

# Mass Spectrometric Determination of Heat of Sublimation of Uranium

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The vapour pressure of uranium was determined between 1720 and 2340°K:  $-\log P_a(\text{atm}) = (26,210 \pm 270)/T - (5,920 \pm 0.135)$ . The heat of sublimation calculated therefrom is  $\Delta H_{s,0}^\circ(\text{U}) = 129.0 \pm 2.0$  kcal/g atom. This result is in agreement with independent measurements of the vapour pressure of uranium as well as with the values derived from thermochemical cycles based on the dissociation energies of the monoxide and dioxide of uranium and on the vaporization of the monocarbide, the dicarbide and the monosulphide of uranium.

The first measurements of the vapour pressure of uranium by different techniques carried out within the Manhattan project<sup>1</sup> gave discordant results. Although other estimates<sup>1</sup> of the heat of sublimation  $\Delta H_{s,0}^\circ(\text{U})$  ranged from 67 to 152 kcal/g atom, the value  $\Delta H_{s,0}^\circ(\text{U}) = 125^\dagger$  kcal/g atom<sup>2</sup> was deduced from these measurements. These determinations were strongly influenced by interaction with the crucible materials and by the presence of oxygen, the influence of which, although realized, was not studied in detail.

Subsequent determinations<sup>3</sup> by the effusion method, using tantalum Knudsen cells with fission counting of the condensate and including a study of the influence of oxygen, or measurements<sup>4</sup> of the weight loss with a microbalance from composite beryllia-tungsten crucibles, led to a value  $\Delta H_{s,0}^\circ(\text{U}) = 117^\dagger$  kcal/g atom both by the second and third law methods.

From mass spectrometric pressure measurements for uranium contacted by alumina and contained in a molybdenum crucible,  $\Delta H_{s,0}^\circ(\text{U}) = 126^\dagger$  kcal/g atom was calculated<sup>5</sup> by the third law method. The latter pressures, already confirmed<sup>6, 7</sup> and again obtained here, are in agreement with indirect values for the heat of sublimation derived from thermochemical data for the gaseous oxides<sup>8-10</sup> and for the carbides of uranium.<sup>8, 10-13</sup>

The objection<sup>14</sup> that the high value of the heat of sublimation results from a pronounced lowering of the uranium activity by oxygen has been discussed.<sup>15, 16</sup> It was shown<sup>6, 15</sup> that oxygen does not strongly influence the uranium activity, but leads to the formation of the UO molecule, whose pressure in the  $(\text{U—O})(l) + \text{UO}_{2-x}(s)$  system is about ten times higher than that of uranium<sup>5-7, 9, 10, 15, 16, 18</sup> in the temperature interval 1700-2200°K. In view of the close agreement between the pressures<sup>3</sup> of uranium leading to  $\Delta H_{s,0}^\circ(\text{U}) = 117$  kcal/g atom and those<sup>5-7, 9, 10, 17, 18</sup>

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† These values are those given in the publications referred to. The numerical values of the thermodynamic functions used here lead to slightly different figures given in table 2.

in the two-phase  $(\text{U—O})(l) + \text{UO}_{2-x}(s)$  system, it was further suggested<sup>6, 15</sup> that these pressures<sup>3</sup> concern the two-phase system. The latter is almost certainly the case for measurements<sup>4</sup> made with beryllia crucibles as a result of the reduction of BeO by uranium.<sup>19</sup>

The mass spectrometric studies<sup>6, 7</sup> of the vapour pressure of uranium were extended to cover a wider range of experimental conditions. All results from this laboratory are presented here.

## EXPERIMENTAL AND RESULTS

The general experimental procedure<sup>20, 21</sup> for the thermochemical study of vaporization processes by the combination of a Knudsen cell and a mass spectrometer and the instrument<sup>22</sup> used were described earlier. The description of a modified Knudsen cell assembly, with which the majority (numbers 35-72 in table 1) of the experiments discussed here were performed, has been given elsewhere.<sup>9, 12</sup> This assembly was built to make twin-cell measurements possible and also to increase the resolution of effusion from perturbing effects, such as interboundary and surface migration.

One of the problems in selecting container materials was that of interactions with liquid uranium. Since we wanted to leave the question of the influence of oxygen on the partial pressure of uranium open, urania, which has good characteristics as a crucible, was used only for the study of the  $(\text{U—O})(l) - \text{UO}_{2-x}(s)$  two-phase system. The solubility<sup>23</sup> of tungsten and tantalum in uranium being low, it was assumed that for uranium possible deviation from Raoult's law used to estimate the activity of this element in the corresponding cells, introduce only small uncertainties in the evaluation of its vapour pressure. These refractory metals were therefore used. In the initial<sup>6</sup> experiments, (numbers 11-15) sintered tungsten and tantalum were employed. Uranium exhibits, however, a marked tendency toward interboundary migration and creep,<sup>5, 24</sup> especially at the higher temperatures in the experiments. This was observed *in situ* by monitoring the intensity distribution in the molecular beam during the experiment and by micrographic and autoradiographic examination of the cells thereafter. In the final measurements, vacuum-melted tantalum was used successfully while tungsten single crystals rapidly gave rise to surface migration. Prior to the experiments, the vacuum-melted cells were outgassed under vacuum above 2200°C. The experiments were interrupted when the measurement of the intensity profile<sup>20, 21</sup> showed surface vaporization to contribute to the intensity in the molecular beam. The effusion orifice had a knife-edged circular shape, except in experiments 41·03, 41·04 and 41·05, where a cylindrical canal with a Clausing factor of 0·63 was used.

The high purity uranium was kindly made available by the Metallurgy Department, Centre d'Etudes Nucléaires, Saclay (France). The main impurities were oxygen (32 p.p.m.); chlorine (70 p.p.m.); carbon (11 p.p.m.). The samples, 2-600 mg in weight, were cleaned by washing with boiling concentrated nitric acid or by electro-polishing in a glycerine + sulphuric acid mixture<sup>3</sup> (expt. 15·02). In one experiment (15·03), about 1 atom % carbon powder was added to the sample to eliminate the oxygen, estimated to represent also 1 atom %. This procedure<sup>25</sup> proved to be effective (see table 1).

Ionization of the neutrals was performed by impact with electrons, whose energy could be varied between 5 and 80 eV. For most of the measurements for uranium, 12 eV electrons were used to avoid interference with  $\text{U}^+$  produced by fragmentation from UO when the latter was present. The average ionization potentials measured by the linear extrapolation method, in which the energy scale was calibrated against the ionization potential of silver,  $\text{U}^+ : 6·1 \pm 0·3$ ;  $\text{UO}^+ : 5·7 \pm 0·4$ ;  $\text{UO}_2^+ : 5·5 \pm 0·4$  eV

TABLE 1.—VAPOUR PRESSURE AND HEAT OF SUBLIMATION OF URANIUM

I expt.	II cell ( <i>o</i> )	III pressure standard	IV $\frac{I(UO_2)}{I(U^{+})}$ ( <i>d</i> )	V seq.	VI <i>T</i> °K	VII $-\log P$ atm	VIII $-\Delta(G^\circ -$ $\frac{H_0}{T})/T$ cal/deg.	IX $\Delta H_0^{(III)}$ kcal/g atom	X $\Delta H_0^{(e)}$ kcal/g atom	XI $\Delta H_0^{(II)}$ kcal/g atom	XII $\Delta H_0^{(II)}$ kcal/g atom ( <i>T</i> = 1905)	XIII $\Delta S_0^{(II)}$ cal/deg.
11.01( <i>b</i> )	W(sint.)	UO	t.p.	1	1721	9.12	32.27	127.5	127.7 ± 0.9	123.6 ± 4.3	114.2 ± 4.3 ( <i>T</i> = 1905)	24.8 ± 2.3
			t.p.	2	1775	8.63	32.22	127.3				
			t.p.	3	1822	8.28	32.09	127.5				
			< 0.02	13	1833	8.33	32.06	128.6				
			< 0.02	14	1864	8.06	31.98	128.4				
			< 0.02	12	1873	7.91	31.95	127.6				
			2.4	4	1874	7.78	31.95	126.6				
			< 0.02	15	1898	7.75	31.89	127.8				
			0.02	11	1909	7.66	31.86	127.7				
			1.3	5	1916	7.50	31.84	126.8				
			0.8	6	1948	7.22	31.76	126.2				
			< 0.02	16	1959	7.39	31.73	128.4				
			0.03	10	1962	7.35	31.72	128.2				
			< 0.02	17	1989	7.15	31.66	128.1				
			0.5	7	2014	6.82	31.60	126.5				
			0.04	9	2044	6.90	31.53	129.0				
13.05( <i>b</i> )	Ta(sint.)	Ag	0.06	8	2061	6.82	31.48	129.2				
			t.p.	2	1920	7.41	31.83	126.2	127.0 ± 0.8	121.4 ± 9.2	111.6 ± 9.2 ( <i>T</i> = 2027)	24.0 ± 4.6
			t.p.	1	1945	7.35	31.77	127.2				
			t.p.	4	2086	6.55	31.43	128.1				
			t.p.	3	2096	6.30	31.41	126.3				
			t.p.	5	2106	6.33	31.38	127.1				

TABLE I (contd.)

I expt.	II cell (a)	III pressure standard	IV $\frac{K(\text{UO}_2^+)}{I(\text{U}^{+})}$ (d)	V seq.	VI $T^\circ$ °K	VII $-\log P$ atm	VIII $-\Delta(G^\circ -$ $H^\circ)/T$ cal/deg.	IX $\Delta H^\circ_{\text{f}}(\text{II})$ kcal/g atom	X $\Delta H^\circ_{\text{f}}(\text{e})$ kcal/g atom	XI $\Delta H^\circ_{\text{f}}(\text{II})$ kcal/g atom	XII $\Delta H^\circ_{\text{f}}(\text{II})$ kcal/g atom ( $T = 2060$ )	XIII $\Delta S^\circ_{\text{f}}(\text{II})$ cal/deg.
15.01(b)	Ta(sint.)	Ag	t.p.	2	1959	7.36	31.73	127.9	126.9 $\pm$ 0.8	125.6 $\pm$ 7.2	115.7 $\pm$ 7.2 ( $T = 2060$ )	26.1 $\pm$ 3.5
			t.p.	1	1964	7.18	31.72	126.8				
			t.p.	3	1987	6.96	31.66	126.2				
			t.p.	4	1994	6.94	31.64	126.4				
			t.p.	5	2039	6.60	31.54	125.9				
			t.p.	6	2073	6.49	31.46	126.8				
			t.p.	7	2117	6.32	31.36	127.6				
			t.p.	8	2159	6.01	31.26	126.9				
			t.p.	10	2166	6.11	31.24	128.2				
			t.p.	9	2174	5.83	31.23	125.9				
15.03(b)	W(sint.)	Ag	2 $\rightarrow$ 1	1	1832	8.31	32.06	128.4	127.9 $\pm$ 0.6	—	—	—
			0.2	2	1878	7.84	31.94	127.3				
			< 0.02	3	1920	7.62	31.83	128.1				
35.01	W(s.c.)	Ag	t.p.	1	1895	7.86	31.89	128.6	128.6	—	—	—
40.01	Ta(v.m.)	Ag	t.p.	1	1885	7.92	31.92	128.5	128.9 $\pm$ 0.4	—	—	—
			t.p.	2	1981	7.35	31.68	129.4				
41.03	UO <sub>2</sub> (sint.)	Ag	t.p.	1	1879	8.03	31.93	129.0	129.1 $\pm$ 0.3	125.7 $\pm$ 2.5	116.0 $\pm$ 2.5 ( $T = 1988$ )	25.1 $\pm$ 1.2
			t.p.	2	1995	7.49	31.74	129.0				
			t.p.	3	1968	7.37	31.71	128.8				
41.04			t.p.	1	2012	7.12	31.60	129.1				
41.05			t.p.	1	2023	7.08	31.57	129.4				
			t.p.	2	2103	6.58	31.39	129.3				

TABLE 1 (contd.)

expt.	I) cell (a)	II) pressure standard	IV) $\frac{I(\text{UO}_2)}{I(\text{U}^{+})}$ (d)	V seq.	VI $T$ °K	VII $-\log P$ atm	VIII $-\Delta(G^\circ - \frac{H^\circ}{T})$ cal/deg.	IX $\Delta H^\circ_{\text{sub}}(\text{II})$ kcal/g atom	X $\Delta H^\circ_{\text{sub}}(\text{e})$ kcal/g atom	XI $\Delta H^\circ_{\text{sub}}(\text{II})$ kcal/g atom	XII $\Delta H^\circ_{\text{sub}}(\text{II})$ kcal/g atom (T = 2203)	XIII $\Delta S^\circ_{\text{sub}}(\text{II})$ cal/deg.
44.01	Ta(v.m.)	UO	t.p.	1	1870	8.11	31.96	129.2	128.8 ± 0.6	126.8 ± 3.1	116.5 ± 3.1	25.6 ± 1.4
			t.p.	2	2053	6.68	31.51	127.5				
			<1.6	5	2195	6.05	31.18	129.2				
			3	4	2211	5.93	31.15	128.9				
			1	6	2220	5.85	31.13	128.5				
			<1	7	2226	5.85	31.11	128.8				
			>4	3	2247	5.65	31.07	127.9				
			0.6	8	2318	5.41	30.93	129.1				
			0.5	9	2324	5.39	30.92	129.2				
			0.4	10	2324	5.39	30.92	129.2				
			0.3	11	2339	5.37	30.89	129.7				
48.03	UO <sub>2</sub> (sint.) in W(sint.)	Ag	t.p.	1	1887	8.15	31.91	130.6	130.7 ± 0.2	—	—	—
			t.p.	2	2008	7.34	31.61	130.9				
49.01	W(s.c.)	UO	t.p.	1	1896	8.03	31.89	130.1	129.8 ± 0.3	—	—	—
			t.p.	2	1907	7.96	31.86	130.2				
			t.p.	3	2020	7.08	31.58	129.2				
72.01(c)	Ta(v.m.)	Ag	t.p.	3	1794	8.75	32.16	129.5	129.4 ± 0.4	133.5 ± 1.5	124.0 ± 1.5	29.1 ± 0.7
			t.p.	5	1831	8.37	32.06	128.8			(T = 1953)	
			t.p.	2	1848	8.34	32.02	129.7				
			t.p.	1	1853	8.31	32.01	129.8				
			t.p.	4	1869	8.16	31.96	129.5				
			t.p.	10	1888	7.96	31.91	129.0				
			t.p.	11	1892	7.95	31.90	129.2				
			t.p.	6	1913	7.82	31.85	129.4				
			t.p.	7	1941	7.62	31.78	129.4				
			t.p.	17	1951	7.47	31.75	128.6				
			t.p.	16	1965	7.43	31.72	129.1				
			t.p.	12	1966	7.39	31.71	128.8				
			t.p.	18	1966	7.44	31.71	129.3				

TABLE 1 (contd.)

I expt.	II cell (a)	III pressure standard	IV $\frac{I(UO_2)}{I(U)} \cdot \frac{d}{d}$	V seq.	VI T °K	VII -log P atm	VIII $-\Delta(G^\circ - \frac{H^\circ}{T})/T$ cal/deg.	IX $\Delta H^\circ_{298}$ kcal/g atom	X $\Delta H^\circ_{298}$ kcal/g atom	XI $\Delta H^\circ_{298}$ kcal/g atom	XII $\Delta H^\circ_{298}$ kcal/g atom	XIII $\Delta S^\circ_{298}$ cal/deg.
72.01	Ta(v.m.)											
			t.p.	8	1977	7.34	31.68	129.0				
			t.p.	9	1983	7.26	31.67	128.7				
			t.p.	15	2018	7.01	31.58	128.5				
			t.p.	13	2032	6.99	31.55	129.1				
			t.p.	19	2047	6.85	31.52	128.7				
			t.p.	14	2089	6.66	31.42	129.3				
			t.p.	20	2116	6.46	31.36	128.9				
			t.p.	21	2160	6.18	31.26	128.6				
			t.p.	22	2358	5.45	—	— (f)				

column	IX	X	XI	XII	XIII
average		128.6 $\pm$ 1.2(h)	126.1 $\pm$ 4.1(h)		
all expt.	128.4 $\pm$ 1.2(g)		128.5 $\pm$ 2.0(g)	118.8 $\pm$ 2.0(g) (T = 1988)	26.8 $\pm$ 1.0(g,i)
average		128.9 $\pm$ 0.6(k)	128.6 $\pm$ 3.2(k)		
selected expt.	129.0 $\pm$ 1.2(j)		129.6 $\pm$ 1.2(j)	119.9 $\pm$ 1.2(j) (T = 2000)	27.1 $\pm$ 0.6(j,i)

(a) W(sint), Ta(sint): sintered tungsten or tantalum cell without insert; W(s.c.): tungsten single crystal cup; Ta(v.m.) tantalum vacuum melted cell; UO<sub>2</sub> (sint): sintered UO<sub>2</sub>.

(b) The difference in the pressures and in the  $\Delta H^\circ_{298}$  values for these experiments and those given earlier,<sup>6, 15</sup> results from the application of the solubility corrections, from the use of different numerical values for the free energy functions of gaseous and liquid uranium (Stull and Sinke throughout in ref. (6), (15), which together lead to +0.6 kcal and for the relative cross-section of uranium.  $\sigma(U) = 75$  instead of  $\sigma(U) = 50$ , which corresponds to +1.5 kcal.

(c) the sample was about a 1 : 1 mixture of U and UO<sub>2</sub>.

(d) this ratio is a qualitative measure of the oxygen content of the sample and is therefore reported; t.p. designates the ratio in the two phase system (U—O)(l) + UO<sub>2-x</sub>(s).

(e) average third law value per experiment.

(f) not calculated, see text.

(g) unweighted second and average third law values over all points in all the experiments (11.01–72.01).

(h) unweighted average of the second law and of the average third law values per experiment (experiments 11.01–72.01)

(i)  $\Delta S^\circ_{2000} = 26.8$  cal deg.<sup>-1</sup> from thermal data.

(j) unweighted second and average third law values over all points in the selected experiments (15.03–44.01, 49.01 and 72.01).

(k) unweighted average of the second law and of the average third law values per experiment in the selected experiments (15.03–44.01, 49.01 and 72.01).

are identical with the values  $U^+$ :  $6.11 \pm 0.05$ ;  $UO^+$ :  $5.72 \pm 0.06$ ;  $UO_2^+$ :  $5.5 \pm 0.1$  eV obtained by the R.P.D. method.<sup>26</sup>

In the  $UO_2$  crucibles, the ratios of intensities  $I(UO^+)/I(U^+)/I(UO_2^+)$  were approximately 10/1/1. These ratios were also observed in part of the tungsten and tantalum cells during the entire experiment (table 1). Outgassing tantalum at 2200°C and other precautions (cleaning of uranium and as much as possible avoidance of gettering of oxygen during the heat-up), have apparently not been sufficient to remove oxygen in these experiments. This observation, already made earlier<sup>15</sup> may explain the analogy between the uranium pressures measured under analogous circumstances by the conventional effusion method<sup>3</sup> and the total pressures in the  $(U-O)(l)-UO_{2-x}(s)$  system. Another implication of the observations, in particular that the  $I(UO^+)/I(U^+) = 10$ , is so easily obtained and maintained, is that the oxygen solubility in uranium in equilibrium with  $UO_{2-x}$  is probably, at least below 2000°K, not as high as given in a recent phase diagram<sup>27</sup> (about 18 atom % compared to about 0.3 %<sup>28</sup> at 2000°K).

In the experiments in which the  $I(UO^+)/I(U^+)$  ratio decreased by auto-deoxidation<sup>6, 15</sup> below the value characteristic of the  $(U-O)(l)-UO_{2-x}(s)$  two-phase system, particular attention was paid to the measurement of the uranium intensity at constant temperature. In no instance was the  $U^+$  intensity observed to change appreciably as would be expected if oxygen did strongly influence the activity of liquid uranium.

To examine further this question, a direct comparison was made with twin Knudsen cells<sup>7, 9, 12</sup> between the uranium pressure above single-phase uranium contained in tantalum and above uranium contacted by tantalum in a  $UO_2$  crucible. The measurements gave for the ratio  $P_U((U-O)(l)-Ta(s))/P_U((U-O)(l)-UO_{2-x}(s)-Ta(s))$ :  $1.00 \pm 0.05$  at 1970°K;  $1.04 \pm 0.05$  at 2107°K;  $1.10 \pm 0.10$  at 2211°K. The corresponding ratios of oxygen activity, deduced from  $I(UO^+)/I(U^+)$  were 1/2.3, 1/4.8 and 1/7.2 respectively. The decrease of uranium activity in the two-phase system with temperature is confirmed by the comparison of the pressure measured in experiment 72.01 at 2358°K with that extrapolated from the measurement between 1794 and 2160°K. The ratio  $P(\text{measured})/P(\text{extrapolated})$  is 2 but may represent the variation of the cumulative effects of tantalum and oxygen rather than that of oxygen alone from 2160 to 2360°K. For this reason the heat of sublimation of uranium was not calculated from the pressure measured at 2358°K.

In one experiment in a tantalum cell, a search was made for the molecule  $U_2$  up to temperatures of 2480°K. This molecule was not observed, the upper limits for the ratio  $I^+(U_2)/I^+(U)$  being  $5 \times 10^{-4}$ , leading to an upper limit of 80 kcal/mole for the dissociation energy  $D_0^0(U_2)$ .

The pressures (fig. 1, table 1) were calibrated<sup>20, 21</sup> in most of the experiments by quantitatively vaporizing known amounts of silver (2.5 mg). In three, the known  $UO$  and  $UO_2$  pressures in the two-phase system were used as pressure standards. The latter were determined independently<sup>10</sup> by condensation of a known fraction of the effusate or by quantitative vaporization experiments. The relative products of the ionization cross-sections and multiplier yields were chosen as  $\sigma\gamma(U) = 1.15$ ,  $\sigma\gamma(Ag) = 1$ ,  $\sigma\gamma(UO) = 0.80 \pm 0.10$  and  $\sigma\gamma(UO_2) = 0.55 \pm 0.10$  by extrapolation of measurements<sup>9</sup> of the latter three. Together with the calibration curve of the multiplier, the ratio for  $\sigma(Ag)/\sigma(U)$  corresponds to using  $\sigma(U) = 75$  in the Otvos and Stevenson<sup>29</sup> scale, in which  $\sigma(Ag) = 35$ . The former value was also recently calculated in a treatment<sup>30</sup> in which the method of Otvos and Stevenson is refined. The value  $\sigma(U) = 50$ <sup>5</sup> used previously<sup>5-7, 15</sup> was deduced from the ionization cross-section of  $UF_4$ . It has since been shown<sup>31</sup> that ionization by electron impact of

halides, in particular fluorides, leads generally to cross-sections well below these expected from the additivity rule of the atomic cross-sections.<sup>29</sup> For this reason,  $\sigma(\text{U}) = 50$  is considered too low.

The pressures, presented in table 1 in order of increasing temperatures, were corrected for the solubility<sup>23</sup> of tantalum and tungsten in uranium assuming the solutions to be ideal. These corrections were applied even when the uranium was contained in urania crucibles within tantalum or tungsten cells to take the interactions via the gas phase into account. No corrections for the presence of oxygen were made in any case. The uncertainty limit,  $\pm 2.0$  kcal/g atom to be ascribed to the third law

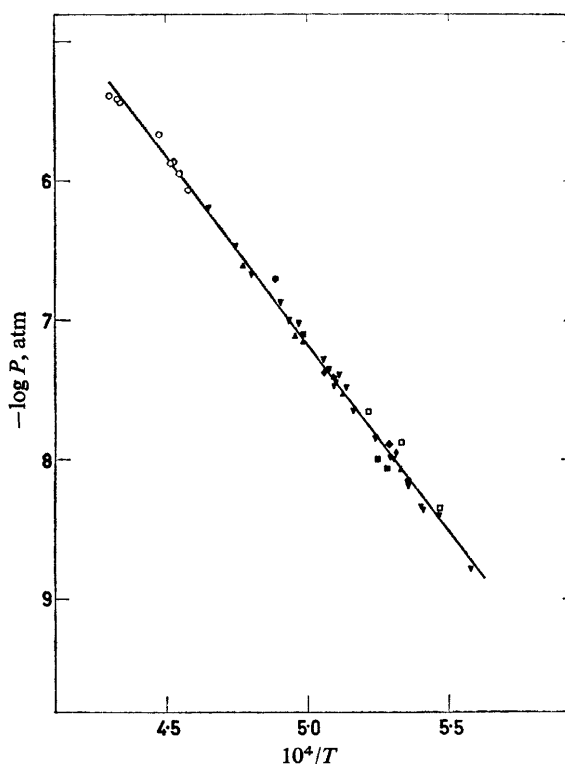


FIG. 1.—Uranium vapour pressure (atm).  $\square$ , expt. 15.03 (single phase);  $\blacklozenge$ , 35.01 (two phase);  $\blacklozenge$ , 40.01 (two phase);  $\blacktriangle$ , 41.03; 41.04; 41.05 (two phase);  $\bullet$ , 44.01 (two phase);  $\circ$ , 44.01 (single phase);  $\blacksquare$ , 49.01 (two phase);  $\blacktriangledown$ , 72.01 (two phase).

value selected below takes into account an uncertainty of  $\pm 1\%$  in the absolute temperature, which includes the precision of the measurements ( $\pm 5^\circ$ ) and a pessimistic estimate of possible gradients throughout the cell, of  $\pm 20\%$  in the calibration of the mass spectrometer, of  $\pm 30\%$  in the relative ionization cross-sections of uranium and silver, of  $\pm 10\%$  in the activity correction and of  $\pm 0.3$  cal/deg. in the free energy functions.

## DISCUSSION

### PRESENT MEASUREMENTS

The heat of sublimation of uranium was calculated by the second and third law procedures. For gaseous uranium the thermodynamic functions given by Feber and Herrick<sup>32</sup> were used; for liquid uranium they were calculated from the data for the



solid given by Stull and Sinke<sup>33</sup> together with the heat of fusion,<sup>34</sup>  $\Delta H_f^\circ = 1,900 \pm 130$  cal/g atom and the heat capacity  $C_p = 11.45$ <sup>34</sup> cal/g atom deg. for liquid uranium. The numerical values for  $\Delta(G^\circ - H_0^\circ)/T$  are given in column 8, table 1. Column 9 gives the  $\Delta H_{s,0}^\circ$  value for each individual point. Column 10 gives the average third law value per experiment with its standard deviation. Columns 11-13 summarize the second law results obtained from the least-squares calculations.

In mass spectrometric measurements of the type reported here, instrumental factors, e.g., the pressure calibration, are the same for all points in a given experiment and could therefore introduce systematic errors. To avoid the risk of giving excessive weight to experiments with large numbers of points, it was therefore verified that in the third law evaluation the averages and their standard deviations calculated by giving equal weight to each point and to each experiment, irrespective of the number of points, do not differ significantly. For consistency with the second law evaluation, the average of the points was considered in the result retained below.

The third law results in particular indicate that the measurements in sintered materials yield somewhat lower  $\Delta H_{s,0}^\circ(\text{U})$  values than those in vacuum melted cells. Although as noted earlier,<sup>10, 35</sup> there are indications that the uranium pressure in tungsten containers is somewhat higher than for other materials, other effects might explain the above differences. For sintered materials, in particular in the experiments 13.05 and 15.01, interboundary migration was observed to be pronounced. Whether or not for tungsten the latter phenomenon and possibly a lower heat of sublimation of uranium are related to a positive heat of formation of U-W solutions, tentatively suggested,<sup>36</sup> is not clear. It was also observed that the migration of uranium was gradual, occasionally intermittent and probably enhanced when its oxygen content decreased. For these reasons and because of the scatter in the points, shown both in the second and third law evaluations of the data, the experiments 11.01, 13.05 and 15.01 were omitted in selecting the heat of sublimation of uranium, although retaining them would not appreciably alter the result (see table 1). Experiment 48.03 was not included because the amount of free uranium was very small.

On the influence of oxygen, the third law results, (point averages as well as experiment-averages) show that between 1800 and 2200°K there is no significant lowering of the vapour pressure of uranium by this element. In agreement therewith the measurements in twin tantalum cells show that, for a two to seven fold variation of the oxygen activity, the variation of the uranium activity is between 0 and 20 % at most and increases with temperature ( $1.00 \pm 0.05$  at 1970°K;  $1.04 \pm 0.05$  at 2110°K;  $1.10 \pm 0.10$  at 2210°K). These results thus confirm the upper limit given earlier for the decrease in activity of uranium contacted by urania, a factor of 1.6.<sup>15</sup> Unfortunately the uncertainties associated with the above activity ratios and in particular the marked difference in the oxygen solubility in the alternate phase diagrams,<sup>27, 28</sup> do not make it possible to discuss whether or not there are marked positive or negative deviations from ideality in the U—O system. For a number of metals, at absolute temperatures roughly half those of interest here, e.g., Pb,<sup>37</sup> Sn,<sup>38</sup> Fe,<sup>40</sup> Ti,<sup>39, 40</sup> Zr,<sup>39</sup> it has, however, been shown that up to several atomic %, Henry's law is valid for oxygen, and hence<sup>41</sup> Raoult's law for the metal. If this, especially since the temperature is higher, is also the case here, the present results, if attributed to oxygen alone, suggest that the oxygen solubility in uranium contacted by urania is about 4 at. % at 2100°K and 9 at. % at 2200°K, i.e., intermediate between the values in the conflicting phase diagrams, 0.25<sup>28</sup> or 22<sup>27</sup> and 0.4<sup>28</sup> or 28<sup>27</sup> atom % at the same temperatures. By logarithmic extrapolation against  $T^{-1}$ , the present data further suggest that at temperatures higher than 2200°K the solubility of oxygen in uranium may tend towards the high values.<sup>27</sup> A concentration of about 25 at. % is then

estimated at 2360°K, where the activity of uranium contacted by tantalum and  $\text{UO}_{2-x}$  is about 0.5. If the effects of oxygen and tantalum are additive and since the correction for the solubility of tantalum is already made, the activity coefficient of uranium in the (U—O) saturated solution at this temperature would then be 0.7. For comparison, the activity coefficient of uranium contacted by UC at 2173°K, where the carbon concentration in solution is 20 at. %, is about 0.3.<sup>11</sup> In keeping with the above arguments concerning the influence of solutes at low concentration and of independent measurements<sup>11</sup> for the U—C system, the presence of carbon in one experiment (15.03) at a concentration well below 1 at. % should not introduce a pronounced lowering of the uranium activity.

Since neither oxygen nor carbon should appreciably influence the vapour pressure of uranium, the results of experiments 15.03 to 44.01, 49.01 and 72.01 in table 1 were treated by a least-square calculation in which equal weight was given to each point. The resulting expression for the vapour pressure as a function of  $T^{-1}$  is

$$-\log P_U(\text{atm}) = (26,210 \pm 270)/T - (5.920 \pm 0.135). \quad (1)$$

This corresponds to a second law heat of evaporation  $\Delta H_{e,T}^\circ(\text{U}) = 119.9 \pm 2.5$  kcal/g atom (uncertainty = 2 standard deviations) at the central temperature 2000°K and to a heat of sublimation at 0°K,  $\Delta H_{s,0}^\circ(\text{U}) = 129.6 \pm 3.0$  kcal/g atom. For comparison, the second law heat of evaporation, obtained by averaging the values for experiments 41.03, 44.01 and 72.01 is  $\Delta H_0^\circ = 128.6 \pm 3.2$  kcal/g atom. The second law entropy of evaporation resulting from eqn. (1) is  $27.1 \pm 0.6$  cal/deg. g atom, compared to the value used in the third law evaluation,  $\Delta S_{2000} = 26.8$  cal/deg. g atom. The average third law value, calculated by averaging the values for all points in expt. 15.03 to 44.01, 49.01 and 72.01 is  $\Delta H_{s,0}^\circ(\text{U}) = 129.0 \pm 1.2$  kcal/g atom.

Together with the thermodynamic functions used here, it yields the following equations to represent the vapour pressure of uranium up to the boiling point, 4690°K, calculated therefrom:

$$\log P_U(\text{atm}) = -28,192/T + 0.930 \log T - 1.023 \times 10^{-3}T + 5.802, \quad (298-1406^\circ\text{K}); \quad (2)$$

$$\log P_U(\text{atm}) = -28,192/T - 2.43 \log T + 1494, \quad (1406-4690^\circ\text{K}). \quad (3)$$

#### LITERATURE DATA

The vapour pressures and heat of sublimation of uranium obtained above are in agreement with the initial mass spectrometric measurement,<sup>5</sup> corrected as before for the solubility of molybdenum and recalculated with the same relative ionization cross-section and free-energy functions as used here:  $\Delta H_{s,0}^\circ(\text{U}) = 129.8 \pm 5$  kcal/g atom. The present results also agree within the experimental uncertainty with measurements by vapour condensation in absence of UO performed since this work was concluded,  $\Delta H_{s,0}^\circ(\text{U}) = 130.3 \pm 0.3$  in W,  $130.8 \pm 0.3$  in Ta,  $131.2 \pm 0.6$  in TaC,  $131.5 \pm 0.8$  kcal/g atom in  $\text{ZrB}_2$  cups.<sup>35</sup> Further it is almost identical with the uranium pressure determined<sup>42</sup> in tungsten Knudsen cells for the (U saturated with P) +  $\text{UP}_{1-x}$  ( $x = 0.035 \pm 0.015$ ) two-phase system, obtained both by preferential \* vaporization of phosphorus from uranium phosphide and by adding excess uranium to UP.

\* An earlier mass spectrometric study of uranium phosphide (K. A. Gingerich and P. K. Lee, *J. Chem. Physics*, 1964, 40, 3520, suggested this compound to vaporize congruently between 1750 and 2250°K. Migration of uranium interfered, however, appreciably with effusion, as shown by the marked difference in pressures resulting from the total weight loss determination and from the silver calibration. In addition, the presence of important temperature gradients in the Knudsen cell in the investigation was later pointed out (K. A. Gingerich, *J. Chem. Physics*, 1966, 44, 1717).

Between 2073 and 2423°K, the uranium pressure in this system is given by the relation <sup>42</sup>

$$-\log P_U(\text{atm}) = (25898 \pm 192)/T - (5.68 \pm 0.09). \quad (4)$$

Assuming uranium to have an activity close to unity in the whole temperature interval, its second law heat of vaporization is  $\Delta H_{2250}^\circ = 118.5 \pm 1.8$ , or  $\Delta H_0^\circ = 128.9 \pm 2.0$  kcal/g atom. The corresponding third law value calculated here, which shows no trend with temperature is  $\Delta H_{s,0}^\circ(\text{U}) = 130.0 \pm 2$  kcal/g atom.

In addition to these direct measurements, concordant values for the heat of sublimation of uranium result from thermochemical cycles involving the carbides, the oxides and the sulphide of uranium. These indirect values are, however, considered less accurate than the direct determinations as a result of the increased number of thermodynamic data required. In these, the existence of homogeneity ranges for most uranium compounds, the need to know or estimate the stoichiometry of the vaporization process and the variation of the thermodynamic functions with composition are important factors.

The pressure data, thermodynamic functions and the heat of formation of UC,  $\Delta H_{f,298}^\circ(\text{UC}) = -23.2 \pm 1.0$  and of  $\text{UC}_{1.9}$ ,  $\Delta H_{f,298}^\circ(\text{UC}_{1.9}) = -21.1 \pm 1.4$  kcal/mole have been discussed earlier.<sup>10-13</sup> In the present evaluation for the reaction  $\text{UC}_{1.9}(s) \rightarrow \text{U}(g) + 1.9\text{C}(\text{graphite})$  the numerical values of the free-energy function given in ref. (11b) were used; in the non mass-spectrometric pressure determinations,<sup>43-45</sup> the correction for the presence of  $\text{UC}_2(g)$  was taken from ref. (13); in the mass spectrometric studies,<sup>11a, 46</sup> the pressures, based on the earlier value of the relative ionization cross section of uranium  $\sigma(\text{U}) = 50$ , have been reduced by 50 % to be consistent with the cross-section  $\sigma(\text{U}) = 75$  used here. The two mass spectrometric <sup>11a, 46</sup> and one <sup>44</sup> conventional Knudsen cell pressure determinations, shown <sup>47</sup> to be highly internally consistent, then lead to a value  $\Delta H_{s,0}^\circ(\text{U})$  in excellent agreement with that determined here. Two conventional pressure determinations lead to a somewhat lower value for  $\Delta H_{s,0}^\circ(\text{U})$ . Of these, one <sup>45</sup> is considered <sup>47</sup> to give too high pressures because of re-evaporation from the heat shields and because of the presence of oxygen resulting from the mode of preparation of the sample.<sup>11a</sup> As discussed elsewhere,<sup>11a</sup> similar difficulties have also been encountered in part at least of the other set <sup>43</sup> of experiments of this type.

In the evaluation of the data for  $\text{U}_{1-x}\text{C}_{1+x}(s) \rightarrow (1-x)\text{U}(g) + (1+x)\text{C}(g)$  throughout the homogeneity range and for the congruently vaporizing composition  $\text{UC}_{1.08 \pm 0.03}$ , the numerical values for the free-energy function of UC given in ref. (11b) have been used, the homogeneity range being treated as an ideal solution of UC and  $\text{UC}_{1.9}$ . The uranium pressures from ref. (11a) were lowered in the ratio  $\sigma(\text{U}) = 50/\sigma(\text{U}) = 75$ , the value  $\sigma(\text{U}) = 75$  having already been used in ref. (12). The rates of evaporation from ref. (48) were used as such, the reasons for adopting unit evaporation coefficients having been discussed.<sup>12</sup>

The uranium pressure above uranium sulphide between 1825 and 2300°K is given by <sup>49a</sup>

$$-\log P_U(\text{atm}) = (29600 \pm 170)/T - (7.323 \pm 0.081), \quad (5)$$

whereas the relative pressures of uranium and sulphur exclusive of an instrumental factor proportional to the effective ionization cross section are given by

$$\log(I_U T) = -(29,600 \pm 170)/T + (17.589 \pm 0.081), \quad (6)$$

$$\log(I_S T) = -(28,410 \pm 400)/T + (15.79 \pm 0.19). \quad (7)$$

The temperature dependences of the uranium and sulphur pressures thus differ by more than the uncertainties associated with the measurements and show an increase of the  $P_U/P_S$  ratio with temperature. It is therefore suggested here that the compound  $US_{1.00}$  does not vaporize congruently as assumed in ref. (49a) but changes in composition within an homogeneity range towards  $US_{1-x}$  (with  $x = f(T)$ ), until the phase limit is reached. By comparing the uranium decomposition pressure with the vapour pressure determined here the latter would occur at  $2350 \pm 100^\circ\text{K}$  in agreement with a number of observations (49b). Neglecting in first approximation differences in entropy and enthalpy of  $US_{1\pm x}$  and of  $US$ , the cycle based on the vaporization of uranium monosulphide is:

	2nd law	3rd law
$US(s) \rightarrow U(g) + S(g)$	$\Delta H_{2000}^\circ = 265.5 \pm 2.0$	$274.2 \pm 5$
	$\Delta H_{298}^\circ = 269.7 \pm 3.0$	
$S(g) \rightarrow S(\text{rhomb})$	$\Delta H_{298}^\circ = -66.4 \pm 0.5$	
$U(s) + S(s) \rightarrow US(s)$	$\Delta H_{f,298}^\circ = -73.2 \pm 3.5^{50}$ or $-78.9 \pm 12^{51}$	
$U(s) \rightarrow U(g)$	$\Delta H_{298}^\circ = 130.1 \pm 5$ or $124.4 \pm 12$	$134.6 \pm 6$ or $128.9 \pm 12$

In the calculations for this cycle the following thermodynamic quantities were used for  $US(s)$ :  $S_{298}^\circ = 18.6$  cal/mole deg.;  $H_{298}^\circ - H_0^\circ = 2667$  cal/mole<sup>52</sup>;  $S_{2000}^\circ - S_{298}^\circ = 26.2 \pm 1.5$  cal/mole deg.;  $H_{2000}^\circ - H_{298}^\circ = 23.9 \pm 1.5$  kcal/mole, the latter two quantities being obtained by extrapolating up to  $2000^\circ\text{K}$  the heat capacity measurement carried out between  $400$  and  $1400^\circ\text{K}$ .<sup>53</sup> The second law heat of decomposition was obtained by summing the heats of vaporization of uranium,  $\Delta H_{2000}^\circ$  (6) =  $135.5 \pm 0.8$  and of sulphur,  $\Delta H_{2000}^\circ$  (7) =  $130.0 \pm 1.8$  kcal/g atom resulting from eqn. (6) and (7) above. For the third law calculation, the uranium pressure  $-\log P_U = 7.5 \pm 0.1$  atm at  $2000^\circ\text{K}$  is that resulting from eqn. (5) above; the sulphur pressure,  $-\log P_S = 7.9 \pm 0.2$  atm was calculated from the relative intensities given by eqn. (6) and (7) rather than from the condition of congruency,  $P_S = P_U \times [(32)/238]^{1/2}$  (even if the result is identical). Relative multiplier yields proportional to  $M^{-1/2}$  were therefore used and relative ionization cross-sections  $\sigma_U = 75$ ,  $\sigma_S = 19 \pm 6$ <sup>29, 30</sup> at the maximum of the ionization efficiency curve, reduced proportionally to the ratio  $(E_i - IP_i)/IP_i$ , where  $E_i$  is the energy employed for the intensity measurement;<sup>49</sup> and  $IP_i$  the ionization potential ( $E_S = 12.4$ ;  $E_U = 11.4$ ;  $IP_S = 10.4$ ;  $IP_U = 6.1$  eV).

There appears to be some disagreement between the second law and third law results. This would disappear if, as done in ref. (49),  $US$  were assumed to vaporize congruently throughout the whole temperature interval with  $\Delta H_{2000}^\circ$  (8) =  $2\Delta H_{2000}^\circ$  (6) =  $271.0$  or  $\Delta H_{298}^\circ$  (8) =  $275.6$  kcal/mole. Taking into account the uncertainties in the vaporization behaviour (congruent or not), in the pressure, in the entropy at  $2000^\circ\text{K}$  and its variation with composition if applicable, and in the heat of formation of  $US$ ,<sup>50, 51</sup> we conclude that the thermodynamic data for this compound are consistent with the other values for the heat of sublimation of uranium, but that they cannot at present be used to derive a precise value for the latter quantity.

The values for the heat of sublimation of uranium resulting from the measurements of the heats of vaporization of  $\text{UO}(g)$  and  $\text{UO}_2(g)$  and the independent measurement of their dissociation energies were obtained from the following data :



By combining eqn. (9), (11), (12), (13) and (14) and eqn. (9)-(13) and (15), there results  $\Delta H_{s,0}^\circ(\text{U}) = 130.0 \pm 3.5$  and  $129.5 \pm 3.0$  kcal/g atom respectively.

TABLE 2.—HEAT OF SUBLIMATION OF URANIUM, REVIEW

I reaction studied $\text{U}(l) \rightarrow \text{U}(g)$	II temp. interval °K	III ref.	IV $\Delta H_0^\circ$ (reaction) kcal/mole	V $\Delta H_{s,0}^\circ(\text{U})$ kcal/g atom
	1720-2340	this work		$129.0 \pm 2.0$
	1630-1970	3		$117.6 \pm 0.4^{(1)}$
	1875-1970	5		$129.8 \pm 5.0^{(1a)}$
	1800-2175	11		$\geq 127.9^{(2)}$
				$\leq 132.3^{(1a,3)}$
	1700-2200	35		$130.3-131.5$
	2073-2473	42		$130.0 \pm 2.0^{(1)}$
$\text{U}_{1-x}\text{C}_{1+x}(s) \rightarrow (1-x)\text{U}(g) + (1+x)\text{C}(g)$				
$x = -0.0025; 0.038;$ $0.042; 0.054$	2040-2470	11	$322.1 \pm 2.0$	$128.6 \pm 2.5$
$x = 0.26; 0.28; 0.30;$ $0.305; 0.306; 0.317$	2100-2450	11	$325.8 \pm 2.0$	$128.8 \pm 2.5$
$x = 0.02$	2250-2510	7, 12	$323.3 \pm 2.0$	$129.7 \pm 2.5$
$x = 0.04$ (free surface con-	2250-2500	48	$322.4 \pm 2.0$	$128.7 \pm 2.5$
$x = 0.04$ gruent vaporiza-	2470-2510	7, 12	$323.5 \pm 2.0$	$129.8 \pm 2.5$
tion)				
$\text{UC}_{1.9}(s) \rightarrow \text{U}(g) + 1.9\text{C}$ (graphite)	1930-2360	43	$(147.9 \pm 3.0)$	$(126.3 \pm 3.5)$
	2228	44	$148.6 \pm 3.0$	$127.0 \pm 3.2$
	2050-2500	44	$150.3 \pm 3.0$	$128.7 \pm 3.3$
	2010-2900	45	$(145.2 \pm 3.0)$	$(123.6 \pm 3.5)$
	2150-2700	46	$151.1 \pm 3.7$	$129.5 \pm 3.8$
	2150-2450	11	$150.5 \pm 1.7$	$128.9 \pm 2.0$
$\text{US}(s) \rightarrow \text{U}(g) + \text{S}(g)$	1825-2400	49	$273.8 \pm 5.0$	$130 \pm 5.0$
$\text{UO}_2(s) \rightarrow \text{UO}_2(g)$	1900-2420	9, 12	$152.5 \pm 1.5$	$129.5 \pm 3.0$
$\frac{1}{2}\text{U}(l) + \frac{1}{2}\text{UO}_2(s) \rightarrow \text{UO}(g)$	1720-2100	9, 12	$136.5 \pm 1.5$	$130.0 \pm 3.5$

(1) recalculated to conform with the free energy functions and where applicable.

(1a) also with the relative ionization cross-section of uranium used in this paper.

(2,3) respectively 2nd and 3rd law heat of vaporization of uranium contacted by UC assuming the (U saturated with C) solution to be an ideal one.<sup>11</sup> The second and third law results are therefore lower and upper limits respectively for the actual heat of sublimation.



As can be seen in table 2, in which the available data have been summarized, the direct and indirect values for the heat of sublimation of uranium are mutually in excellent agreement. It is therefore considered that the overall evidence establishes the high value of the heat of sublimation of this element.

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