

Uranium Monosulfide. III. Thermochemistry, Partial Pressures, and Dissociation Energies of US and US₂

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Uranium Monosulfide. III. Thermochemistry, Partial Pressures, and Dissociation Energies of US and US₂*

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A mass-spectrometric study of the sublimation of uranium monosulfide has been performed over the temperature range 1825° to 2400°K. The data are combined with the previous measurements of absolute rate of effusion by means of a new method of calculation which effects an absolute pressure calibration of the spectrometer and allows a determination of the partial pressures of U, US, and US₂ in the vapor, the enthalpies and entropies of sublimation to atoms and molecules, and the dissociation energies of US and US₂. The partial pressures of U, US, and US₂ at 2020°K are in the ratios 1/0.27/0.001. The data for the several sublimation processes are as follows:

Reaction	log <i>P</i> (atm)	ΔH°_{2020} kcal/mole	ΔS°_{2020} cal/mole·deg
US(s) = US(g)	$\log P_{US} = (7.606 \pm 0.091) - (31\,030 \pm 190)/T$	142.0 ± 0.9	34.8 ± 0.4
US(s) = U(g) + S(g)	$\log P_U = (7.323 \pm 0.081) - (29\,600 \pm 170)/T$	270.9 ± 0.16	65.0 ± 0.7
2US(s) = US ₂ (g) + U(g)	$\log P_{US_2} = (6.36 \pm 0.26) - (33\,430 \pm 580)/T$	288.4 ± 3.7	62.6 ± 1.2

The quoted uncertainties are standard deviations. The dissociation energies for US and US₂ and the estimated uncertainties are

$$D_0(\text{US}) = 133.8 \pm 2.3 \text{ kcal/mole or } 5.80 \pm 0.10 \text{ eV,}$$

$$D_0(\text{US}_2) = 252 \pm 4 \text{ kcal/mole or } 10.9 \pm 0.2 \text{ eV.}$$

INTRODUCTION

WE have previously published^{1,2} mass-effusion and mass-spectrometric studies of the sublimation and thermochemical properties of uranium monosulfide. An extensive thermodynamic treatment of the vaporization reactions was presented. The accuracy of that treatment, however, was limited by the mass-spectrometric results because estimated ionization cross sections were used, because some error due to fragmentation may have been introduced, and because only ratios of ion currents, but not the individual currents resulting from each vapor species, could be measured. We have recently described³ a method for combining weight-loss and mass-spectrometric effusion measurements to determine uniquely the partial pressures of the vapor species without the need for estimating relative ionization cross sections. The pressures so determined can be combined with the ion-current data to calculate the instrumental sensitivity to each vapor

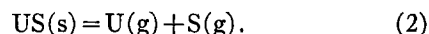
species. We have, therefore, performed a new mass-spectrometric study of the sublimation of uranium monosulfide in order to take advantage of improved instrumentation,⁴ and the results are combined herein with our previous mass-effusion measurements in a redetermination of the thermochemical properties of uranium monosulfide and a measurement of the dissociation energies of US and US₂.

PREVIOUS WORK

In Papers I and II it was shown that uranium monosulfide sublimes congruently at the stoichiometric composition by two processes of comparable importance between 1840° and 2730°K, namely,



and



The total rate of effusion from a tungsten cell was measured at temperatures from 1840° to 2730°K by collection of samples of the effusate on platinum disks and determination of the amount of uranium present by α counting. The data were treated to yield the "effective pressure," P_E , calculated as though gaseous US were the only vapor species. Thus, if P_{US} and P_U

* Based on work performed under the auspices of the U.S. Atomic Energy Commission and supported in part at the University of Iowa under contract No. AT(11-1)-1182 by the Commission.

¹ E. D. Cater, P. W. Gilles, and R. J. Thorn, *J. Chem. Phys.* **35**, 608 (1961), hereinafter called Paper I.

² E. D. Cater, E. G. Rauh, and R. J. Thorn, *J. Chem. Phys.* **35**, 619 (1961), hereinafter called Paper II.

³ E. D. Cater and R. J. Thorn, *J. Chem. Phys.* (to be published).

⁴ See, for example, R. J. Ackermann and E. G. Rauh, *J. Chem. Phys.* **36**, 448 (1962).

are the partial pressures of US and U in the vapor, and M_{US} and M_U are their respective molecular weights, then

$$P_E = P_{US} + P_U (M_{US}/M_U)^{1/2} \quad (3)$$

The data were plotted as $\log P_E$ vs $10^4/T$, and both linear and nonlinear least-squares analyses were made. The results were the two equations

$$\log P_E = (-29\,970 \pm 90)/T + (7.666 \pm 0.038) \quad (4)$$

and

$$\log P_E = -1.7382 + (3.1274 \times 10^4)/T - (1.3181 \times 10^8)/T^2 + (0.093776 \times 10^{12})/T^3 \quad (5)$$

The nonlinear Eq. (5) fits the data slightly better than the linear Eq. (4) since a slight curvature of $\log P_E$ vs $10^4/T$ was observed. The errors in Eq. (4) are standard deviations.

METHOD

In a mass-spectrometric measurement of effusate from a cell at temperature $T^\circ\text{K}$, the partial pressure P_i of Vapor Species i in the cell is related to the ion current I_i by the equation,

$$K_i P_i = I_i T, \quad (6)$$

where the proportionality constant K_i is the over-all instrumental sensitivity to Species i .

Now, for sublimation of uranium monosulfide at two temperatures, T_1 and T_2 , let the effective pressures be $P_E^{(1)}$ and $P_E^{(2)}$ and the partial pressures and ion currents due to the species U and US be $P_U^{(1)}$, $P_U^{(2)}$, $I_U^{(1)}$, $I_U^{(2)}$, $P_{US}^{(1)}$, $P_{US}^{(2)}$, $I_{US}^{(1)}$, $I_{US}^{(2)}$, respectively. As shown elsewhere,³ one can combine Eqs. (3) and (6) to obtain the relation

$$P_U^{(1)} = \frac{P_E^{(2)} - [I_{US}^{(2)} T_2 / I_{US}^{(1)} T_1] P_E^{(1)}}{[(I_U^{(2)} T_2 / I_U^{(1)} T_1) - (I_{US}^{(2)} T_2 / I_{US}^{(1)} T_1)] (M_{US}/M_U)^{1/2}} \quad (7)$$

Thus, if P_E and the ion currents are known at T_1 and T_2 , one can obtain uniquely the values of the partial pressures of U and US at T_1 and T_2 , and also the proportionality constants, K_U and K_{US} . In order to obtain the best values for use in Eq. (7), we have calculated ion currents and pressures from least-squares fits to our present experimental data and previous pressure measurement of effective pressures. We have also selected several sets of T_1 and T_2 in order to examine the consistency of the data.

EXPERIMENTAL MEASUREMENTS

A sample of US, prepared at the time of our previous work by reaction of metallic uranium with hydrogen sulfide followed by vacuum annealing in tungsten at 2200°C , was used. The particular sample had been sublimed to the underside of the crucible lid during the annealing, as had the samples previously studied. An effusion study was performed by heating the sample in a well-outgassed (at 2700°C) tungsten cell in a Bendix time-of-flight mass spectrometer operated under conditions of continuous ion formation only slightly different from those described by Studier.⁵ Temperatures were measured by sighting through a shuttered window directly into the orifice with a Leeds and Northrup disappearing filament optical pyrometer. The pyrometer had been calibrated from first principles at the copper point and upwards by the method of rotating sectors.⁶ Corrections were made for the transmissivity of window and prism. Ion currents attributable to four vapor species could be simultaneously

measured on calibrated strip-chart recorders. The apparatus and technique used have been previously described.⁴ All recorded ion currents were corrected for background. A check was made to show that the observed ion peaks were due to species effusing from the orifice.

RESULTS

The general vaporization behavior observed was essentially that described earlier.² The primary species U^+ , UO^+ , US^+ , UOS^+ , and S^+ were observed initially. The oxygenated species disappeared after a small fraction of the sample had been vaporized. US_2^+ and $(US)_2^+$ were observed at the highest temperatures. Measurement of the ion current due to S^+ was hampered by the background at Mass 32.

Appearance potential curves were obtained for the ions U^+ and US^+ . The observed appearance potentials were, respectively, 6.0 and 6.3 eV. That for U^+ , 6.0 eV is in agreement with the ionization potential of uranium, 6.11 ± 0.05 eV.⁷ The two ion currents increased rapidly up to energies of about 17 eV, beyond which they increased only gradually. The ratio of the ion currents, I_U/I_{US} , was essentially constant at energies from about 11 to 17 eV and increased at higher energies. It is clear that both ions are primary species. Fragmentation of gaseous US to give U^+ may be the cause of the increasing ratio I_U/I_{US} at energies above 17 eV.

Figure 1 shows the dependence of ion current on temperature for the primary species U^+ , US^+ , S^+ , and US_2^+ . The data on U^+ and US^+ were recorded in three series, designated A, B, and C. In each series, several data were recorded at temperatures sequentially in-

⁵ M. H. Studier, Rev. Sci. Instr. **34**, 1367 (1963).

⁶ See, for a description of the equipment used, R. J. Thorn and G. H. Winslow, Am. Soc. Mech. Engs., Paper No. 63-WA-224 (1963).

⁷ J. B. Mann, J. Chem. Phys. **40**, 1632 (1964).

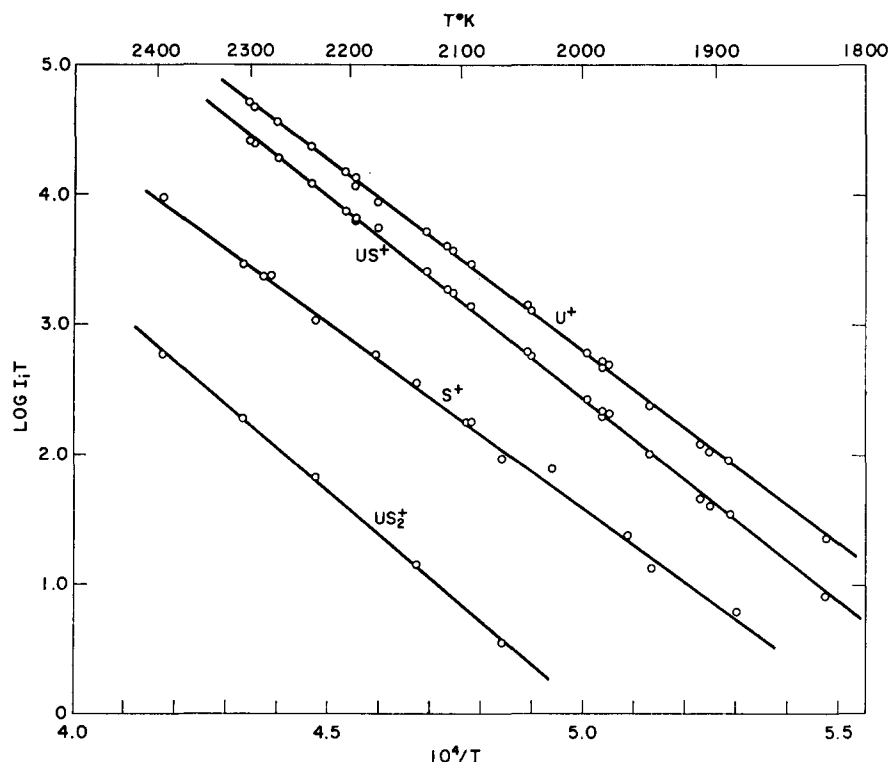


FIG. 1. $\log I_i T$ vs $10^4/T$ for U^+ , S^+ , US^+ , and US_2^+ from the sublimation of uranium monosulfide. Data for U^+ and US^+ recorded at 11.4 eV; data for S^+ and US_2^+ recorded at 12.4 eV.

creased, then several with temperatures sequentially decreased. Electrons of fixed energy—approximately 11.5 eV—were employed. At this energy, no detectable fragmentation of US to give U^+ would occur. No dependence of ion current on time or temperature order was observed; thus, the instrumental sensitivity was constant in each series and our previous report of congruent vaporization is confirmed. However, slight changes of instrumental sensitivity occurred between the series. The data shown in Fig. 1 have been normalized at the temperature 2020°K by the addition of 0.02 to the $\log I_{U^+} T$ and $\log I_{US^+} T$ values for Series B and the subtraction of 0.02 from the values for Series C. The result is that the respective values of $\log I_{U^+} T$ and $\log I_{US^+} T$ calculated at 2020°K from linear least-squares fits to the data for each series individually are equal. It should be noted that the slopes and intercepts from the least-squares equations for the individual series agreed within their standard deviations for both U^+ and US^+ . After each change in temperature, the several ion currents attained their new constant values in a short time and at the same rate. Hence, no indication was obtained of a departure from stoichiometry of the solid sample. This inference can be made because very slight changes of stoichiometry of the solid may cause appreciable differences in the rates at which the different species attain their final equilibrium values. In general, near a stoichiometric composition the partial pressure of the gaseous species corresponding to the composition of the solid does not change rapidly with composition, but the partial pressures of both

the elemental components change very rapidly. This is a result which is described by the defect theory of nonstoichiometry. Ackermann *et al.*⁸ observed this behavior in the vaporization of thorium dioxide.

The data shown in Fig. 1 for S^+ and US_2^+ were recorded as Series D on a later day than Series A, B, and C. A new portion of solid monosulfide was used. Electrons of 12.4 eV energy were used. At lower energies, the signal from S^+ was too low for accurate measurement. At higher energies, the background at Mass 32 was much increased. Data for U^+ and US^+ in Series D agreed with the data from Series A, B, and C. No appearance potential curves for S^+ and US_2^+ were taken. Ion currents from $(US)_2^+$ and U_2S^+ were observed at the highest temperatures and higher electron energies, but the signals were too weak for accurate measurement. The U_2S^+ was surmised to be a fragment and $(US)_2^+$, a primary species.

Linear least-squares equations for the variation of $\log I_i T$ with $1/T$ for the various species are

$$\log(I_{U^+} T) = (17.589 \pm 0.081) - (29\,600 \pm 170)/T, \quad (8)$$

$$\log(I_{US^+} T) = (17.938 \pm 0.091) - (31\,030 \pm 190)/T, \quad (9)$$

$$\log(I_{S^+} T) = (15.79 \pm 0.19) - (28\,410 \pm 400)/T, \quad (10)$$

$$\log(I_{US_2^+} T) = (16.76 \pm 0.26) - (33\,430 \pm 580)/T. \quad (11)$$

In addition to the linear treatments of the data, the following four-parameter least-squares fits for U^+ and

⁸ R. J. Ackermann, E. G. Rauh, R. J. Thorn, and M. E. Cannon, *J. Phys. Chem.* **67**, 762 (1963).

TABLE I. Calculated instrumental sensitivities^a for U and US.

Temperature used		Linear treatment			Nonlinear treatment		
$10^4/T_1$	$10^4/T_2$	$10^{-10}K_U$	$10^{-10}K_{US}$	K_U/K_{US}	$10^{-10}K_U$	$10^{-10}K_{US}$	K_U/K_{US}
5.5	4.1	1.88	1.94	0.970	1.79	1.38	1.30
5.3	4.2	1.83	2.23	0.822	2.75	1.01	2.72
5.1	4.5	1.84	2.14	0.830	3.79	0.916	4.13
4.9	4.7	1.86	2.14	0.868	5.80	0.62	9.36
4.9	4.3	1.81	2.30	0.788	-4.12	45.0	-0.092
5.3	4.7	1.86	2.12	0.877	1.47	1.04	1.41
		Av 1.845	Av 2.145	Av 0.860			

^a The units of the K 's are 10^{10} ion-current units·deg/atm.

US⁺ were obtained:

$$\log I_U T = 14.864 - (1.9519 \times 10^4)/T \\ - (0.06548 \times 10^8)/T^2 - (0.00521 \times 10^{12})/T^3, \quad (12)$$

$$\log I_{US} T = 17.127 - (3.6261 \times 10^4)/T \\ + (0.3209 \times 10^8)/T^2 - (0.0366 \times 10^{12})/T^3. \quad (13)$$

Examination of the residuals from the $\log IT$'s calculated from Eqs. (8), (9), (12), and (13) show that the latter two equations give a better fit to the data.

THERMOCHEMICAL TREATMENT

In order to determine the instrumental sensitivities to U and US, partial pressures were calculated from Eqs. (7) and (3) for several choices of T_1 and T_2 in the range of measurement. Values of P_E , $I_U T$, and $I_{US} T$ were obtained from both the linear Eqs. (3), (8), and (9) and the nonlinear Eqs. (5), (12), and (13). The resulting instrumental sensitivities, K_U and K_{US} , and their ratios are presented in Table I. It is clear that the linear equations for $\log P_E$, $\log I_U T$, and $\log I_{US} T$ give nearly constant values for K_U and K_{US} , whereas the nonlinear equations yield K 's that are mutually inconsistent. The average values of K_U and K_{US} from the linear treatment are taken for use below. The linear equations for $\log P_E$, $\log I_U T$, and $\log I_{US} T$ are employed for calculation of the thermochemical properties of uranium monosulfide.

Two comments should be made regarding the numbers in Table I. First, if it is assumed that the variation of $\log I_U T$ and of $\log I_{US} T$ with reciprocal temperature is truly linear, it is mathematically impossible that $\log P_E$ should vary linearly with $1/T$. However, the deviation from linearity of $\log P_E$ would correspond to something like ± 0.01 over the mutual temperature range, and so from a practical standpoint, the mutual inconsistency of Eqs. (3), (8), and (9) is negligible. The second comment is that, while the nonlinear least-squares eqs. (5), (12), and (13) yield slightly smaller residuals than do the linear equations, the deviations from linearity are very small (see Fig. 1 of Paper I), and it is apparent that the nonlinear equations are mutually inconsistent from the standpoint of

the present calculations. Examination shows that the downward curvatures of the $\log IT$ curves are slightly too great to be consistent with the curvature of $\log P_E$. We believe the data are sufficiently precise that the inconsistency demonstrates a systematic experimental difference between measurements of the ion currents and measurements of absolute rate of effusion rather than random experimental error. Other experiments we have performed indicate that space-charge effects in the ion source could give rise to the extra downward curvature of the $\log IT$ curves. In the continuous mode of operation⁶ of the time-of-flight mass spectrometer ions are formed continuously in the source region and retained there in the potential well of the electron beam. At 100- μ sec intervals the ions then in the source region are drawn out into the flight tube by a short (2 μ sec) electrostatic pulse. At the higher pressures in the effusion cell, a large concentration of ions develops in the source, the space charge is partially neutralized, and a larger percentage of the ions is lost to the walls before the draw-out pulse. Thus, beyond a certain point, the plot of $\log IT$ vs $1/T$ begins to take on a slight downward departure from linearity.

The instrumental sensitivities, $K_U = 1.85 \times 10^{10}$ and $K_{US} = 2.15 \times 10^{10}$ current units·deg/atm, may be combined with Eqs. (8) and (9) to yield the variation of $\log P_U$ and $\log P_{US}$ with $1/T$, and the resulting equations are

$$\log P_U (\text{atm}) = (7.323 \pm 0.081) - (29\,600 \pm 170)/T \quad (14)$$

and

$$\log P_{US} (\text{atm}) = (7.606 \pm 0.091) - (31\,030 \pm 190)/T. \quad (15)$$

Because P_{US_2} is a very small contributor to P_E , it cannot be calculated directly, although in principle by using three temperatures, one can extend Eq. (7) to include P_{US_2} . For purposes of calculation, we take the instrumental sensitivity for US₂ to be 2.50×10^{10} by assuming the proportional increase from US to US₂ to be the same as that from U to US. The resulting equation for the partial pressure of US₂ is

$$\log P_{US_2} = (6.36 \pm 0.26) - (33\,430 \pm 580)/T, \quad (16)$$

TABLE II. Thermodynamic values for reactions involving uranium monosulfide in the temperature range 1825° to 2400°K (pressures in atmospheres).

Reaction	Eq. Const $K =$	$\log K =$	ΔH_{2020}° (kcal/mole)	ΔS_{2020}° (cal/deg·mole)
I. $\text{US(s)} = \text{US(g)}$	P_{US}	$(7.606 \pm 0.091) - (31\ 030 \pm 190)/T$	142.0 ± 0.87	34.80 ± 0.42
II. $\text{US(s)} = \text{U(g)} + \text{S(g)}$	$P_{\text{U}}P_{\text{S}} = P_{\text{U}}^2(M_{\text{S}}/M_{\text{U}})^{1/2}$	$(14.211 \pm 0.162) - 59\ 240 \pm 340/T$	270.9 ± 1.56	65.03 ± 0.71
III. $2\text{US(s)} = \text{US}_2(\text{g}) + \text{U(g)}$	$P_{\text{U}}P_{\text{US}_2}$	$(13.68 \pm 0.27) - (63\ 030 \pm 670)/T$	288.4 ± 3.1	62.60 ± 1.24
IV. $\text{US(g)} = \text{U(g)} + \text{S(g)}$	$P_{\text{U}}^2(M_{\text{S}}/M_{\text{U}})^{1/2}/P_{\text{US}}$	$(6.605 \pm 0.186) - (28\ 170 \pm 390)/T$	128.9 ± 1.8	30.23 ± 0.82
V. $\text{US}_2(\text{g}) = \text{U(g)} + 2\text{S(g)}$	$P_{\text{U}}^3(M_{\text{S}}/M_{\text{U}})P_{\text{US}_2}$	$(14.74 \pm 0.30) - (55\ 370 \pm 650)/T$	253.3 ± 3.0	67.44 ± 1.37
Entropies at 2020°K (cal/deg·mole)				
		Source		
U(g)	58.85	Stull and Sinke, Ref. 11		
S(g)	50.19	Stull and Sinke, Ref. 11		
US(s)	44.01 ± 0.71	This work		
US(g)	78.81 ± 0.82	This work		
US(g)	(79.5 ± 2)	Estimated		
US ₂ (g)	91.77 ± 1.88	This work		

in which standard deviations are given. The actual error due to the assumed instrumental sensitivity is unknown. Thus at 2020°K, gaseous US₂ has a partial pressure only 0.10% of P_{E} .

In Table II the several equilibrium constants of interest are listed, and their variations with temperature are evaluated from Eqs. (14), (15), and (16).

The relation

$$\log K = \Delta S^{\circ}/R' - \Delta H^{\circ}/R'T \quad (17)$$

in which $R' = 2.303R = 4.576$ cal/deg·mole, provides the so-called second-law heats and entropies of reaction; these also appear in Table II.

In order to calculate the dissociation energy of US and of US₂, and in order to estimate the entropy of US(g) for a check on the second-law value given in Table II, we have estimated molecular parameters and other functions as follows: For the internuclear spacing in gaseous US, we take 2.20 Å, 20% less than the U-S distance in the solid,¹ and a vibrational frequency of 516 cm⁻¹, 40% less than the symmetrical stretching frequency, 860 cm⁻¹, in the uranyl ion.⁸ Ackermann *et al.*⁹ have argued that the frequency 860 cm⁻¹ is a good approximation to the vibrational frequency of the UO molecule, and the frequency of the US molecule should be less by the order of 40% or so. For lack of any experimental information, we assume the ground electronic state to have a degeneracy between two and eight (with an appropriate allowance on the estimated error). The resulting estimate for the entropy of US(g) at 2020°K is 79.5 ± 2 eu. This estimated uncertainty allows for $\pm 20\%$ in the internuclear spacing and $\pm 50\%$ in the vibrational frequency. The estimated entropy for US(g) agrees with the value 78.8 eu obtained from

the intercept in the second-law treatment and the data for the gaseous elements (Table II). This agreement is taken as an indication that the second-law value is reliable. In fact, if the estimated molecular parameters are correct, the ground-state degeneracy is most likely two, three, or four.

Westrum and Walters¹⁰ reported for solid US, $S_{298}^{\circ} = 12.08$ eu and $(H_{298}^{\circ} - H_0^{\circ}) = 2667$ cal/mole. Referring to Table II, one obtains $(S_{2020}^{\circ} - S_{298}^{\circ})$ (US, s) = 31.93 eu, corresponding to an average heat capacity of the solid $C_P(\text{US}) = 16.7$ cal/deg·mole or $8.4R$. This average heat capacity gives $(H_{2020}^{\circ} - H_{298}^{\circ})$ (US, s) = 28.4 kcal/mole.

From the above-estimated molecular constants one calculates for gaseous US $(H_{2020}^{\circ} - H_0^{\circ})$ (US, g) = 17.4 kcal/mole. Combined with the enthalpy functions for the elements¹¹ this yields the dissociation energy of gaseous US, $D_0(\text{US}) = 133.8 \pm 2.3$ kcal/mole or 5.80 ± 0.10 eV, where the error contains the standard deviations of the slopes and an estimate of the error in the enthalpy function.

To estimate the dissociation energy of US₂ from the heat of Reaction V, Table II, requires an estimate of the function $(H_{2020}^{\circ} - H_0^{\circ})$ (US₂). If the stretching frequencies are taken as $500 \text{ cm}^{-1} \pm 50\%$ and the bending frequencies as $250 \text{ cm}^{-1} \pm 50\%$, then for either an assumed linear or bent molecule, $(H_{2020}^{\circ} - H_0^{\circ})$ (US₂) = 27.0 ± 3.0 kcal/mole. The dissociation energy of US₂(g) at 0°K is thus 252 ± 4 kcal/mole or 10.9 ± 0.2 eV, and the average bond energy of the U-S bond is 5.45 ± 0.1 eV.

⁹ R. J. Ackermann, M. S. Chandrasekharaiah, and E. G. Rauh, Argonne National Laboratory Report, ANL-7048 (1965).

¹⁰ E. F. Westrum, Jr., and R. R. Walters, reported by E. F. Westrum, Jr., and F. Gronwald, in *Thermodynamics of Nuclear Materials* (International Atomic Energy Agency, Vienna, 1962), pp. 24-32.

¹¹ D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements* (American Chemical Society, Washington, 1956).

TABLE III. Comparison of results of present study with those of Papers I and II.*

	ΔH_T° (old) (kcal/mole)	ΔH_T° (new) (kcal/mole)	ΔS_T° (old) (eu)	ΔS_T° (new) (eu)	Pressure at 2020°K (atm)	
					Old	New
US(s) = US(g)	150.3±2.1	142.0±0.9	38.4±0.6	34.8±0.4	$P_{US}=1.34\times 10^{-8}$	1.76×10^{-8}
US(s) = U(g) + S(g)	271.2±4.0	270.9±1.6	65.5±1.6	65.0±0.7	$P_U=5.03\times 10^{-8}$	4.68×10^{-8}
U(g) + S(g) = US(s) at 298°K	-273±5	-280±4				
US(g) = U(g) + S(g) at 0°K		133.8±2.3				

* See Refs. 1 and 2.

These values may be compared with the dissociation energies¹² of UO and UO₂, $D_0(\text{UO})=7.8\pm 0.3$ eV and $D_0(\text{UO}_2)=14.7\pm 0.3$ eV.

DISCUSSION

The results of the present study are compared to those of Papers I and II in Table III and in Fig. 2. The values assigned to the sublimation to atoms and the partial pressures of U are much less affected by the new experiments than those involving gaseous US. This is to be expected because the partial pressure of U is greater than that of US and a small fractional change in the calculated P_U gives a larger fractional change

in P_{US} . The fact that both the heat and entropy of sublimation to molecules increased can also be rationalized as follows: First, in the earlier study a sensitivity ratio, $K_{US}/K_U=1.4$, was assumed, whereas in the present work the ratio is shown to be $K_{US}/K_U=1.16$. Second, the slope of the plot $\log I_{US}/I_U$ vs $10^4/T$ in Paper II was too negative by 9.2 kcal/mole when compared with the present results. A re-examination of the mass-spectrometric data of Paper II (taken with 50- and 20-eV energies) shows that the 50-eV points tended to be bunched at the higher temperatures while the 20-eV points were mostly spread among the lower temperatures. The 20-eV data gave ratios of I_{US}/I_U in fair agreement with the data in the present paper. The 50-eV data undoubtedly were affected by fragmentation and give ratios I_U/I_{US} too high. Therefore the slope was excessively negative in Paper II. Hence, the less accurate thermodynamic values of Papers I and II differ in an explainable way from the values obtained here.

In conclusion, we present these results as a strong argument for combining the results of careful measurements of absolute rate of effusion with mass-spectrometric studies; neither alone gives a complete picture.

For the major vapor species U and US we have determined the sensitivities of the mass spectrometer; only for the minor species US₂ was an estimate necessary. Note again that these are over-all instrumental sensitivities and contain both the ionization cross sections and detector efficiencies. One does not necessarily expect these numbers to agree with relative ionization cross sections determined in instruments equipped to determine cross sections and detector sensitivities independently. It is interesting to examine the presently obtained sensitivities to U and S atoms in this respect. The effusion rates of U and S must be equal to maintain stoichiometry in the condensed phase. The ion-current ratio at 12.4-eV energy is approximately $I_U/I_S\approx 20$ so that the sensitivity ratio at the energy is 7.3. However, at higher energies the plateau values for U and S give $I_U/I_S\approx 11$. These numbers may be compared with the values of relative cross sections on the scale of Otvos and Stevenson¹³ for sulfur¹³ and for uranium,¹² $\sigma_S=12.8$, $\sigma_U=50\pm 5$ or $\sigma_U/\sigma_S=4.0\pm 0.4$.

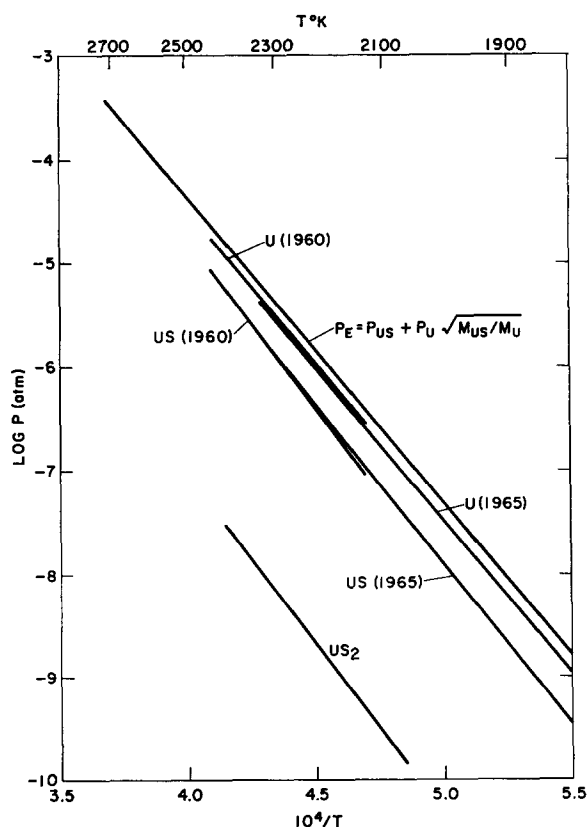


FIG. 2. Variation of pressure with temperature. Plot of $\log P_E = \log[P_{US} + P_U(M_{US}/M_U)^{1/2}]$, $\log P_{US}$, and $\log P_U$ vs $10^4/T$ from Paper I and $\log P_{US}$, $\log P_U$, and $\log P_{US_2}$ vs $10^4/T$ from present study. The latter values are taken to be "best" values.

¹² G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960).

¹³ J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. **78**, 546 (1956).