The Low Temperature Heat Capacities, Enthalpies, and Entropies of UF4 and UF6

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The Low Temperature Heat Capacities, Enthalpies, and Entropies of UF_4 and UF_6*

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The heat capacity of UF_4 has been measured from 20° to 350°K and that of UF_6 from 14° to 370°K. Molar heat capacities have been tabulated at 5-degree intervals and extrapolated to 0°K. From them the entropies and enthalpies of the compounds have been found by integration and tabulated. The triple point temperature of UF_6 was found to be 337.212°K (64.052°C) and the heat of fusion was found to be 19,193 j mole^{-1}.

THE heat capacities of UF_4 and UF_6 were measured in the Low Temperature Laboratory of the National Bureau of Standards between April and October 1942.[1] The work has been the subject of reports A-201 and A-607 to the OSRD.

MATERIALS

The materials were prepared at Columbia University shortly before our measurements were made. The UF_4, a green powder, was received in a glass bottle sealed with wax. It was stated to contain about two percent of UO_2F_2. As this impurity may be expected to have a heat capacity not greatly different from that of UF_4, it should not introduce serious error.

The UF_6 was brought to us in a glass trap, as a colorless or slightly yellowish crystalline solid. It was handled entirely in apparatus from which air and moisture had been evacuated. The method of transfer from the trap to the calorimeter involved distillation, and would tend to eliminate impurities of higher or lower vapor pressure than UF_6. Graphs of the melting range of UF_6 are shown in Fig. 1. They indicate, with the usual assumptions regarding freezing-point depression, that the mole fraction of impurity was 2×10^{-4}. Considering the corrosive nature of the substance, this is quite gratifying. There may, of course, have been some gaseous and liquid-insoluble impurities which the melting curve would not show up.

EXPERIMENTAL

The UF_4 was measured in a platinum calorimeter previously used in measurements on a synthetic rubber.[2] Temperatures were measured

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* This document is based on work performed for the Atomic Energy Project, and the information covered therein will appear in Division VIII of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the National Bureau of Standards.

[1] The heat capacity of UF_5 also was subsequently measured by Robert D. Rands, Jr. Although this material (a gray powder) was protected from water vapor, analyses made by Homer F. Priest at Columbia University, both before and after our measurements, showed a substantial change in the sample. For this and other reasons we have decided not to publish the results, but take this opportunity of calling them to the attention of anyone who might wish to make use of them in a subsequent investigation.

[2] Norman Bekkedahl and Russell B. Scott, "Specific heat of the synthetic rubber hycar-O.R.," J. Research Nat. Bur. Stand. **29**, 87 (1942), RP1487.
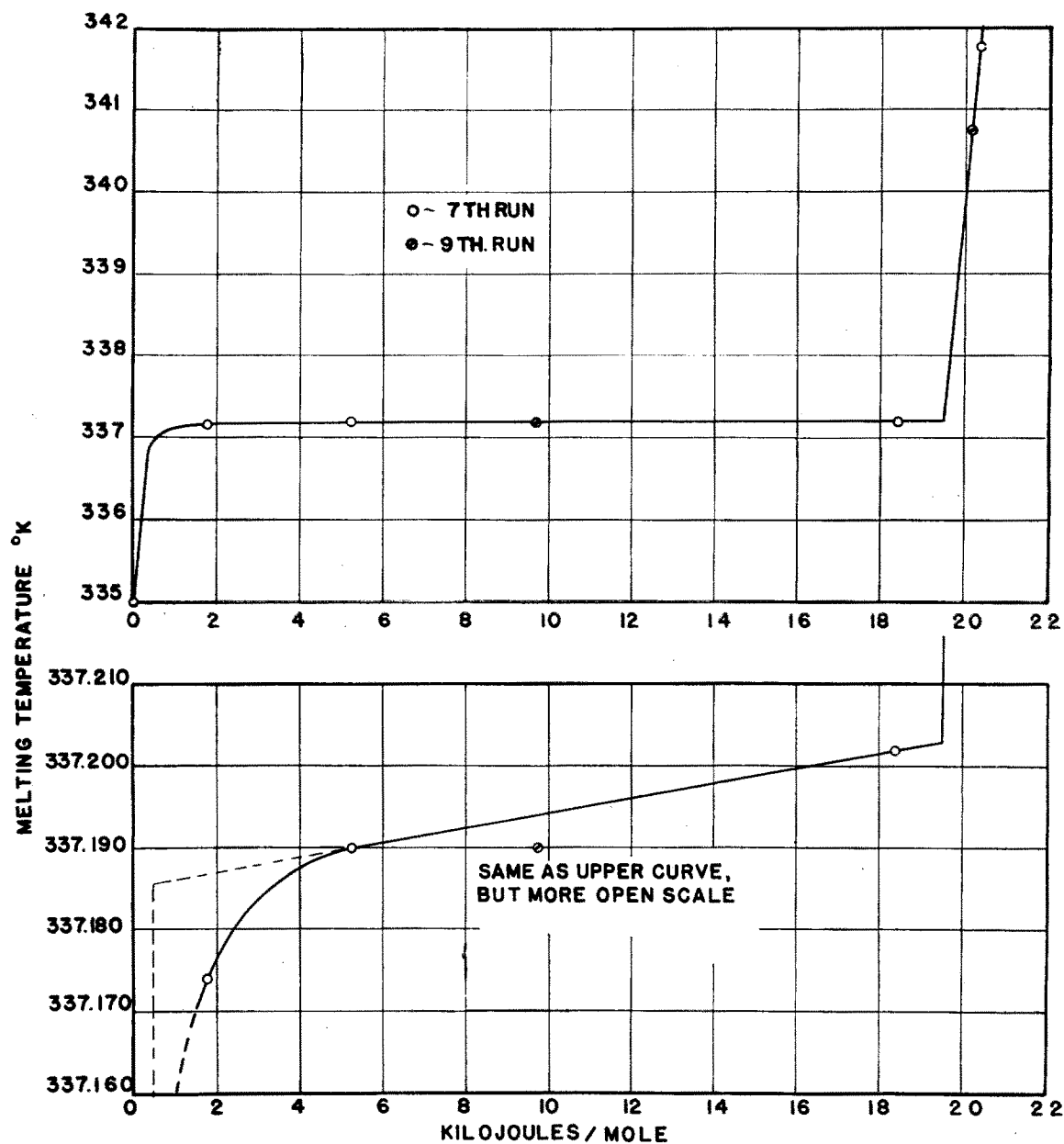
FIG. 1. Melting data for the UF$_6$ sample; the energy supplied is measured from an arbitrary zero (335°K).

with the 90 Pt:10 Rh resistance thermometer M4, which served also as a heater. The calorimeter was filled with UF$_4$ and soldered shut. When proved vacuum tight, a small protruding tube was opened, the calorimeter placed in a glass container and evacuated for about 48 hours. It was then filled with helium to a pressure of one atmosphere and quickly soldered shut in an atmosphere of helium. The calorimeter was weighed, installed in the cryostat, and measurements made. After removal the weight was checked and the calorimeter opened by unsoldering with a flame. After thoroughly brushing out the UF$_4$, the empty calorimeter, lid, and solder were weighed. The net weight was taken to be the difference between this value and the

gross weight of the unopened calorimeter. The values, after correction to vacuum, are

UF$_4$	123.849 g
He (calculated)	0.005 g
Tare weight	188.060 g.

Taking the molecular weight to be 314.07, the calorimeter contained 0.39433 mole of UF$_4$.

To check the weighings, the removed UF$_4$ was weighed. It weighed somewhat more than expected and proved to be gaining weight at a rate of more than 1 mg min.$^{-1}$. The weight was observed at intervals for several days. After an initial rise of about 450 mg, the change was found to be erratic. It is attributed to absorption of water vapor from the air. It is thought that any water in the sample in the calorimeter would have been substantially removed by the initial two-day evacuation, so that the results are not in error from this source. The tare heat capacity had been determined previous to the present measurements, but a correction was made for a small difference in the weight of solder used to close the calorimeter.

The UF$_6$ was measured in a special fluted copper calorimeter. The corrugations in this calorimeter (see Fig. 2) permitted it to be deformed by the material, which undergoes a very large expansion at or just below the melting point. The corrugated design proved to be very necessary. After the measurements the calorimeter showed marked distortion, and immersion in water showed a volume increase of about ten percent. A 95 Sn:5 Sb solder was used for all joints that came in contact with UF$_6$. Temperatures were measured with a pure platinum resistance thermometer (thermometer P). The heater consisted of a resistance of about 50 ohms of AWG 34 double glass insulated constantan wire wound bifilarly on the outside of the platinum case of the thermometer. It was imbedded directly in solder, where it worked satisfactorily without developing grounds.

The short filling tube was connected to a glass train consisting of a trap containing the supply of UF$_6$, an empty bulb, and a bulb full of helium. By opening glass break seals and suitably changing temperatures the charge was transferred first to the empty bulb and then collected in the calorimeter as a liquid. After cooling below the

triple point, helium was admitted above the UF$_6$, the small copper tube was pinched off and immediately soldered shut. On completion of the measurements the gross weight of calorimeter and charge was determined. Then the calorimeter was drilled open in an atmosphere of dry CO$_2$, transferred to a helium atmosphere, and attached to a vacuum system. The UF$_6$ was vaporized into a dry-ice trap, after which the emptied calorimeter was filled with helium and closed with a weighed amount of solder. The tare weight was then determined. Making due allowance for the small amounts of solder, drill chips, and helium fillings, the weights (reduced to vacuum) are as follows:

UF$_6$	128.565 g
Tare weight	71.211 g.

Taking the molecular weight to be 352.07, the calorimeter contained 0.36517 mole of UF$_6$. The material is known to attack copper, but a protective coating is formed which slows down the rate of attack. Most of the reaction probably took place as the result of the first filling, which was unsuccessful. Even attack by the sample whose heat capacity was measured would not necessarily cause error, because the tare heat capacity was measured after the UF$_6$ was removed. If as a result of attack some of the UF$_6$ was reduced to UF$_4$ and copper fluoride was formed, these products, being non-volatile, would have remained in the calorimeter during the tare measurements, so that their heat capacities would have been eliminated from the net heat capacity.

The electrical measurements, control circuits, and procedures for both UF$_4$ and UF$_6$ were
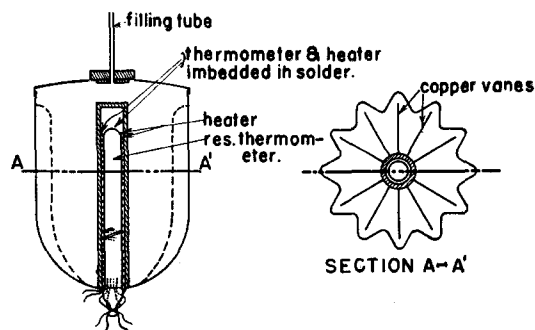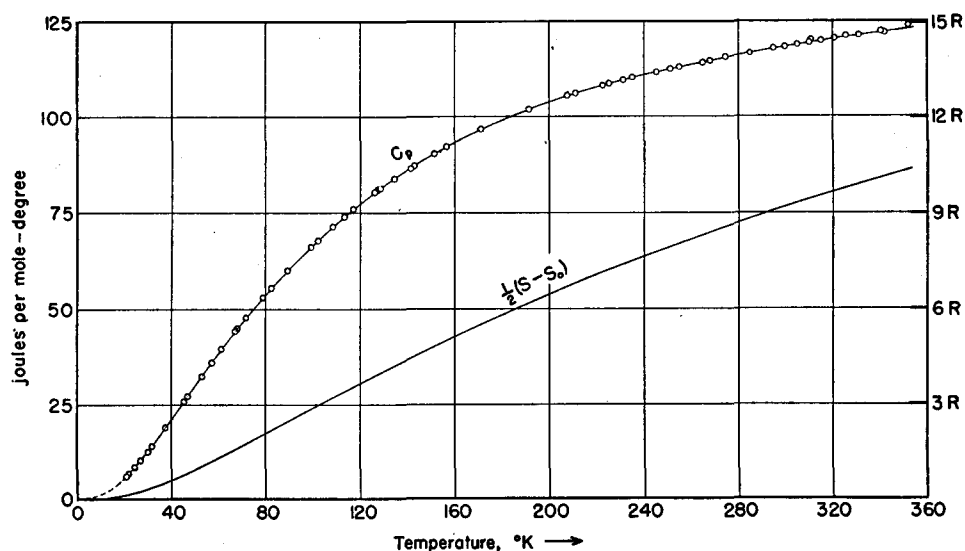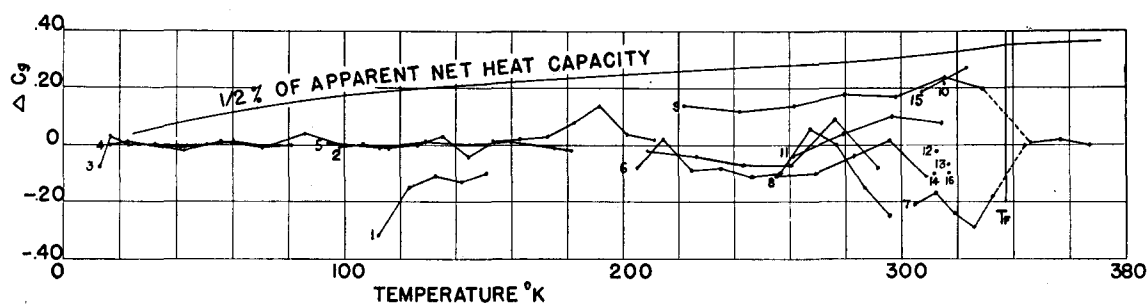

FIG. 2. Diagram of the sample container used for UF$_6$.

FIG. 3. Molar heat capacity and entropy of UF_4.

FIG. 4. Deviations of observed gross heat capacity of UF_6 from the smooth tabular values of heat capacity. The runs are numbered to indicate the order in which they were taken.

similar to those described in a recent publication.[3]

The observed heat capacities were plotted as deviations from approximate functions. Smooth curves were drawn through the points, from which values were read at five-degree intervals. These were added to the approximate functions to give tables of both gross and tare heat capacities, from which a table of net heat capacities was obtained by subtraction. Computations were made so as to avoid error resulting from the finite temperature interval of each measurement. A number of approximate functions were used. For example, the heat capacity of the calorimeter containing UF_6 was repre-

sented below 165°K, by C (approximate, j deg.$^{-1}$) $= 80D(x)$, with x, the argument of the Debye function, set equal to $350/(T+16)$. After removal of the UF_6 the tare heat capacity was represented throughout the entire temperature range by C (approximate, j deg.$^{-1}$) $= 27D(x)$, with $x = 315/T$.

The scattering of the data for UF_4 was found by reading the distance of each point from the smooth curve of a deviation plot of the gross heat capacity. These values were divided by the number of moles of UF_4 in the calorimeter, and gave a mean deviation from the smooth curve of $0.06 - j$ mole^{-1} deg.$^{-1}$. Figure 3 is a graph of the molar heat capacity showing the sixty experimental points.

For UF_6 the deviations were found by a different procedure, somewhat preferable to that

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[3] Russell B. Scott, Cyril H. Meyers, Robert D. Rands, Jr., Ferdinand G. Brickwedde, and Norman Bekkedahl, "Thermodynamic properties of 1,3-butadiene in the solid, liquid, and vapor states," J. Research Nat. Bur. Stand. 35, 39 (1945), RP1661.

used for UF$_4$. The gross heat capacity table was integrated over the interval of each individual measurement, the result subtracted from the actual energy input, and the difference divided by ΔT. This gives the deviation of each experimental point from the table. The deviations of the ninety-six experimental points are shown in Fig. 4. They refer to the actual gross heat capacity rather than the molar heat capacity. The mean deviation is 0.08$-$j deg.$^{-1}$.

In the case of UF$_6$ it was necessary to apply a vapor correction both to the heat capacity and to the heat of fusion. This was done according to the procedure outlined in reference 4. The vapor-pressure data of Crist and Weinstock and those of Haworth and Simon were represented by two equations intersecting at 337.212°K (64.052°C) which is the triple-point temperature found in the present investigation. The equations are: $\log_{10}P$ (solid, mm Hg) $=(-2559.5/T)$ $+10.648$ and $\log_{10}P$ (liquid, mm Hg) $=(-1511.3/T)+7.5396$. These equations give a triple point pressure of 1142-mm Hg. The vapor correction reaches about five percent of the net heat capacity just below the triple point, but drops again when the material melts because of the great reduction in vapor volume. The volume of the calorimeter after measurements were completed was determined from the mass of water required to fill it. The value found, 56.27 cm³, was used in all the corrections. The specific volume of the liquid was computed from the

TABLE I. Vapor correction to the heat capacity of UF$_6$, and contribution of $\int V dP$ to the enthalpy. C is the uncorrected heat capacity and C_{sat} the desired heat capacity of saturated condensed phase. Vapor pressures were computed from the equations given in the text.

T °K	p mm Hg	$C-C_{\text{sat}}$ j mole^{-1} deg.$^{-1}$	$\int V dP$ j mole^{-1}
230	0	0	
235	1	0	
240	1	0.03	
245	2	0.03	
250	3	0.06	
255	4	0.08	
260	6	0.14	
265	10	0.19	
270	15	0.25	
275	22	0.36	
280	32	0.52	
285	47	0.68	0
290	66	0.96	1
295	94	1.26	1
300	131	1.67	1
305	180	2.19	2
310	246	2.85	2
315	333	3.64	3
320	446	4.66	4
325	592	5.89	6
330	780	7.39	7
335	1018	9.20	10
337.212	1142	—	11
340	1243	2.08	12
345	1442	2.27	15
350	1666	2.41	18
355	1916	2.60	21
360	2195	2.77	24
365	2507	2.90	28
370	2851	3.09	33

equation

$$v/v_f = \rho_f/\rho = 1 + 1.727 \times 10^{-3}(T-T_f) + 3.59 \times 10^{-6}(T-T_f)^2,$$

taken from the work of Wechsler and Hoge,[5]

FIG. 5. Molar heat capacity and entropy of UF$_6$.
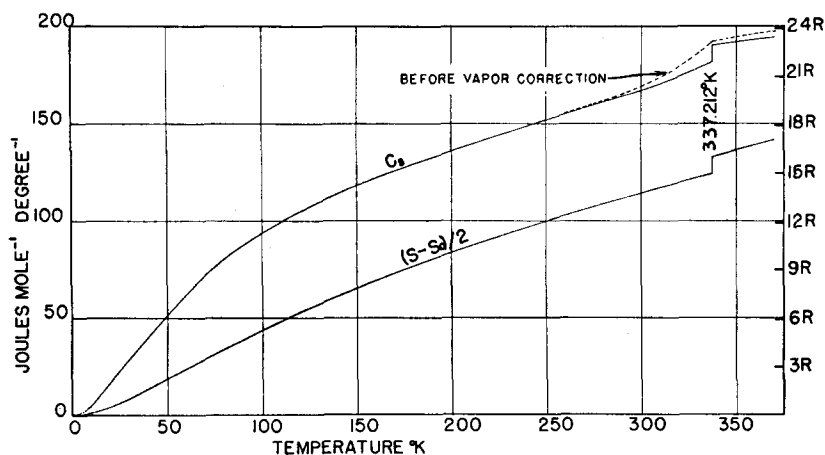
[4] Harold J. Hoge, "Heat capacity of a two-phase system, with applications to vapor corrections in calorimetry," J. Research Nat. Bur. Stand. 36, 111 (1946), RP1693.
[5] Martin T. Wechsler and Harold J. Hoge, Report A-456; see also the later report A-1591.

TABLE II. Thermodynamic properties of UF₄; $S-S_0 = \int (C_p/T)dT$; $H-H_0 = \int C_p dT$; the energy unit is the international joule ($=1/4.1833$ cal.).

T °K	C_p j mole⁻¹ deg.⁻¹	$S-S_0$ j mole⁻¹ deg.⁻¹	$H-H_0$ j mole⁻¹
0	0	0	0
5	0.08	0.03	0.1
10	0.68	0.22	1.7
15	2.24	0.76	8.5
20	5.13	1.7	26.1
25	7.93	3.2	58.1
30	11.80	4.9	107.3
35	16.15	7.1	177.2
40	20.49	9.5	268.8
45	24.84		
50	29.22	15.0	517.2
55	33.51		
60	37.72	21.1	852
65	41.84		
70	45.81	27.6	1270
75	49.55		
80	53.14	34.2	1766
85	56.59		
90	59.88	40.8	2331
95	63.00		
100	65.96	47.4	2961
105	68.84		
110	71.60	54.0	3649
115	74.26		
120	76.76	60.5	4391
125	79.19		
130	81.50	66.8	5183
135	83.66		
140	85.66	73.0	6020
145	87.57		
150	89.39	79.0	6895
155	91.14		
160	92.83	84.9	7806
165	94.42		
170	95.92	90.6	8750
175	97.33		
180	98.66	96.2	9724

TABLE II.—*Continued*.

T °K	C_p j mole⁻¹ deg.⁻¹	$S-S_0$ j mole⁻¹ deg.⁻¹	$H-H_0$ j mole⁻¹
185	99.93		
190	101.12	101.6	10,723
195	102.24		
200	103.32	106.8	11,745
205	104.36		
210	105.35	111.9	12,789
215	106.32		
220	107.24	116.9	13,852
225	108.10		
230	108.92	121.7	14,933
235	109.71		
240	110.47	126.3	16,030
245	111.20		
250	111.89	130.9	17,142
255	112.56		
260	113.20	135.3	18,267
265	113.81		
270	114.41	139.6	19,405
273.16	114.80	140.9	19,767
275	115.03		
280	115.63	143.8	20,556
285	116.20		
290	116.75	147.8	21,717
295	117.28		
298.16	117.62	151.1	22,674
300	117.81	151.8	22,890
305	118.33		
310	118.84	155.7	24,074
315	119.35		
320	119.85	159.5	25,267
325	120.33		
330	120.81	163.2	26,470
335	121.28		
340	121.74	166.8	27,683
345	122.20		
350	122.64	170.4	28,905

with a triple-point density $\rho_f = 3.674$ g cm⁻³ taken from Priest.[6] For the solid the data were scanty, and a density of 4.93-g cm⁻³ was used at all temperatures. Better values of some of these quantities have since become available, but because of the large uncertainty in the volume of the calorimeter at any particular time the correction has not been recalculated. During the entire time it was in use, which included one unsuccessful filling, the calorimeter increased in volume by 5.4 cm³. In view of this the vapor correction can hardly be considered accurate to better than fifteen percent. Table I contains values of the vapor correction. In Fig. 5 the uncorrected heat capacity is shown by the dashed curve.

Two determinations of the triple-point temperature and heat of fusion of UF₆ were made. The

[6] Homer F. Priest, Report A-139.

results are plotted in Fig. 1. The second gave a somewhat lower temperature and a heat of fusion lower by 1.6 per mille. Possibly the material had become less pure. The mean of the two runs gave a value of 19,193 j mole⁻¹ for the heat of fusion after making the vapor correction discussed above. Corrections were made for the heat capacity of the material below and above the triple point. From Fig. 1 the change in melting temperature as the last half of the material melts in 9 millidegrees. Adding this amount to the highest point in the melting range gives 337.212°K for the triple point of pure UF₆.

THERMODYNAMIC PROPERTIES

The calculation of the heat-capacity tables has already been outlined. Extrapolation of the molar heat capacity of UF₄ from 20° to 0°K was performed with the equation $C = 3R[D(150/T) + 0.0041T^3]$. Extrapolation of the molar heat capacity of UF₆ from 14° to 0°K was performed

TABLE III. Thermodynamic properties of UF_6; C_{sat} is the heat capacity of 1 mole of condensed phase in equilibrium with saturated vapor; $H-H_0 = \int C_{sat} dT + \int V dP$; $S-S_0 = \int (C_{sat}/T) dT$; for vapor corrections and $\int V dP$, see Table I; the energy unit is the international joule ($=1/4.1833$ cal.).

T °K	C_{sat} j mole⁻¹ deg.⁻¹	$H-H_0$ j mole⁻¹	$S-S_0$ j mole⁻¹ deg.⁻¹	$T(S-S_0)$ j mole⁻¹
0	0	0	0	0
20	17.00	117.1	8.2	164
25	23.14	217.6	12.7	318
30	28.95	347.9	17.4	522
35	34.59	506.8	22.3	780
40	40.31	694.0	27.3	1092
45	46.01	909.8	32.3	1454
50	51.62	1154	37.5	1875
55	57.13	1426	42.7	2348
60	62.33	1725	47.9	2874
65	67.23	2049	53.1	3452
70	71.80	2396	58.2	4074
75	76.24	2767	63.3	4748
80	80.32	3158	68.4	5472
85	84.24	3570	73.4	6239
90	87.80	4000	78.3	7047
95	91.03	4447	83.1	7894
100	94.07	4910	87.8	8780
105	96.92	5388	92.5	9712
110	99.65	5879	97.1	10,681
115	102.34	6384	101.6	11,684
120	104.91	6902	106.0	12,720
125	107.35	7433	110.3	13,788
130	109.73	7976	114.6	14,898
135	112.00	8530	118.8	16,038
140	114.20	9096	122.9	17,206
145	116.28	9672	126.9	18,400
150	118.39	10,258	130.9	19,635
155	120.38	10,855	134.8	20,894
160	122.33	11,462	138.7	22,192
165	124.27	12,079	142.4	23,496
170	126.14	12,705	146.2	24,854
175	128.00	13,340	149.9	26,232
180	129.80	13,985	153.5	27,630
185	131.45	14,638	157.1	29,064
190	133.31	15,299	160.6	30,514
195	134.98	15,970	164.1	32,000

TABLE III.—*Continued.*

T °K	C_{sat} j mole⁻¹ deg.⁻¹	$H-H_0$ j mole⁻¹	$S-S_0$ j mole⁻¹ deg.⁻¹	$T(S-S_0)$ j mole⁻¹
200	136.60	16,649	167.5	33,500
205	138.24	17,336	170.9	35,034
210	139.96	18,032	174.3	36,603
215	141.31	18,735	177.6	38,184
220	143.17	19,446	180.9	39,798
225	144.73	20,165	184.1	41,422
230	146.26	20,893	187.3	43,079
235	147.82	21,628	190.4	44,744
240	149.36	22,371	193.6	46,464
245	150.89	23,122	196.7	48,192
250	152.40	23,880	199.7	49,925
255	153.88	24,646	202.8	51,714
260	155.38	25,419	205.8	53,508
265	156.86	26,199	208.7	55,306
270	158.37	26,987	211.7	57,159
273.16	*159.32*	*27,490*	*213.5*	*58,320*
275	159.87	27,783	214.6	59,015
280	161.30	28,586	217.5	60,900
285	162.72	29,396	220.4	62,814
290	164.15	30,214	223.2	64,728
295	165.71	31,039	226.0	66,670
298.16	*166.75*	*31,565*	*227.8*	*67,921*
300	167.35	31,871	228.8	68,640
305	169.10	32,714	231.6	70,638
310	170.96	33,564	234.4	72,664
315	172.88	34,424	237.1	74,686
320	174.85	35,295	239.9	76,768
325	176.82	36,176	242.6	78,845
330	178.93	37,066	245.3	80,949
335	181.01	37,969	248.0	83,080
337.212	181.92	38,371	249.2	84,033
melts	($L=19,193$,	$L/T_f=56.9$)		
337.212	190.73	57,564	306.1	103,221
340	191.09	58,098	307.7	104,618
345	191.78	59,058	310.5	107,122
350	192.52	60,022	313.3	109,655
355	193.26	60,989	316.0	112,180
360	193.83	61,960	318.7	114,732
365	194.46	62,935	321.4	117,311
370	195.04	63,914	324.0	119,880

with the equation $C = 3R[D(73/T) + E(110/T)]$. The symbols D and E represent the Debye and Einstein specific heat functions. The heat capacity given for UF_6 is C_{sat}, which refers to the condensed phase in equilibrium with saturated vapor. Since UF_4 has no appreciable vapor pressure in the range of our measurements, C_{sat} and C_p are not significantly different for it, and the curve in the graph has been labeled C_p.

Table II gives the heat capacity, enthalpy, and entropy of UF_4 at uniform temperature intervals. Table III gives the same quantities for UF_6, and also $T(S-S_0)$. Enthalpies were computed by integrating $dH = C_{sat} dT + V dP$ along the saturation curve, using Simpson's rule and the values of C in the tables. The contribution of the last term was nearly negligible, as may

be seen from Table I. Entropies were obtained along the same path by a similar integration of $dS = (C/T) dT$. The heat capacities and entropies are plotted in Figs. 3 and 5.

DISCUSSION OF RESULTS

The measurements on UF_4 gave no particular difficulty. Those made on UF_6 were complicated by the deformation of the calorimeter which made the vapor corrections uncertain. There was some lack of reproducibility in the heat capacity of UF_6. This may be seen in Fig. 4, where the initial points of the various runs are numbered in chronological order. Between about 300°K and the triple point there was a tendency for the calorimeter to drift down after it would normally have come to temperature equilibrium. Above

the triple point the tendency was to drift upward. The upward drift may have been due to chemical reaction. For this reason the calorimeter was kept at high temperatures no longer than absolutely necessary, and it is thought that change in chemical composition produced by reaction was not serious. Some tests were made to relate the irregularities in heat capacity with past thermal history, but these were inconclusive.

Considering errors arising from the experimental measurements as well as those resulting from possible impurities, the data for UF_6 are not considered reliable to much better than one percent. This is about equal to the extreme spread of the points in Fig. 4. The errors in the UF_4 data are probably only about half as large, but the uncertainty resulting from impurity is larger, so that the over-all accuracy for the two compounds is probably about the same. The errors in the other quantities in the tables are probably about the same as those in the heat capacities from which they are derived.

The Vapor Pressure of Uranium Hexafluoride*

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The vapor pressure of uranium hexafluoride, UF_6, has been measured from 273°K to 358°K. The measurements were made by a null method in an all metal apparatus with a brass sylphon bellows. The data are represented by the equations:

$$\text{Solid} - \text{vapor } \log_{10}P(\text{mm Hg}) = -3.77962 \log_{10}T - (3123.479/T) + 21.87103,$$
$$\text{Liquid} - \text{vapor } \log_{10}P(\text{mm Hg}) = -3.72662 \log_{10}T - (2065.679/T) + 18.60033.$$

The constants in the equations were adjusted so that the equations would give the same heat of fusion and triple-point temperature as was determined by Brickwedde, Hoge, and Scott. The vapor pressure at the triple point is 1133 ± 7 mm. The sublimation point at which the vapor pressure is 1 atmosphere is 56.5°C. The heat of vaporization has been calculated using the Berthelot equation to obtain the vapor volume. From this and the entropies measured by Brickwedde, the absolute entropy of the gas has been calculated.

INTRODUCTION

THE vapor pressure of uranium hexafluoride had been previously measured by Ruff and Heinzelmann[3] over the temperature range 37–56.2°C. Their results are not precise showing large deviations from linearity in a $\log P$ against $1/T$ plot. The vapor pressures obtained by them are always higher than those obtained in the present work, the percentage differences being very much greater at lower pressure. This situation could be explained by the presence of a volatile impurity in their sample, e.g., HF. The purpose of the present work was to improve the accuracy of these measurements as well as to extend the range of measurement.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. This consists of a reservoir in a thermostat and a brass sylphon bellows for the measurement of pressure by a null method. At the time the experiments were made, it was thought that only a limited number of metals were safe materials for use with UF_6. Accordingly, the vessels and connecting tubes were of copper, the pack-

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