isopiestic method which consisted of equilibrating a sample of urania with the vapor phase arising from a saturated mixture of urania-liquid uranium inside a closed container.

A slip-cast, thin-walled cup was fabricated from pure urania powder and outgassed at 1800°C for about 2 hr in a vacuum of 10^{-6} mm Hg. A charge of uranium wire was placed inside the cup, which was then placed in the center of a well-outgassed tantalum crucible. Several small pieces of urania (about 1-2 g) were placed around the urania cup and in the space between the cup and the tantalum crucible wall. By this arrangement the

Fig. 1. Crucible Assembly for Determination of the Lower Phase Boundary of Urania

liquid uranium and that part of the urania used for analysis were physically separated. The lid was then placed in position and the whole assembly, shown in Fig. 1, was introduced into the vacuum system and evacuated to a pressure less than 10^{-6} mm Hg. The crucible assembly was heated inductively to the desired temperature, held at that temperature for sufficient time to achieve equilibrium, and then quickly cooled. The minimum times necessary for equilibration of the urania pieces were based on the observed vapor pressure of the urania-liquid uranium mixtures and the time required to transfer from the mixture to these pieces quantities of UO(g) sufficient to reduce them to compositions near those observed by Martin and Edwards. The equilibration times given in Table 1 are greater by factors of 2-20 than these minimum times. The

composition of the urania phase was determined by oxidation of the urania pieces to U_3O_8 by heating in air to 850°C . The results are presented in Table 1 and in Fig. 2. Below 2100°C these results are in good agreement with those of Martin and Edwards,¹¹ who analyzed the oxide growths that formed at the urania-liquid uranium interface.

TABLE 1. Composition of the Lower Phase Boundary of Urania

No.	Temperature, $^\circ\text{C}$	Time of Equilibration	O/U Ratio
1	1832	90 min	1.93
2	1977	90 min	1.87
3	1807	60 min	1.99*
4	1804	135 min	1.98*
5	2090	35 min	1.84 ₅
6	2070	60 min	1.83 ₅
7	1590	49 hr	1.96
8	1918	3 hr	1.88
9	1750	16 hr	1.93
10	2136	60 min	1.82
11	1822	10 hr	1.83**
12	1832	9 hr	1.92
13	2230	20 min	1.84 [†]
14	2220	15 min	1.82 ₅
15	2200	39 min	1.82

*The reason for the large discrepancy between these points and No. 1 is not known.

**The urania cup was found cracked at the end of the run.

[†]Uranium was found exhausted at the end of the run.

Fig. 2. Composition of Urania Saturated with Uranium as a Function of Temperature

Attempts to measure the composition of the phase boundary above 2200°C by this method were unsuccessful because large amounts of the material were lost through the taper fit between the lid and the crucible. Further measurements at these higher temperatures with some modification of this procedure are in progress.

B. Measurements of the Total Effusion Rate

The effusion rates of the vapors in equilibrium with the mutually saturated urania-liquid uranium phases were measured by the effusion method. The theory and the application of this method to determine the vapor pressures

in the range from 10^{-9} to 10^{-2} mm Hg are sufficiently well known to require no further discussion here. The effusion rates were determined by collection of a definite fraction of the effusate on platinum targets and analysis of the target deposit for uranium content by alpha or fission counting. The experimental details, apparatus, preparation of targets, temperature measurements, and calibration have been described.⁸

Before measurements could be made it was necessary to find a suitable container for the liquid uranium. Tungsten and molybdenum were incompatible with liquid uranium at temperatures above 1600°C , tantalum above 1750°C ; in addition to their dissolution in liquid uranium, they were wetted easily by liquid uranium at these temperatures. This resulted in the creep of liquid uranium out of the effusion cell through the taper fit and subsequent evaporation to form a heavy, conducting film on the surrounding fused-silica condenser. This sublimate heated inductively and became a secondary evaporation source for uranium-bearing species. After some experimentation a urania cup of the type used in the isopiestic measurements was found to be a satisfactory container for liquid uranium at temperatures as high as 2300°C . Below 1750°C a tantalum cup functioned satisfactorily.

The effusion measurements were carried out over the temperature range $1540\text{--}2315^{\circ}\text{K}$. For measurements at the higher temperatures, $1825\text{--}2315^{\circ}\text{K}$, the samples consisted of normal uranium metal in a normal urania cup and were prepared in the same manner as in the isopiestic measurements. At the lower temperatures, $1540\text{--}2030^{\circ}\text{K}$, the sample consisted of uranium metal (enriched in U^{234} and U^{235}) and urania prepared

from the enriched metal, and was contained in a well-outgassed tantalum cup. The effusion cells (see Fig. 3), were made from dense tantalum or tungsten.

Fig. 3. Schematic Diagram of the Effusion Cell

The uranium content of the targets was determined by radiochemical methods. It can be shown that for uranium samples of natural isotopic composition, measurement of the α activity may be used to determine uranium concentrations above the microgram range, whereas for the enriched samples employed in this study the method is applicable to a uranium concentration above 10^{-8} g. The uranium content of all the targets, both for enriched samples and those of natural isotope

composition, were analyzed by a proportional counter with an overall counting efficiency of 0.517. Those targets which contained less than 10^{-8} g of uranium were assayed by fission-rate counting of the U^{235} . Concentrations of the order of 10^{-8} to 10^{-10} g of U^{235} can be determined with good precision by this method.

Two suitable targets which were previously analyzed by α counting were used as standards in the fission counters. The fission rate of the sample was compared simultaneously with that of a standard in the same thermal-neutron flux and the amount of uranium in the sample was calculated directly from the measured fission-rate ratio.

Previously^{8, 12} it was shown in this Laboratory that the platinum targets cooled by liquid nitrogen in the effusion apparatus collected practically all uranium-bearing species. In this investigation the condensation efficiency was checked in the same manner and found to be greater than 99.5%

For a thin-edged orifice, the effusion rate of a given molecular species is given¹³ by the expression

$$Z_i = \frac{1}{4} n \left(\frac{8 RT}{\pi M_i} \right)^{\frac{1}{2}} \text{ molecules cm}^{-2} \text{ sec}^{-1}, \quad (1)$$

where Z_i is the number of molecules leaving the orifice in unit time per unit area, n is the vapor density of the molecules inside the effusion cell, M_i is the molecular weight of the species, T is the temperature in degrees Kelvin, and R is the gas constant. If a fraction of this effusate is collected on a circular target of area much larger than the orifice area and parallel to the plane of the orifice, the rate of collection is related to the pressure of the vapors inside the effusion cell by means of the equation

$$p_i = \frac{w_i}{at} \sqrt{\frac{2\pi RT}{M_i}} \left(\frac{d^2 + r^2}{r^2} \right), \quad (2)$$

where p_i is the partial pressure of species i , w_i is the mass of the species " i " collected on the target in time t , a is the area of the orifice, d is the orifice-to-collimator distance, and r is the radius of collimator. A collimator radius of 9.58 mm was used throughout the measurements. The pressure p_i calculated from Eq. (2) is the steady-state pressure of the species inside the effusion cell and is related to the thermodynamic equilibrium pressure by the equation

$$p_i = p_{eq} / \left(1 + \frac{a}{A\alpha} \right). \quad (3)$$

Here p_{eq} is the equilibrium pressure, A the evaporating surface area, and α is the evaporation coefficient of the species "i." Since the ratio of a/A was less than 10^{-2} , p_i was considered to be nearly equal to p_{eq} for all the species under discussion.

The composition of the vapor in equilibrium with urania-liquid uranium was shown mass spectrometrically to be predominantly UO and is described later. Hence, an apparent vapor pressure p_e for the system was calculated from the measured effusion rates by assuming UO to be the only molecular species in the vapor. The results are presented in the Tables 2 through 9 in the order of measurement.

TABLE 2. Vaporization Data for Urania-Uranium System: Series B*

Temp (°K)	Time (sec)	α activity (c/m)**	Weight W(UO) (g x 10 ⁵)	P_e (atm)
2268	1159	70.3	9.88	3.73×10^{-5}
2268	1144	69.6	9.79	3.74×10^{-5}
2094	4140	24.6	3.46	3.67×10^{-6}

*Tungsten effusion cell. Liquid uranium contained in a dense urania cup. Natural isotopic composition. Orifice diameter at 298°K was 1.17₇ mm, and orifice-to-collimator distance was 89.30 mm.

**Corrected for a background of 0.76 c/m.

TABLE 3. Vaporization Data for Urania-Uranium System: Series C*

Temp (°K)	Time (sec)	α activity (c/m)**	Weight W(UO) (g)	P_e (atm)
2037	3615	6.9 ₅	$9.8_0 \times 10^{-6}$	$1.0_4 \times 10^{-6}$
2330	616	72.9	1.02×10^{-4}	6.83×10^{-5}
2100	2700	17.6	2.48×10^{-5}	3.58×10^{-6}
2341	554	73.6	1.04×10^{-4}	7.69×10^{-5}
2225	1504	51.3	7.22×10^{-5}	1.93×10^{-5}

*Tungsten effusion cell. Liquid uranium contained in thin-walled urania cup. Natural isotopic composition. Orifice diameter and orifice-to-collimator distance were 1.23₅ mm and 90.26 mm, respectively, at room temperature.

**Corrected for a background of 0.79 c/m.

TABLE 4. Vaporization Data for Urania-Uranium System: Series D*

Temp (°K)	Time (sec)	α activity (c/m)**	Weight W(UO) (g)	P_e (atm)
2050	3734	8.6 ₅	$1.2_2 \times 10^{-5}$	$1.5_4 \times 10^{-6}$
2131	2010	22.7	3.20×10^{-5}	7.67×10^{-6}
2202	2274	17.3	2.40×10^{-5}	5.24×10^{-6}
2279	1170	18.9	2.66×10^{-5}	1.14×10^{-5}
2199	1416	9.0 ₆	1.27×10^{-5}	$4.4_1 \times 10^{-6}$
2049	3732	11.4	1.61×10^{-5}	2.03×10^{-6}
1937	10836	5.4 ₀	$7.6_0 \times 10^{-6}$	$3.2_2 \times 10^{-7}$

*Tungsten effusion cell. Liquid uranium contained in a thin-walled urania cup. Natural isotopic composition. Orifice diameter and orifice-to-collimator distance were 1.12₉ mm and 91.35 mm, respectively, at room temperature.

**Corrected for a background of 0.89 c/m.

TABLE 5. Vaporization Data for Urania-Uranium System: Series E*

Temp (°K)	Time (sec)	α activity (c/m)**	Weight W(UO) (g)	P_e (atm)
1825	10554	~0.5	$\sim 7 \times 10^{-7}$	$\sim 2 \times 10^{-8}$
1879	5949	0.8 ₉	$1.2_5 \times 10^{-6}$	$7.4_9 \times 10^{-8}$
1939	6157	2.5 ₇	$3.6_2 \times 10^{-6}$	$2.1_2 \times 10^{-7}$
2027	5772	9.4 ₇	$1.3_3 \times 10^{-5}$	$8.5_2 \times 10^{-7}$
2111	2385	14.3	2.02×10^{-5}	3.19×10^{-6}
2189	1839	36.0	5.06×10^{-5}	1.06×10^{-5}
2317	667	65.9	9.28×10^{-5}	5.50×10^{-5}
2257	876	51.1	7.18×10^{-5}	3.19×10^{-5}
2069	1640	4.4 ₀	$6.1_9 \times 10^{-6}$	$1.4_1 \times 10^{-6}$
2163	684	8.9 ₉	$1.2_5 \times 10^{-5}$	$7.0_0 \times 10^{-6}$
1915	2736	1.0 ₀	$1.4_1 \times 10^{-6}$	$1.8_4 \times 10^{-7}$

*Tantalum effusion cell. Liquid uranium contained in thin-walled urania cup. Natural isotopic composition. Molybdenum radiation shield. Orifice diameter and orifice-to-collimator distance were 1.39₉ mm and 91.10 mm, respectively, at room temperature. Liquid uranium and the urania cup were heated to 1800°C for 2 hr before the commencement of the run.

**Corrected for a background of 0.79 c/m.

TABLE 6. Vaporization Data for Urania-Uranium System: Series F*

Temp (°K)	Time (sec)	α activity (c/m)**	$W_{\alpha}(\text{UO})$ (g)	$(p_e)_{\alpha}$ (atm)	$W_f(\text{UO})$ (g)	$(p_e)_f$ (atm)
1701	5814	3.8 ₅	$5.1_0 \times 10^{-8}$	$3.6_1 \times 10^{-9}$		
1917	2625	74.8	9.85×10^{-7}	1.65×10^{-7}		
2027	2044	348	4.59×10^{-6}	1.01×10^{-6}		
1821	3251	18.3	2.42×10^{-7}	3.19×10^{-8}		
1574	7484	~0.3	$\sim 4 \times 10^{-9}$	$\sim 2 \times 10^{-10}$		
1857	3269	35.3	4.66×10^{-7}	6.16×10^{-8}		
1978	3282	248	3.28×10^{-6}	4.45×10^{-7}		
2089	1716	735	9.70×10^{-6}	2.59×10^{-6}		
1584	6726	~0.0 ₄	-	-	2.63×10^{-9}	1.58×10^{-10}
1665	3546	1.0 ₅	$1.4_0 \times 10^{-8}$	$1.6_1 \times 10^{-9}$	1.26×10^{-8}	1.48×10^{-9}
1752	2400	3.0 ₉	$4.1_0 \times 10^{-8}$	$7.1_3 \times 10^{-9}$	4.06×10^{-8}	7.21×10^{-9}

*Tungsten effusion cell. Liquid uranium and urania powder were contained in tantalum cup. Enriched Sample 1. Orifice diameter and orifice-to-collimator distance were 1.22₂ mm and 87.2₁ mm, respectively, at room temperature. Molybdenum shield.

**Corrected for a background of 0.77 c/m.

TABLE 7. Vaporization Data for Urania-Uranium System: Series G*

Temp (°K)	Time (sec)	α activity (c/m)**	$W_{\alpha}(\text{UO})$ (g)	$(p_e)_{\alpha}$ (atm)	$W_f(\text{UO})$ (g)	$(p_e)_f$ (atm)
2085	1805	670	9.90×10^{-6}	2.01×10^{-6}		
1852	5732	49.1	7.25×10^{-7}	4.40×10^{-8}		
2001	2701	322	4.76×10^{-6}	6.36×10^{-7}		
1599	11700	~0.5	$\sim 7 \times 10^{-9}$	$\sim 2 \times 10^{-10}$	6.00×10^{-9}	1.68×10^{-10}
1952	5403	275	4.07×10^{-6}	2.69×10^{-7}		
1789	6601	15.5	2.29×10^{-7}	1.20×10^{-8}		
1704	11702	4.1 ₆	$6.1_4 \times 10^{-8}$	$1.7_5 \times 10^{-9}$		
2027	1442	215	3.18×10^{-6}	8.02×10^{-7}		
1931	4866	170	2.52×10^{-6}	1.84×10^{-7}		
1630	10827	0.9 ₇	$1.4_3 \times 10^{-8}$	$4.3_4 \times 10^{-10}$	1.02×10^{-8}	3.10×10^{-10}
1545	21272	1.0 ₃	$1.5_2 \times 10^{-8}$	$2.2_9 \times 10^{-10}$	1.26×10^{-8}	1.91×10^{-10}
2025	3302	318	4.70×10^{-6}	5.20×10^{-7}		
1472	8060	-	-	-	2.87×10^{-9}	1.12×10^{-11}
1543	7509	-	-	-	1.77×10^{-9}	7.60×10^{-11}
1627	3009	-	-	-	4.13×10^{-9}	4.55×10^{-10}
1575	2400	-	-	-	9.90×10^{-9}	1.35×10^{-10}
1954	972	50.4	7.44×10^{-6}	2.78×10^{-7}	-	-

*Tantalum effusion cell. Liquid uranium and urania contained in tantalum cup. Enriched Sample 2. Orifice diameter 1.390 mm and orifice-to-collimator distance 89.20 mm at room temperature. Molybdenum shield.

**Corrected for a background of 0.76 c/m.

TABLE 8. Vaporization Data for Urania-Uranium System: Series H*

Temp (°K)	Time (sec)	α activity (c/m)**	W_{α} (UO) (g)	$(P_e)_{\alpha}$ (atm)	W_f (UO) (g)	$(P_e)_f$ (atm)
1807†	4536	2.0 ₄	$3.0_2 \times 10^{-8}$	$4.0_5 \times 10^{-8}$	8.78×10^{-9}	1.18×10^{-8}
2122†	474	6.1 ₇	$9.1_2 \times 10^{-8}$	$1.2_7 \times 10^{-6}$		
1916	1714	1.7 ₉	$2.6_5 \times 10^{-8}$	$9.6_8 \times 10^{-8}$	2.61×10^{-8}	9.56×10^{-8}
1703	6149	~0.3	$\sim 4 \times 10^{-9}$	$\sim 4 \times 10^{-9}$	2.62×10^{-9}	2.53×10^{-9}
1872	5032	3.0 ₁	$4.4_5 \times 10^{-8}$	$5.4_6 \times 10^{-8}$	3.48×10^{-8}	4.28×10^{-8}
2022	588	3.6 ₇	$5.4_2 \times 10^{-8}$	$5.9_5 \times 10^{-7}$	5.46×10^{-8}	5.95×10^{-7}
2205	323	29.3	4.34×10^{-7}	9.05×10^{-6}	-	-
1956	3769	11.1	1.65×10^{-7}	2.77×10^{-7}	-	-
1574	11835	~0.1	-	-	2.85×10^{-10}	1.39×10^{-10}
2200	254	19.5	2.89×10^{-7}	7.66×10^{-6}	-	-

*Tungsten effusion cell. Urania and liquid uranium contained in tantalum cup. Enriched Sample 2. Orifice diameter 0.313 mm and orifice-to-collimator distance 85.28 mm at room temperature. Molybdenum shield.

**Corrected for a background of 0.79 c/m.

†System not yet equilibrated. Points rejected.

TABLE 9. Vaporization Data for Urania-Uranium System: Series J*

Temp (°K)	Time (sec)	α activity (c/m)**	W_{α} (UO) (g)	$(P_e)_{\alpha}$ (atm)	W_f (UO) (g)	$(P_e)_f$ (atm)
1725	6378	4.9 ₀	$7.2_4 \times 10^{-8}$	$2.3_2 \times 10^{-9}$	-	-
1574	10848	~0.3	$\sim 4 \times 10^{-9}$	$\sim 7 \times 10^{-11}$	3.95×10^{-9}	7.12×10^{-11}
1624	13488	1.4 ₂	$2.1_0 \times 10^{-8}$	$3.0_8 \times 10^{-10}$	2.28×10^{-8}	3.35×10^{-10}
1679	7164	2.8 ₀	$4.1_4 \times 10^{-8}$	$1.1_6 \times 10^{-9}$	4.14×10^{-8}	1.17×10^{-9}
1651	10776	2.2 ₉	$3.3_8 \times 10^{-8}$	$6.2_4 \times 10^{-10}$	3.26×10^{-8}	6.04×10^{-10}
1600	5970	~0.4	$\sim 6 \times 10^{-9}$	$\sim 2 \times 10^{-10}$	5.34×10^{-9}	1.76×10^{-10}

*Tantalum effusion cell. Urania and liquid uranium contained in tantalum cup. Enriched Sample 2. Orifice diameter 1.79 mm and orifice-to-collimator distance 87.89 mm at room temperature. Molybdenum shield.

**Corrected for a background of 0.79 c/m.

Series B, C, and D were interrupted because of the formation of a metallic-looking deposit on the inner wall of the quartz condenser. The temperature of a run became unsteady once the film became visible. This deposit may have acted as a secondary evaporating source for the uranium-bearing species and may have given rise to apparently high values for the total effusion rates. In addition, in Series D, sublimates collected on the target were nonuniform in some cases. The results of Series B, C, and D

are given in the tables to show the erratic behavior and generally high vapor pressures, but were not included in the final evaluation of the data. In Series E through J a slotted molybdenum radiation shield, described elsewhere,¹⁴ was used to prevent the deposit from being continuous and thus from absorbing energy from the rf field.

The sample for Series E was of natural isotopic composition with metallic impurities less than 25 ppm. For Series F the sample was prepared from isotopically enriched uranium, 93.18% U^{235} and 1.11% U^{234} , and contained less than 200 ppm of metallic impurities. For Series G through J the isotopic composition was 93.229% U^{235} and 0.986% U^{234} , and contained less than 250 ppm of metallic impurities. The specific activities of these materials were calculated from the half-lives given by Seaborg *et al.*¹⁵

The data of Series E through J, shown on a $\log p_e$ vs $1/T$ plot in Fig. 4, are expressible by the least-squares equation

$$\log p_e = (7.250 \pm 0.146) - (27024 \pm 255)/T. \quad (4)$$

Fig. 4. Plot of $\log p_e$ (atm) vs $10^4/T$ for Mixtures of Urania-Liquid Uranium (Series E, F, G, H, and J)

The errors quoted here and in the remainder of the paper are standard deviations. The agreement between the results using samples of natural isotopic content (Series E) and those with enriched U^{235} and U^{234} (Series F, G, H, and J) is good. Furthermore, the variation of the orifice area from $7.69 \times 10^{-4} \text{ cm}^2$ (Series H) to $2.52 \times 10^{-2} \text{ cm}^2$ (Series J) produced no apparent effect on the observed rates of effusion.

In several cases a direct comparison is possible between the weights and pressures of uranium-bearing species determined by α counting, $W_\alpha(UO)$ and $(p_e)_\alpha$, and those determined by fission counting, $W_f(UO)$ and $(p_e)_f$, respectively. In general, the agreement is good when the α count is greater than 1-2 counts/min. In the least-squares treatment of the data given by Eq. (4) the re-

sults of fission counting were used in preference to those of α counting because of the greater sensitivity of the former method.

The agreement between the results of the present investigation and those for a mixture of urania-liquid uranium previously reported by Ackermann, Gilles, and Thorn⁸ is excellent. At a temperature of 2071°K, these investigators reported a value of the pressure, 1.14×10^{-3} mm Hg, which corresponds to the total pressure of uranium-bearing species (assuming the atomic weight of the vapor is 235) in equilibrium with urania-liquid uranium. If the value of the molecular weight of UO ($M = 254$) is used and the resultant value of the pressure is converted to atmospheres, one obtains $p = 1.45 \times 10^{-6}$ atm, which is to be compared with the value $p_e = 1.59 \times 10^{-6}$ atm evaluated from Eq. (4).

III. MASS-SPECTROMETRIC MEASUREMENTS

Several mass-spectrometric measurements with a Bendix time-of-flight spectrometer were made on the U-UO₂ two-phase system. The instrumentation, methods, and techniques used have been reported previously.¹⁴ Preliminary observations were made with a mixture of 100 mg of uranium metal and 20 mg of UO₂ in a tantalum cell. The ions observed at 1800°K were UO⁺, UO₂⁺, and U⁺ in the approximate ratio 10:1:1 in agreement with that reported by Chupka¹⁶ and DeMaria et al.⁷ Several hours of equilibration were required before the ion currents became constant at a given temperature.

The temperature dependences of the ion currents for each species were measured over the range 1800-2200°K at an ionizing electron energy of 10 eV. This energy was selected to prevent fragmentation of UO and UO₂ to U⁺ and UO⁺ for the following reasons. In the normal ionization process the number of ions increases rapidly with increasing energy of the ionizing electrons for a few volts above the threshold of ionization and then approaches a limiting value. In those cases where a primary species of higher molecular weight can give rise to the ion in question through fragmentation, a marked increase in the number of ions is observed at energies above the threshold of ionization by an amount equal to the dissociation energy of the bond broken to produce the ion fragment. This phenomenon has been demonstrated in the fragmentation of YO to Y⁺ (Ref. 17) and of NpO₂ to NpO⁺ (Ref. 18). Since the appearance potentials of U, UO, and UO₂ lie between 4 and 5 eV, and since the dissociation energy of one U-O bond is of the order of 8 eV,^{16,7} U⁺ and UO⁺ ions from fragmentation of UO and UO₂, respectively, may be expected above 12 or 13 eV. Appearance-potential measurements did indeed demonstrate this behavior. Thus an energy between 8 and 12 eV would be optimum for observing these primary ions. This low energy also results in a low background, since the appearance potentials of the residual gases in the vacuum are generally above 12 eV.

From the measurements of the temperature dependence of the pressure of each species in a $\log I^+T$ vs $1/T$ treatment of the data, the

following heats of vaporization were calculated: $\Delta H(U) = 123.2 \pm 1.6$, $\Delta H(UO) = 123.1 \pm 0.5$, and $\Delta H(UO_2) = 140.6 \pm 2.2$ kcal/mole. These heats are reported only for comparison with later results.

In view of the difficulties encountered in Series B, C, and D arising from creep and the dissolution of tantalum in the liquid uranium at temperatures above 2100°K, the cell and sample were replaced, and a second sample was prepared to conform with those used in the total-effusion measurements. It consisted of an 80-mg pellet of uranium metal placed in a shallow cavity in a 200-mg disk of sintered UO_2 ; a relatively small sample was used to hasten equilibration.

Three series of measurements of the temperature dependences of the ion currents over the temperature range 1800-2200°K were made after various lengths of time at temperature. The data, the least-squares equations of the data, and the resulting heats of evaporation of the three species are given in Tables 10, 11, and 12. The data of Series 1 (see Table 10) were taken after 20 min at 2150°K, those for Series 2 (see Table 11) after an additional 200 min at 2150°K, and those of Series 3 (see Table 12) after another 150 min at 2200°K.

TABLE 10. Mass-spectrometric Measurements of Temperature Dependence of Pressures of Gaseous Species in Equilibrium with Urania-Liquid Uranium, Series 1*

T (°K)	U^+	UO^+	UO_2^+
1973	0.192	3.30	0.375
2071	0.645	14.5	1.78
2149	1.65	37.5	5.65
2114	1.27	27.4	3.18
2024	0.440	8.10	0.840
1926	0.100	1.86	0.149
1866	0.040	0.690	0.048
2014	0.354	7.00	0.665
2051	0.615	12.0	1.25
2143	1.82	39.0	4.75

$$\log U^+T = (-24390 \pm 530)/T + (14.950 \pm 0.259) \quad \text{Eq. (a)}$$

$$\log UO^+T = (-26080 \pm 450)/T + (17.079 \pm 0.220) \quad \text{Eq. (b)}$$

$$\log UO_2^+T = (-29920 \pm 250)/T + (17.994 \pm 0.122) \quad \text{Eq. (c)}$$

$$\Delta H(U) = 111.6 \pm 2.4 \text{ kcal/mole}$$

$$\Delta H(UO) = 119.3 \pm 2.1 \text{ kcal/mole}$$

$$\Delta H(UO_2) = 136.9 \pm 1.1 \text{ kcal/mole}$$

*Ionizing electron energy of 10 eV.

TABLE 11. Mass-spectrometric Measurements of
Temperature Dependence of Pressures of Gaseous
Species in Equilibrium with Urania-Liquid
Uranium, Series 2*

T (°K)	U ⁺	UO ⁺	UO ₂ ⁺
2168	3.24	69.0	8.70
2083	1.17	24.0	2.66
1935	0.146	2.72	0.224
1878	0.060	1.04	0.077
2030	0.590	11.8	1.20
2129	2.14	44.5	5.25
2169	3.50	75.0	9.50
2168	3.35	72.5	9.20
1925	0.120	2.26	0.184
1826	0.024	0.395	0.026
1990	0.328	6.35	0.585

$$\log U^+T = (-25540 \pm 110)/T + (15.647 \pm 0.054) \quad \text{Eq. (d)}$$

$$\log UO^+T = (-26810 \pm 150)/T + (17.566 \pm 0.072) \quad \text{Eq. (e)}$$

$$\log UO_2^+T = (-30100 \pm 160)/T + (18.185 \pm 0.078) \quad \text{Eq. (f)}$$

$$\Delta H(U) = 116.9 \pm 0.5 \text{ kcal/mole}$$

$$\Delta H(UO) = 122.7 \pm 0.7 \text{ kcal/mole}$$

$$\Delta H(UO_2) = 137.7 \pm 0.7 \text{ kcal/mole}$$

*Ionizing electron energy of 10 eV.

TABLE 12. Mass-spectrometric Measurements of
Temperature Dependence of Pressures of Gaseous
Species in Equilibrium with Urania-Liquid
Uranium, Series 3*

T (°K)	U ⁺	UO ⁺	UO ₂ ⁺
2080	1.25	26.4	2.86
1933	0.162	3.02	0.224
1822	0.027	0.455	0.029
1877	0.068	1.18	0.086
2006	0.520	10.0	0.960
2187	4.95	110	14.4
2186	4.60	102	13.5

$$\log U^+T = (-25360 \pm 250)/T + (15.621 \pm 0.123) \quad \text{Eq. (g)}$$

$$\log UO^+T = (-26730 \pm 200)/T + (17.593 \pm 0.102) \quad \text{Eq. (h)}$$

$$\log UO_2^+T = (-30240 \pm 310)/T + (18.314 \pm 0.153) \quad \text{Eq. (i)}$$

$$\Delta H(U) = 116.0 \pm 1.1 \text{ kcal/mole}$$

$$\Delta H(UO) = 122.3 \pm 0.9 \text{ kcal/mole}$$

$$\Delta H(UO_2) = 138.4 \pm 1.4 \text{ kcal/mole}$$

*Ionizing electron energy of 10 eV.

The measured heats of evaporation of UO_2 agree in all three series within the standard deviations. However, $\Delta H(\text{U})$ and $\Delta H(\text{UO})$ for Series 1 are low and do not agree within the standard deviations with the corresponding heats in Series 2 and 3. These facts suggest that even with a relatively small sample an appreciable time at temperature is required

to bring both phases into equilibrium. Also, the preliminary values of $\Delta H(\text{U})$, $\Delta H(\text{UO})$, and $\Delta H(\text{UO}_2)$ suggest that the dissolved tantalum plays a role in the equilibrium. Since the results of Series 2 and 3 agree within the standard deviations, only the data of Series 2 are shown in the $\log I^+T$ vs $1/T$ plot of Fig. 5.

Fig. 5. Plot of $\log I^+T$ vs $10^4/T$ for Mass-spectrometric Measurements of U, UO , and UO_2 in Equilibrium with Urania-Liquid Uranium; Series 2

Mass-spectrometric observations of the vapor species over urania were made with a 1.1-g sample of initial composition $\text{UO}_{2.005 \pm 0.004}$. The only primary ions observed were UO^+ , UO_2^+ , and UO_3^+ at all temperatures in the range of observation. Measurements of the temperature dependences of UO^+ and UO_2^+ were made at an ionizing electron energy of 10 eV as before, but since the appearance potential of UO_3^+ is of the order of 10 eV,^{16,7}

it was necessary to employ a higher energy for the measurements of UO_3 . An energy of 22 eV was selected because this energy was essentially the limiting value for UO_3^+ . Thus, in order to obtain meaningful ion ratios and temperature-dependence measurements, observations were made on UO^+ and UO_2^+ at 10 eV, and on UO_2^+ and UO_3^+ at 22 eV. By means of the UO_2^+ , which was measured at both energies, the UO^+ ion current could be normalized to 22 eV.

Initial data and the appropriate heats of evaporation are given in Table 13 and shown in Fig. 6. During measurements the ion currents were not strictly constant at a fixed temperature, the UO^+ increasing slowly, the UO_3^+ decreasing slowly, and the UO_2^+ remaining nearly constant, indicating a decreasing O/U ratio in the condensed phase. The sample was then allowed to equilibrate further for about 4 hr at $\sim 2300^\circ\text{K}$, after which the ion currents were essentially constant. The ion currents were also constant at lower temperatures, indicating that the composition established at 2300°K was maintained at the lower temperatures. The data for the temperature dependences of UO^+ and UO_2^+ at 10 eV are given in Tables 14 and 16, and for UO_2^+ and UO_3^+ at 22 eV in Table 15. The

least-squares equations for the data and the heats of evaporation are also given. Since the same heat of evaporation of UO_2^+ was obtained at 10 and 22 eV, the data for UO_2^+ at 10 eV were normalized to those of UO_2^+ at 22 eV at the mid-temperature of the observations, and the same normalization factor was then applied to the UO^+ . The normalized data and equations are given in Fig. 7.

TABLE 13. Preliminary Mass-spectrometric Observations of Temperature Dependence of Pressures of Gaseous Species in Equilibrium with $\text{UO}_{2.005}$

T (°K)	UO^+ (at 10 eV)	UO_2^+ (at 10 eV)	UO_2^+ (at 22 eV)	UO_3^+ (at 22 eV)
2103	0.023	8.20	10.1	0.740
2185	0.100	27.0	31.5	1.68
2148	0.050	14.3	17.5	0.980
2062	0.100	3.90	4.70	0.310
$\Delta H(\text{kcal/mole})$	~ 167	~ 142	~ 142	~ 129

TABLE 14. Mass-spectrometric Measurements of Temperature Dependence of Pressures of Gaseous Species in Equilibrium with $\text{UO}_{1.994}$, Series A

T (°K)	UO^+ (at 10 eV)	UO_2^+ (at 10 eV)
2326	2.64	118
2263	1.50	55.5
2187	0.760	22.0
2105	0.360	6.80
2008	0.140	1.50
2060	0.228	3.54
2145	0.550	13.6
2225	1.12	39.0
2294	2.10	91.0

Fig. 6. Plot of $\log I^+T$ vs $10^4/T$ for Mass-spectrometric Measurements of UO , UO_2 , and UO_3 above $\text{UO}_{2.005} \pm 0.004$

$$\log \text{UO}^+T = (-19880 \pm 220)/T + (12.330 \pm 0.102) \quad \text{Eq. (j)}$$

$$\log \text{UO}_2^+T = (-29410 \pm 460)/T + (18.137 \pm 0.212) \quad \text{Eq. (k)}$$

$$\Delta H(\text{UO}) = 91.0 \pm 1.0 \text{ kcal/mole}$$

$$\Delta H(\text{UO}_2) = 134.6 \pm 2.1 \text{ kcal/mole}$$

TABLE 15. Mass-spectrometric Measurements of Temperature Dependence of Pressures of Gaseous Species in Equilibrium with $\text{UO}_{1.994}$, Series B

T (°K)	UO_2^+ (at 22 eV)	UO_3^+ (at 22 eV)
2323	127	1.43
2257	57.5	0.450
2185	22.2	0.106
2105	6.60	0.018
2145	12.4	0.046
2224	37.0	0.236
2291	85.0	0.810

$$\log \text{UO}_2^+ T = (-29610 \pm 330)/T + (18.221 \pm 0.148) \quad \text{Eq. (l)}$$

$$\log \text{UO}_3^+ T = (-43500 \pm 460)/T + (22.264 \pm 0.207) \quad \text{Eq. (m)}$$

$$\Delta H(\text{UO}_2) = 135.5 \pm 1.5 \text{ kcal/mole}$$

$$\Delta H(\text{UO}_3) = 199.1 \pm 2.1 \text{ kcal/mole}$$

TABLE 16. Mass-spectrometric Measurements of Temperature Dependence of Pressures of Gaseous Species in Equilibrium with $\text{UO}_{1.994}$, Series C

T (°K)	UO^+ (at 10 eV)	UO_2^+ (at 10 eV)
2322	2.28	110
2227	0.920	32.0
2107	0.306	5.80
2010	0.124	1.32
2062	0.208	3.10
2174	0.600	16.6
2278	1.58	67.5

$$\log \text{UO}^+ T = (-19910 \pm 350)/T + (12.280 \pm 0.162) \quad \text{Eq. (n)}$$

$$\log \text{UO}_2^+ T = (-29840 \pm 250)/T + (18.269 \pm 0.116) \quad \text{Eq. (o)}$$

$$\Delta H(\text{UO}) = 91.1 \pm 1.6 \text{ kcal/mole}$$

$$\Delta H(\text{UO}_2) = 136.5 \pm 1.1 \text{ kcal/mole}$$

Fig. 7. Normalized Plot of $\log I^+ T$ vs $10^4/T$ for Mass-spectrometric Measurements of UO , UO_2 , and UO_3 above $UO_{1.994 \pm 0.004}$

$$\log I_{UO}^+ T = (-19890 \pm 180)/T + (12.334 \pm 0.084) \quad \text{Eq. (p)}$$

$$\log I_{UO_2}^+ T = (-29630 \pm 190)/T + (18.231 \pm 0.087) \quad \text{Eq. (q)}$$

$$\log I_{UO_3}^+ T = (-43500 \pm 460)/T + (22.264 \pm 0.207) \quad \text{Eq. (r)}$$

The composition of the residue was determined by combustion analysis to be $UO_{1.994 \pm 0.004}$. Since UO , UO_2 , and UO_3 are the only significant vapor species, from inspection of Fig. 7 one sees that the overall composition of the vapor is somewhat temperature dependent, being approximately UO_2 at the highest temperature but slightly richer in uranium at the lower temperatures. However, the composition of the solid will not be changed appreciably because at $2000^\circ K$ the loss of material, predominantly UO_2 , is of the order of a few $\mu g/\text{min}$. For this reason and because of the reproducibility of the data in retracing the temperature range, one concludes that during the measurements the composition of the solid phase was essentially unchanged.

IV. THERMODYNAMIC ANALYSIS

A. Calculations of the Partial Pressures in Equilibrium with Urania-Liquid Uranium

It can be easily shown by means of Eq. (2) that the "effective" pressure of the uranium-bearing species given by Eq. (4) is related to the individual partial pressures of species observed mass spectrometrically via the equation

$$p_e = p_{\text{UO}} + \left(\frac{M_{\text{UO}_2}}{M_{\text{UO}}} \right)^{\frac{1}{2}} p_{\text{UO}_2} + \left(\frac{M_{\text{U}}}{M_{\text{UO}}} \right)^{\frac{1}{2}} p_{\text{U}}. \quad (5)$$

The partial pressure of a given atomic or molecular species is related to the ion current I_i^+ , the cross section σ_i , the detector efficiency ϵ_i , and the absolute temperature T by the expression

$$I_i^+ \approx \sigma_i \epsilon_i p_i / T. \quad (6)$$

The individual partial pressures of U, UO, and UO₂ can be evaluated from the effective pressure, from the mass-spectrometric ion currents, and from the estimation of the detector efficiencies and the relative ionization cross sections. In the region of relatively low electron energies (10 and 20 eV) utilized in this study, the method for estimating cross sections proposed by Otvos and Stevenson¹⁹ is not applicable since it is restricted to electron energies in excess of 70 eV. It is intuitively reasonable that a uranium atom with all six of its valence electrons unbonded might have a larger probability (cross section) for ionization than a molecule of UO in which two of these electrons are directly involved in bonding with the oxygen atom. By similar reasoning, molecules of UO₂ and UO₃ would have successively smaller cross sections. However, the increase in geometric size of the respective molecules would tend to counter the trend produced by the decreasing number of unbonded valence electrons.

In the present study the total-effusion-rate data (see Fig. 4) will be analyzed by using two sets of estimates of relative ionization cross sections: $\sigma_{\text{U}}:\sigma_{\text{UO}}:\sigma_{\text{UO}_2} = 1:1:1$ and $3:2:1$, together with the arbitrary assumption of equal multiplier efficiencies for all species. Equation (5) can be rewritten to yield the partial pressure of UO:

$$p_{\text{UO}} = p_e / [1 + (1.031)(p_{\text{UO}_2}/p_{\text{UO}}) + (0.968)(p_{\text{U}}/p_{\text{UO}})]. \quad (7)$$

By assuming equal relative ionization cross sections and by substituting the appropriate values for p_e , $p_{\text{UO}_2}/p_{\text{UO}}$, and $p_{\text{U}}/p_{\text{UO}}$ from

Eq. (4) and Eqs. (d), (e), and (f) of Table 11 at two representative temperatures, one arrives at the linear equation for $\log p_{\text{UO}}$, Eq. (t) of Table 17.

Similarly, Eq. (5) was solved for p_{UO_2} and p_{U} by use of the same cross-section estimates, yielding Eqs. (u) and (s) of Table 17. The entire calculation procedure was then repeated for the other set of estimated cross sections: $\sigma_{\text{U}}:\sigma_{\text{UO}}:\sigma_{\text{UO}_2} = 3:2:1$. All the calculated equations are given in Table 17 in the form $\log p_i = A_i + (B_i/T)$, and Eqs. (5), (s), (t), and (u) are plotted in Fig. 8.

TABLE 17. The Partial Pressures of U, UO, and UO₂ in Equilibrium with Mutually Saturated Urania-Liquid Uranium: $\log p_i = A_i + (B_i/T)$

Vapor Species	Relative Ionization Cross Sections					
	$\sigma_{\text{U}} = \sigma_{\text{UO}} = \sigma_{\text{UO}_2}$			$1/3 \sigma_{\text{U}} = 2/3 \sigma_{\text{UO}} = \sigma_{\text{UO}_2}$		
	A_i	B_i	Eq.	A_i	B_i	Eq.
U	5.194 ± 0.140	$-25,620 \pm 300$	s	4.880 ± 0.140	$-25,410 \pm 300$	v
UO	7.109 ± 0.140	$-26,870 \pm 300$	t	6.964 ± 0.140	$-26,655 \pm 300$	w
UO ₂	7.728 ± 0.140	$-30,165 \pm 300$	u	7.894 ± 0.140	$-29,970 \pm 300$	x

Fig. 8. Partial Pressures of U, UO, UO₂, and O in Equilibrium with Urania-Liquid Uranium and the "Effective" Pressure from Fig. 4

In Table 18 the heats of evaporation observed mass spectrometrically (Table 11) are compared with those evaluated from the constants B_i given in Table 17. Both sets of estimated cross sections evidently yield heats of evaporation that are compatible with the observed values within the respective standard deviations. In other words, the experimental precision is not sufficient to distinguish between the two sets of estimated cross sections. In further calculations the equations derived from the assumption of equal cross-sections will be employed. The agreement of the heats of evaporation shown in Table 18, therefore, demonstrates that the mass-spectrometric data appear to be basically consistent with the observed mass-effusion data and, in particular, the agreement between the mass-effusion data and the mass-spectrometric measurements of the principal vapor species UO(g) is very good.

TABLE 18. Comparison of Calculated and Mass-spectrometrically Measured Heats of Sublimation

Vapor Species	ΔH° (obs), kcal/mole (from Table 11)	ΔH° (calc), kcal/mole $\sigma_U = \sigma_{\text{UO}} = \sigma_{\text{UO}_2}$	ΔH° (calc), kcal/mole $1/3 \sigma_U = 2/3 \sigma_{\text{UO}} = \sigma_{\text{UO}_2}$
U	116.9 ± 0.5	117.2 ± 1.2	116.3 ± 1.2
UO	122.7 ± 0.7	123.0 ± 1.2	122.0 ± 1.2
UO_2	137.7 ± 0.7	138.0 ± 1.2	137.1 ± 1.2

For the mass-spectrometric study of the equilibrium

the data in Tables 10, 11, and 12 normalized to 22 eV permit the evaluation and analysis of the equilibrium constant:

$$K = p_{\text{UO}}^2 / p_U p_{\text{UO}_2}. \quad (9)$$

The results are shown in Fig. 9 for Series 1, 2, and 3, and the least-squares equation representing the data is

$$\log K = (1.268 \pm 0.058) + (2091 \pm 117)/T. \quad (10)$$

The data are seen to possess good precision with the exception of a few points, most of which correspond to the initial observations from Series 1, where the equilibration of the urania-liquid uranium sample was very likely not complete. These data were therefore discarded in the calculation of Eq. (10).

Fig. 9. Plot of Log K vs $10^4/T$ for the Equilibrium $\text{UO}_2(\text{g}) + \text{U}(\text{g}) = 2\text{UO}(\text{g})$

B. The Standard Free Energy of Formation of Gaseous Uranium Monoxide

It is now instructive to evaluate the maximum and minimum values of the standard free energy of formation of gaseous uranium monoxide from the results previously presented. Consider the homogeneous and heterogeneous equilibria

If in reaction (11) the two reactants remain pure, i.e., there is no mutual solubility of the two phases, then

$$\Delta G_{11}^\circ = 2\Delta G_f^\circ(\text{UO}, \text{g}) - \Delta G_f^\circ(\text{UO}_2, \text{s}) = -R'T \log p_{\text{UO}}^2 \quad (13)$$

where $R' = 2.303 R$. By utilizing Eq. (t) from Table 17 together with $\Delta G_f^\circ(\text{UO}_2, \text{s}) = -258,650 + 40.64 T$ from Coughlin,^{20*} one calculates $\Delta G_f^\circ(\text{UO}, \text{g}) \leq -30.8 \text{ kcal/mole}$ at 2000°K , which value represents the minimum negative value, since it has been assumed that the two reactants in Eq. (11) remain at unit activity.

*The linear equation for $\Delta G_f^\circ(\text{UO}_2, \text{s})$ given by Coughlin differs from the more precise three-term equation proposed by Rand and Kubaschewski²¹ by less than 700 cal over the temperature range $1800\text{--}2400^\circ\text{K}$.

If, however, one attempts to account for the effect of mutual solubility of the two condensed phases by ascertaining the reduction in the partial pressures of U(g) and $\text{UO}_2\text{(g)}$ in Eq. (12) compared with their respective vapor pressures, a more realistic value of $\Delta G_f^\circ(\text{UO}, \text{g})$ can be obtained. The partial pressure of $\text{UO}_2\text{(g)}$ is reduced at most by a factor of two based on a comparison of the vapor pressure measurements of the nearly stoichiometric urania phase⁸ with Eq. (u) of Table 17, for $\log p_{\text{UO}_2}$, which corresponds to the partial pressure of $\text{UO}_2\text{(g)}$ above $\text{UO}_{1.94}\text{(s)}$ at 2000°K (see Fig. 2). The virtual agreement of various values of the heats of sublimation of $\text{UO}_2\text{(g)}$ resulting from condensed phases of different compositions, namely, $\Delta H = 135.6 \pm 0.9$ for $\text{UO}_{1.994}\text{(s)}$, $\Delta H = 136.9 \pm 1.1$, 137.7 ± 0.7 and 138.4 ± 1.4 for urania saturated with liquid uranium, and $\Delta H = 137.1 \pm 1.7$ kcal/mole reported by Ackermann *et al.*⁸ indicates that the partial pressure of $\text{UO}_2\text{(g)}$ does not depend markedly on the composition of the urania phase.

In the case of the vapor pressure of uranium, the measurements of Rauh and Thorn¹² are greater by approximately a factor of ten than those reported by DeMaria *et al.*,⁷ and recently repeated by Drowart *et al.*²² Ackermann, Rauh, and Thorn²³ have recently commented on this discrepancy and have observed mass spectrometrically that in experiments in which the procedure of Rauh and Thorn was repeated the vaporizing species were U(g) and UO(g) of comparable intensity, the latter being about twice as intense as the former at the onset of the measurements. From these observations it is possible to set an upper limit for the vapor pressure of uranium at 2000°K which is approximately one-third that reported originally by Rauh and Thorn. Since the equilibrium constant given by Eq. (9) represents a homogeneous equilibrium, it is possible to rewrite Eq. (10) as

$$\log K = 2 \log p_{\text{UO}}^\circ - \log p_{\text{U}}^\circ - \log p_{\text{UO}_2}^\circ, \quad (14)$$

where the superscripts refer to the case where the reactants are the pure components. By substituting the value of the maximum vapor pressure of liquid uranium at 2000°K together with the vapor pressure of UO_2 (Ref. 8) and the value of $\log K$ at 2000°K [see Eq. (10)], one obtains a value of $\log p_{\text{UO}}^\circ = -5.59$. From Eq. (13) one then calculates $\Delta G_f^\circ(\text{UO}, \text{g}) \geq -37.6$ kcal/mole, which represents the maximum negative value. Drowart *et al.*²² state that the vapor pressure of liquid uranium cannot be suppressed by greater than a factor of approximately two as a result of saturation with oxide. Hence, by increasing the partial pressure of uranium in equilibrium with urania-liquid uranium given by Eq. (s) of Table 17 by this factor one obtains via Eqs. (13) and (14) that $\Delta G_f^\circ(\text{UO}, \text{g}) = -33.5$ kcal/mole at 2000°K. This value is seen to be intermediate between the maximum and minimum values and will be accepted for the present as the "best" value, i.e., -33.5 ± 3.0 kcal/mole at 2000°K.

In order to arrive at an equation for the standard free energy of formation of UO(g) , one must calculate free energy functions for this gaseous molecule. Previous estimates of this quantity need revision because better values of the molecular parameters are now available. The molecular parameters used in the calculations are 1.75 Å for the U-O distance²⁴ and 860 cm^{-1} for the vibrational constant,²⁵ which is the symmetrical stretching constant in the uranyl ion. This estimate may be quite reliable since a value of $877\text{--}881\text{ cm}^{-1}$ has been recently measured for ThO(g) by means of the matrix isolation technique.²⁶

The electronic contribution to the free energy function is by far the most difficult to evaluate. The use of the energy levels of gaseous ions or energy levels of gaseous atoms which are iso-electronic to the metal in the gaseous molecule has been proposed by Chandrasekharaiah and Brewer²⁷ and generally produces electronic contributions which are too large. On the other hand, as these authors point out, one cannot simply ignore the contribution of electronic states. In the present study we shall attempt to "average" the two extremes by considering only the ground state of Th(g) , $^3\text{F}_2$, which is iso-electronic with $\text{U}^{+2}(\text{g})$. Admittedly the theoretical support for this procedure is at present quite limited. Values of the free energy function of UO(g) calculated from these assumptions are given in Table 19A. In the range of temperature $1600\text{--}2400^\circ\text{K}$ the standard free energy of formation of UO(g) can be calculated from data given in Table 19A, and the resultant values are represented by the equation

$$\Delta G_f^\circ(\text{UO, g}) = -10,300 - 11.6 T. \quad (15)$$

The maximum uncertainty in this quantity is considerably greater than desired, since it may be as large as $\pm 3\text{ kcal/mole}$, as seen in the previous discussion and is undoubtedly increased by the uncertainty in the free energy functions.

TABLE 19A. Free Energy Functions and the Standard Free Energy of Formation of UO(g)

(cal/mole)

T ($^\circ\text{K}$)	$(G_T^\circ - H_O^\circ)_{\text{UO}}$	$\frac{1}{2}(G_T^\circ - H_O^\circ)_{\text{O}_2}^*$	$(G_T^\circ - H_O^\circ)_{\text{U}}^*$	$\Delta(G_T^\circ - H_O^\circ)$	$\Delta G_f^\circ(\text{UO, g})$
1600	-106,080	-43,460	-30,570	-32,050	-28,670
1800	-121,080	-49,730	-36,840	-34,510	-31,130
2000	-132,290	-56,110	-43,300	-36,880	-33,500
2200	-151,660	-62,580	-49,940	-39,140	-35,760
2400	-167,210	-69,130	-56,780	-41,300	-37,920

*Ref. 28.

TABLE 19B. Equations for the Standard Free Energy of Formation of Some Uranium Oxides

Oxide	$\Delta G_f^\circ (= A + BT)$ cal/mole	Temperature Range ($^\circ\text{K}$)*	Reference
UO(g)	-10,350 - 11.6 T	1600 - 2400	this study
UO ₂ (g)	-121,500 + 4.24 T	1600 - 2400	8, 29
UO ₃ (g)	-198,500 + 19.0 T	1238 - 1360 →	30
UO ₃ (g)	-202,080 + 20.79 T	1400 - 1700	31
UO ₂ (s)	-258,650 + 40.64 T	1500 → 2400	20, 21
O(g)	61,245 - 16.07 T	2000 - 3000	28

*The arrows indicate extrapolations.

C. The Partial Pressure of Oxygen in Equilibrium with Urania-Liquid Uranium

The calculation of the partial pressure of oxygen in equilibrium with the lower phase boundary of the urania (see Fig. 2) can be accomplished by consideration of the equilibrium

For this equilibrium one writes

$$-R'T \left[\log \left(\frac{p_{\text{UO}}}{p_{\text{UO}_2}} \right) p_{\text{O}} \right] = \Delta G_f^\circ(\text{UO}) + \Delta G_f^\circ(\text{O}) - \Delta G_f^\circ(\text{UO}_2). \quad (17)$$

Substitution of the appropriate equations of $\log p_{\text{UO}}$ and $\log p_{\text{UO}_2}$ from Table 17 and the equations for the ΔG_f° 's given in Table 19B leads to the equation

$$\log p_{\text{O}}(\text{atm}) = 7.59 - 40,980/T, \quad (18)$$

which is shown in Fig. 8. Quite clearly the partial pressure of oxygen is considerably smaller than those of the uranium-bearing components.

D. The Evaporation Behavior of the Urania Phase

From the mass-spectrometric data for the equilibrium

given in Fig. 7, one derives the equation

$$\log K = (1.86 \pm 0.28) + (4140 \pm 620)/T, \quad (20)$$

in which the relative ionization cross sections are assumed equal. From the initial measurements (composition of urania phase, $O/U = 2.005 \pm 0.004$) of this equilibrium, given in Table 13, the values of the equilibrium

TABLE 20. Comparison of Values of the Equilibrium Constant of Reaction (19) Resulting from Hyper- and Hypostoichiometric Urania

T (°K)	log K(UO _{2.005})	log K(UO _{1.994})
2103	3.78	3.83
2185	3.77	3.76
2148	3.81	3.79
2062	3.84	3.87

constant can be obtained from the UO₂⁺ and UO₃⁺ data at 22 eV and the UO⁺ data at 10 eV. The results are given in Table 20 and are compared with values calculated from Eq. (20) corresponding to the condensed phase UO_{1.994} $\pm$ 0.004. The agreement between the values of log K obtained from the two systems indicates that a homogeneous equilibrium has been achieved, i.e., there is no significant influence on the measured equilibrium constant by the composition variable of the condensed phase. By combining the data given in Tables 13 through 16 and Fig. 2, one obtains the typical isotherm ($T = 2000^\circ\text{K}$) for pressure vs composition of the urania phase shown in Fig. 10. The partial pressures of the various vapor species are plotted with respect to UO₂(g), which is relatively insensitive to changes in composition as discussed previously. The extreme sensitivity of the partial pressures of UO, UO₃, and U to the composition of the condensed phase is immediately obvious. The partial pressure of uranium is extrapolated to higher values of the O/U ratio based on the fact that the U⁺ primary species was not detected for the condensed phase UO_{1.994}.

It is now possible via a thermochemical cycle based on the equations given in Table 19B to examine the thermodynamic data for UO(g), UO₂(g), and UO₃(g) for internal consistency. By referring to Eq. (19) one can write for the standard free energy of formation of UO(g)

$$\Delta G_f^\circ(\text{UO}) = RT \log K - \Delta G_f^\circ(\text{UO}_3) + 2\Delta G_f^\circ(\text{UO}_2). \quad (21)$$

By substitution of Eq. (20) for log K and the appropriate equations from Table 19B for the free energies of formation of UO₂(g) and UO₃(g),*

*Both equations from UO₃(g) in Table 19B yield the same numerical values at 2000°K.

Fig. 10. Variation of the Partial Pressures of U, UO, and UO₃ with Respect to UO₂ as a Function of Composition of the Urania Phase

one obtains, at 2000°K, $\Delta G_f^\circ(\text{UO}) = -29.6 \text{ kcal/mole.}^*$ Although this value of $\Delta G_f^\circ(\text{UO})$ would appear to confirm the lower limit of the value derived from the analysis of the urania-liquid uranium system, the equation for $\Delta G_f^\circ(\text{UO})$ derived from this cycle is

$$\Delta G_f^\circ(\text{UO}) = -25,600 - 2.0 T, \quad (22)$$

which shows a rather unreasonable value of the entropy of formation. The data and results of the urania-liquid uranium system indicate that ΔS_f° must lie between 10-15 eu, as is generally observed for gaseous monoxides.³² Hence, Eq. (22) indicates that at least one of the equations used in the present calculation is inconsistent. The equation for $\Delta G_f^\circ(\text{UO}_2)$ has been reconfirmed in this study, whereas the equations for $\Delta G_f^\circ(\text{UO}_3)$ involves a lengthy extrapolation. Although the data for log K in Eq. (20) (see Tables 14 and 15) were reproducible in the temperature range from 2105 to 2323°K, this small temperature range may severely limit the accuracy of Eq. (20). Therefore, the uncertainties in both $\Delta G_f^\circ(\text{UO}_3)$ and log K very likely contribute to the inconsistency between Eq. (15) and Eq. (22).

V. SUMMARY

The phase diagram (temperature-pressure-composition) for the uranium-oxygen system from 1600 to 2500°K for the composition range of the bivariant urania phase was investigated in three steps. The composition of the urania phase in equilibrium with liquid uranium was determined by an isopiestic method. This phase dissolves uranium up to a composition given by the ratio O/U = 1.82 at 2500°K. The total volatility rates for urania-liquid uranium mixtures were measured by means of the effusion method from 1580 to 2400°K. An "effective" vapor pressure p_e was calculated from the measured effusion rates, assuming the vapor to be UO(g) . The least-squares treatment of the data resulted in the expression

$$\log p_e(\text{atm}) = (7.25 \pm 0.14) - (27,024 + 255)/T.$$

The mass-spectrometric investigation of the same system has shown the vapor to be predominantly UO(g) with smaller amounts of U(g) and $\text{UO}_2(\text{g})$. The temperature dependence and relative intensities of the species

*The influence of the relative ionization cross sections in the value calculated for $\Delta G_f^\circ(\text{UO})$ will not be large if the cross section for UO_2 is between those of UO and UO_3 , as is easily seen from the form of the equilibrium constant. For example, the assumption of $\sigma_{\text{UO}}:\sigma_{\text{UO}_2}:\sigma_{\text{UO}_3} = 3:2:1$ leads to $\Delta G_f^\circ(\text{UO}) = -30.8 \text{ kcal/mole}^{-1}$.

were measured mass spectrometrically and combined with the total effusion rates to yield the partial pressures for each species:

$$\log p_U(\text{atm}) = (5.194 \pm 0.140) - (25,620 \pm 300)/T;$$

$$\log p_{\text{UO}}(\text{atm}) = (7.109 \pm 0.140) - (26,870 \pm 300)/T;$$

$$\log p_{\text{UO}_2}(\text{atm}) = (7.728 \pm 0.140) - (30,165 \pm 300)/T.$$

The standard free energy of formation of $\text{UO}(\text{g})$ is given by the equation

$$\Delta G_f^\circ(\text{UO}) = -10,300 - 11.6T.$$

The thermodynamic data for $\text{UO}(\text{g})$, $\text{UO}_2(\text{g})$, and $\text{UO}_3(\text{g})$ are examined for internal consistency.

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REFERENCES

1. Robert F. Gould, editor, Non-stoichiometric Compounds, Advances in Chemistry Series, American Chemical Society, Washington, D. C. (1963).
2. Report of the Panel on Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases, Technical Reports Series No. 39, International Atomic Energy Agency, Vienna (1965).
3. Leo Brewer, Chem. Revs. 52, 1 (1953).
4. J. S. Anderson, J. O. Sawyer, H. W. Worner, G. M. Willis, and M. J. Bannister, Nature 185, 915 (1960).
5. E. Rothwell, J. Nucl. Mat. 6, 229 (1962).
6. E. A. Aitken, N. C. Brassfield, and J. A. McGurty, General Electric Nuclear Materials and Propulsion Operation Report TM 63-2-14 (June 1963).
7. G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960).
8. R. J. Ackermann, P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 25, 1089 (1956).
9. A. G. Gray and J. R. Thompson, NBS Grasselli Laboratories Progress Report on Metallurgy for Dec 1944, CT-2618 (1944).
10. Pierre L. Blum, Phillippe Guinet, and Henri Vaugoyeau, Comptes. rend. 257, 3401 (1963).
11. Allan E. Martin and Russell K. Edwards, J. Phys. Chem 69, 1788 (1965).
12. E. G. Rauh and R. J. Thorn, J. Chem. Phys. 22, 1414 (1954).
13. R. G. J. Fraser, Molecular Rays, The MacMillan Company, New York (1931), pp. 14-15.
14. R. J. Ackermann and E. G. Rauh, J. Chem. Phys. 36, 448 (1962).
15. D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Mod. Phys. 30, 814 (1958).
16. W. A. Chupka, ANL-5786 (1957).

17. R. J. Ackermann, E. G. Rauh, and R. J. Thorn, J. Chem. Phys. 40, 883 (1964).
18. R. J. Ackermann, R. L. Faircloth, E. G. Rauh, and R. J. Thorn, J. Inorg. and Nucl. Chem., in press.
19. J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).
20. J. P. Coughlin, U. S. Bureau of Mines Bull. 542 (1954).
21. M. H. Rand and O. Kubaschewski, The Thermochemical Properties of Uranium Compounds, Oliver and Boyd, London (1963).
22. J. Drowart, A. Pattoret, and S. Smoes, J. Chem. Phys. 42, 2629 (1965).
23. R. J. Ackermann, E. G. Rauh, and R. J. Thorn, J. Chem. Phys. 42 2630 (1965).
24. Henry R. Hoekstra, J. Inorganic Chem. 2, 492 (1963).
25. Eugene Rabinowitch, ANL-5122 (1953).
26. Milton J. Linevsky, Air Force Materials Laboratory, Wright-Patterson Air Force Base Technical Report AFML-TR-64-420 (Feb 1965).
27. M. S. Chandrasekharaiah and Leo Brewer, UCRL-8713(revised) (June 1960).
28. D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, Am. Chem. Soc., Washington, D. C. (1956).
29. R. J. Ackermann and R. J. Thorn, Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna (1962), p. 445.
30. R. J. Ackermann, R. J. Thorn, Carl Alexander, and Marvin Tetenbaum, J. Phys. Chem. 64, 350 (1960).
31. Carl Albert Alexander, Doctoral Dissertation, Physical Chemistry, Ohio State University, 1961.
32. R. J. Ackermann, and R. J. Thorn, Ch. 2 of Progress in Ceramic Science, Pergamon Press, Oxford (1961).