The Vapor Pressure of Tetrakis(2,2,6,6-tetramethylheptane-3,5-dionato)uranium

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The Knudsen effusion method was used to measure the vapor pressure of tetrakis(2,2,6,6-tetramethylheptane-3,5-dionato)uranium ($U(thd)_4$) over the temperature range 372–478 K. Sublimation at these temperatures is congruent and mass spectrometry showed that the only important vapor species is the monomeric molecule. The vapor pressure is given by the equation: $\ln P(\mathrm{Pa}) = -(18\,309 \pm 400)T^{-1} + (42.36 \pm 0.6)$. The enthalpy and entropy of sublimation at 425 K are: $\Delta H = 152.2 \pm 3.3$ kJ mol^{-1} and $\Delta S = 256.3 \pm 5$ J K^{-1} mol^{-1}.

Stable, volatile chelates of lanthanides and actinides have been of interest for their potential applications in analytical gas chromotography. Volatile chelates of uranium have recently received attention for their possible use in isotope separation as well. We have taken the opportunity to remeasure the vapor pressure of one of the most stable and volatile of these, tetrakis(2,2,6,6-tetramethylheptane-3,5-dionato)uranium, $U(thd)_4$, by the Knudsen effusion method and to examine the vapor by mass spectrometry.

Swain and Karraker measured the vapor pressure of $U(thd)_4$ from 392 to 409 K by Knudsen effusion (*8*). This is a small temperature range, and since independent information to obtain the enthalpy or entropy of sublimation is not available, we thought it important to study the sublimation of $U(thd)_4$ again. There was also a possible difference in composition between their material and ours as reported melting points differed significantly.

The enthalpy of sublimation derived from our results over the range 372–478 K is in good agreement with Swain and Karraker's value, but the entropy of sublimation from our measurements is 15 J K^{-1} mol^{-1} higher than theirs.

The sublimation of $U(thd)_4$ was studied with a mass spectrometer to eliminate any ambiguity regarding the vapor species. Our mass spectrometric results were consistent with those reported before and confirmed that $U(thd)_4$ sublimes as a simple molecule without decomposition (*4, 8*). The temperature dependence of ion intensities was also consistent with the mass effusion results.

Experimental Section

The $U(thd)_4$ used for these measurements was prepared by addition of Hthd in 95% ethanol to a solution of UCl_4 dissolved in a minimum of 2 N HCl. The product was filtered, vacuum dried, and vacuum sublimed at 215 °C. Elemental analysis gave U, 24.6; C, 53.9; and H, 7.8; theoretical values for $U(thd)_4$ are U, 24.5; C, 54.42; and H, 7.89. The melting point determined on a hot stage microscope was 225.7 ± 1 °C with a melting range of 1.2 °C. Differential thermal analysis showed evidence of a minor impurity with eutectic melting 30° below the melting point and gave a melting point of 220 ± 5 °C. Swain and Karraker reported the melting point of $U(thd)_4$ to be 208 °C (*8*).

Effusion rates were measured from Pyrex glass cells 2 cm in diameter by 3 cm high held in a molybdenum bucket suspended in the center of a tungsten resistance vacuum furnace from an Ainsworth automatically recording semimicrobalance. The automatic recording balance–vacuum furnace system has been described elsewhere (*1, 5*).

Furnace temperature was measured with a sheathed type K thermocouple just beneath the cell and sample temperature was obtained from a calibration curve relating cell temperature to furnace temperature. Accuracy of corrected sample temperatures is believed to be ±0.5 °C. Cell weights could be measured to ±50 μg; precision of weight loss rates ranged from ±0.7 to ±12%.

Effective orifice areas of the cells were determined by measuring effusion rates of anthracene from the cells. Measurements were made from 72 to 123 °C for cell 1 and 54 to 93 °C for cell 2. Data of Bradley and Cleasby were used for anthracene vapor pressures (*2*). The temperature dependence of our anthracene sublimation rates agreed with Bradley and Cleasby within the precision of our measurements. Effective areas from the anthracene calibrations were 0.0611 ± 0.004 mm^2 for cell 1 and 0.530 ± 0.05 mm^2 for cell 2. Areas calculated from geometrical measurements with appropriate Clausing corrections were 0.056 ± 0.005 mm^2 and 0.43 ± 0.02 mm^2 (*3*).

The mass spectrometer is a 60° magnetic sector instrument of 30 cm radius with a Nier type electron impact ion source and a Knudsen cell molecular beam source arranged so the molecular beam, electron beam, and ion beam are mutually orthogonal. Measurements were made at several ion accelerating voltages in the range 4.5–14.5 kV.

The sample was in a stainless steel Knudsen cell 2 cm in diameter by 2 cm high with an orifice 0.5 mm in diameter, 2 mm long. Cell temperature was measured with a Pt-Pt/10% Rh thermocouple to ±0.2 °C. The instrument is described in more detail elsewhere (*1, 6*).

Results

A mass spectrum listing peaks with intensities greater than 1% of the largest peak is given in Table I. The peak for the parent ion, $U(thd)_4^+$, had a relative intensity of ~0.3% of $U(thd)_3^+$. Our results agreed both in mass number and relative intensities with the spectra obtained by K. Ernst from $U(thd)_4$ supplied by Swain and Karraker (*4, 8*).

No ions heavier than $U(thd)_4^+$ were detected although the spectrometer was scanned to *m/e* ~2000. When the shutter between the furnace and ion source was closed, all peaks assigned to the $U(thd)_4$ sample disappeared showing that even peaks at low *m/e* were fragments of noncondensible precursors. We found no significant changes in relative abundances over the temperature range 90–165 °C and, thus, concur with Swain and Karraker's conclusion that $U(thd)_4$ vaporizes congruently as a simple molecule. There are no polymers in the vapor, and partial decomposition does not occur at these temperatures. Table II gives intensities vs. temperature for *m/e* 787 and 955 measured using 20 μA of 70 eV electrons. The ion accelerating potential was 9.5 kV and slit widths were 0.6 mm, giving a re-

Table I. Mass Spectrum of $U(thd)_4$ Taken with an Electron Impact Energy of 70 eV (isotope peaks not listed)

Nominal *m/e*	Rel intens	Identification of ion
111	30	$CHCHCOC(CH_3)_3^+$
168	10	$(thd\text{-}CH_3)^+$
364	7	$U(thd\text{-}C(CH_3)_3)^+$
372	7	$U(thd\text{-}3\text{-}CH_3\text{-}4\text{-}H)^+$
393	50	$U(thd)_3^{2+}$
422	1	$U(thd)^+$
604	1+	$U(thd)_2^+$
620	20	$UO(thd)_2^+$
787	100	$U(thd)_3^+$
955	90	$U(thd)_3(thd\text{-}CH_3)^+$

Table II. Relative Ion Intensities for $U(thd)_4$ Vapor

Sequence	Temp, K	Intensity *m/e* 787	Intensity *m/e* 955
7	354.1	0.49	0.39
4	363.1	2.2	2.6
1	363.3	2.4	2.6
3	387.0	107.5	108.1
6	389.4	115.6	118.5
8	397.1	330.6	278.1
2	403.5	435.8	404.2
5	405.8	474.4	439.4

Table III. Effusion Rates and Vapor Pressure of $U(thd)_4$

Sequence	Temp, K	Rate of wt loss (mg h^{-1})	Precision 2σ in %	Pressure, Pa
		Run 1; Cell 1		
1	389.1	1.43×10^{-2}	1.3	9.41×10^{-3}
3	393.4	2.49×10^{-2}	1.8	1.64×10^{-2}
5	396.0	3.57×10^{-2}	5.5	2.37×10^{-2}
9	404.5	9.81×10^{-2}	2.2	6.58×10^{-2}
8	412.5	0.205	0.7	0.139
2	419.6	0.432	1.6	0.295
7	428.7	1.11	0.8	0.768
4	433.9	1.81	0.8	1.26
6	438.4	2.85	1.6	1.99
	$\ln P = -(18\,285 \pm 326)/T + (42.39 \pm 0.75)$			
		Run 2; Cell 2		
8	372.3	1.22×10^{-2}	3.8	9.02×10^{-4}
2	376.6	2.65×10^{-2}	7.3	1.97×10^{-3}
12	381.5	4.74×10^{-2}	3.4	3.56×10^{-3}
5	386.8	8.27×10^{-2}	2.4	6.25×10^{-3}
10	390.7	0.160	1.5	1.21×10^{-2}
13	395.9	0.326	2.1	2.50×10^{-2}
6	400.8	0.368	2.4	2.83×10^{-2}
11	404.7	0.804	2.1	6.22×10^{-2}
4	409.9	1.12	0.9	8.68×10^{-2}
3	419.2	2.79	1.7	0.219
7	419.5	3.02	0.9	0.238
1	424.2	4.79	0.8	0.379
9	428.4	7.50	1.0	0.597
	$\ln P = -(17\,918 \pm 672)/T + (41.31 \pm 1.6)$			
		Run 3; Cell 1		
27	385.0	8.32×10^{-3}	5.6	5.45×10^{-3}
24	390.1	1.65×10^{-2}	12.6	1.08×10^{-2}
10	393.0	2.06×10^{-2}	0.7	1.36×10^{-2}
13	394.5	2.88×10^{-2}	2.7	1.91×10^{-2}
3	397.4	3.90×10^{-2}	7.0	2.59×10^{-2}
17	399.4	5.03×10^{-2}	4.0	3.35×10^{-2}
26	409.3	0.148	5.1	9.98×10^{-2}
12	417.0	0.316	3.7	0.215
28	418.0	0.340	1.7	0.232
1	425.8	0.715	1.8	0.492
14	426.9	0.938	2.8	0.647
25	427.5	0.894	2.1	0.617
11	430.9	1.17	1.9	0.811
21	433.3	1.69	2.5	1.17
9	436.4	2.00	1.1	1.39
23	437.6	2.19	4.0	1.53
2	440.0	2.77	1.0	1.94
16	441.4	3.16	1.5	2.21
18	442.1	4.11	2.3	2.88
4	444.9	5.19	2.3	3.65
8	445.2	4.85	0.7	3.41
22	447.2	5.47	1.7	3.86
15	455.8	11.88	1.6	8.45
20	457.0	13.29	0.7	9.47
7	459.9	18.24	0.7	13.04
19	464.6	25.78	0.9	18.53
6	469.2	44.30	0.6	32.00
5	478.2	90.91	1.6	66.29
	$\ln P(\text{Pa}) = -(18\,278 \pm 206)/T + (42.29 \pm 0.5)$			

solving power of about 1000. The intensity data for *m/e* 787 are fit by

$$\ln (I^*T) = -(20\,200 \pm 1700)/T + (62.4 \pm 2.1) \qquad (1)$$

During the effusion measurements, rates were constant at a given temperature and reproducible from the time ~10% of a sample had sublimed until ~90% was gone. Residues appeared to be identical with the starting material, consistent with congruent sublimation.

The pressure in a Knudsen cell is given by

$$P = (1/Wa)(m/t)(2\Pi RT/M)^{1/2} \qquad (2)$$

Where m/t = rate of weight loss by effusion through an orifice of area a, R = the gas constant, T = temperature, and M = molecular weight of effusing species (*7*). The Clausing factor, W, gives the fraction of molecules entering an orifice of finite length that actually escape the cell; Wa = effective orifice area.[3] Vapor pressures were calculated from effusion rates using the monomeric molecular weight and effective orifice areas measured by anthracene effusion. Data and results are listed in Table III. Results with the two cells were in good agreement, so orifice area dependence with $U(thd)_4$ was consistent with the anthracene calibrations.

Vapor pressures were fitted to the expression

$$\ln P(\text{Pa}) = -(18\,309 \pm 200)/T + (42.36 \pm 0.5) \qquad (3)$$

by least-squares analysis. Error limits are ±2 standard deviations and reflect only the precision of fit between equation and data. The equation with overall uncertainties including contributions from uncertainty in orifice area and systematic temperature errors is

$$\ln P(\text{Pa}) = -(18\,309 \pm 400)/T + (42.36 \pm 0.7) \qquad (4)$$

The enthalpy of sublimation derived from this equation is $\Delta H_{\text{sub},425} = 152.2 \pm 3.3$ kJ mol^{-1}, in good agreement with Swain and Karraker's value of 149.1 ± 1.5 kJ mol^{-1}. (Note their error limit reflects only their precision and does not include estimated contributions from possible systematic errors.) Our result for the entropy of sublimation to the standard state of 1 atm fugacity is

$$\Delta S_{\text{sub},425} = 256.3 \pm 5.8 \text{ J K}^{-1} \text{ mol}^{-1} \qquad (5)$$

which differs significantly from Swain and Karraker's value of 241.1 ± 2.6 J K^{-1} mol^{-1}.

Figure 1 shows the natural log of vapor pressure as a function of reciprocal temperature and compares our measurements to Swain and Karraker's. Normalized mass spectrometric results are also shown. Our measurements give vapor pressures ~2.4

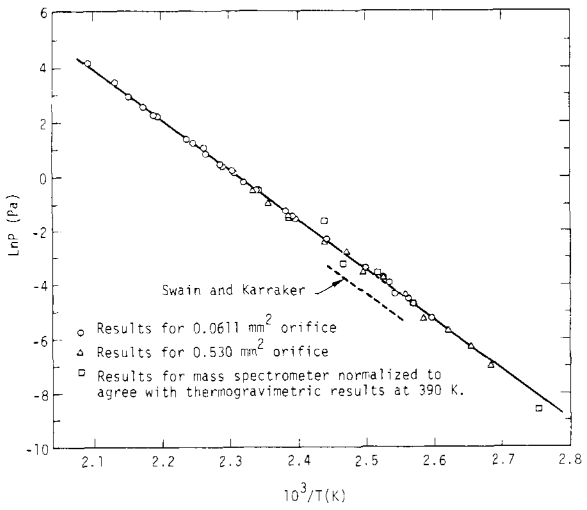

Figure 1. Vapor pressure vs. temperature for U(thd)$_4$.

times the values of Swain and Karraker at a given temperature. The corresponding temperature discrepancies would be about 7.2° at 392 K and 8.1° at 409 K, the lower and upper temperatures of their measurements or 6.5° and 13.8° at our temperature extremes. These differences are far beyond the combined estimated uncertainties for the two studies and we have no explanation for the discrepancy. One suspects a difference in composition because of the difference in melting points, but analyses of the materials were very similar and vapor composition from their material was identical with ours as shown by the mass spectra. It is surprising to find such a large effect on pressure with no detected change in vapor composition and no significant change in enthalpy of sublimation.

The reviewer suggested the discrepancy between our results and those of Swain and Karraker could result from temperature errors due to thermal gradients within the samples. This is possible, and our measurements were more susceptible to this type of error than Swain and Karraker's were because of the temperature gradients in our furnace; the gradients measured between the thermocouples in the furnace and inside the cell varied from about 0° at 100 °C to nearly 25° at 205 °C. Since calibrations were done with empty cells, errors could arise from differences, both conductive and radiative, in thermal transport. However, since the cells were in metal containers, within which the temperature gradient from bottom to top was only 8° at 205 °C, we think a temperature error large enough to explain the difference in results is unlikely.

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The P–V–T Behavior of Acetone in the Dense Gaseous Region

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Experimental PVT data were obtained for acetone in the dense gaseous region for temperatures between 233.7 and 265.3 °C and pressures between 92.4 and 363.8 atm. The experimental pressures and temperatures are presented for each constant mass run, and smoothed compressibility factors resulting from the data are tabulated. The experimental compressibility factors are in good agreement with values calculated from a generalized correlation of this property for polar fluids.

Experimental PVT data were obtained for acetone in the dense gaseous region with a constant volume apparatus. No previous PVT data were available for this substance for the conditions considered. Anderson, Kudchadker, and Eubank (*1*) determined the compressibility factor of acetone for temperatures from 25 to 150 °C and pressures to 7.15 atm. Bridgman (*3*) obtained liquid densities for this substance for elevated pressures and temperatures to 80 °C. Campbell and Chatterlee (*2*) determined saturated liquid and vapor densities for acetone for temperatures from 100 to 235 °C.

Experimental Section

The experimental system was essentially the same as that described in detail previously (*4*, *5*). The constant volume cell was immersed in a molten salt bath controlled internally and externally. The temperature of the bath was measured with protected thermocouples which had been calibrated with a platinum resistance thermometer. The pressure was measured with a dead weight gauge by balancing the test gas with nitrogen by means of a high temperature differential pressure indicator. Modifications were made in the arrangement of the test system, insulation and heating of the bath, and fine pressure control.

The bath assembly was enclosed in a wooden structure 6 ft wide by 7 ft long. One side of the structure served as the control panel. After a vacuum had been obtained, acetone was injected into the system with a syringe. When thermal equilibrium had been reached the temperature and pressure were recorded.

The volume of the test vessel and associated tubing was

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