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THERMODYNAMIC PROPERTIES OF
URANIUM MONONITRIDE

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TABLE OF CONTENTS

	<u>Page No.</u>
Table of Figures -----	3
Abstract -----	5
I. Introduction -----	9
II. Experimental -----	10
A. Method -----	10
B. Apparatus -----	10
C. Material -----	11
D. Experimental Procedure -----	11
III. Results and Discussion -----	12
A. Nitrogen Pressure over UN -----	12
B. Second-Law Analysis -----	12
C. Third-Law Analysis -----	13
IV. Summary -----	14
V. References -----	15

TABLE OF FIGURES

<u>Fig. No.</u>	<u>Title</u>	<u>Page No.</u>
1	Schematic Diagram of Vapor Pressure Apparatus -----	17
2	Uranium Nitride Effusion Data -----	18
3	Pressure of Nitrogen Over UN _(s) -----	19
4	Third-Law Calculations for the Reaction UN _(s) → U _(l) + 1/2 N ₂ (g) -----	20
5	Standard Heat of Formation of UN _(s) -----	21

ABSTRACT

The partial pressure of nitrogen over uranium mononitride was measured by Knudsen effusion experiments over the temperature interval 1910K to 2265K. A linear least squares fit of these data is given by:

$$\log_{10} P_{N_2} \text{ (atm)} = 8.279 - 2.874 \times 10^4 T^{-1}$$

where T is in °K.

Based on the decomposition mechanism

the second-law enthalpy and entropy changes are given by $\Delta H_{2100} = 65.9 \text{ kcal/mole}$ and $\Delta S_{2100} = 19.0 \text{ e.u.}$ A third-law analysis results in a standard heat of formation at 298K of $\Delta H_{f298}^{\circ} = -74.4 \pm 2.0 \text{ kcal/mole.}$

THERMODYNAMIC PROPERTIES OF URANIUM MONONITRIDE

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DATE

I. INTRODUCTION

Uranium mononitride is a potential high temperature nuclear reactor fuel having the highest uranium density of all known uranium compounds. Its thermal conductivity far exceeds UO_2 , and is considerably higher than UC.¹ Interest in UN, however, is often dampened by manifestations of low thermal stability and by a lack of experimental thermodynamic data. It is the purpose of this study to provide a quantitative measure of the thermal stability of UN and to establish some of its thermodynamic properties.

Olson and Mulford² determined the decomposition pressure of the mononitride over the temperature range 2500C to 2850C by observing liquid formation as a function of nitrogen pressure. At a nitrogen pressure of 2.5 atm or greater, congruent melting occurred. The melting point was found to be $2850\text{C} \pm 30\text{C}$. These results were verified by Keller³, $2885\text{C} \pm 30\text{C}$, and by this laboratory⁴, $2860\text{C} \pm 30\text{C}$.

Langmuir evaporation experiments conducted in this laboratory⁵ indicated that uranium mononitride decomposes to nitrogen and uranium, losing nitrogen at a much faster rate than uranium. The surface of a UN specimen was almost completely covered with uranium after being heated for 30 minutes at 1870C in vacuum. X-ray diffraction analysis indicated that recombination of nitrogen and uranium on the cold walls of the apparatus did not occur. Since nitrogen is lost faster than uranium, the decomposition mechanism was concluded to be

Keller⁶ reported nitrogen pressure measurements in an equilibrium system capable of measurements down to 10^{-7} atmospheres. He reports that the nitrogen pressure over UN in the range 10^{-7} atm. to 2.5 atm. may be expressed by the formula

$$\log_{10} P_{\text{N}_2} = 35.1854 - 18.571 \times 10^{-4} \left(\frac{1}{T}\right) + 2.98 \times 10^8 \left(\frac{1}{T}\right)^2 - 18.14 \times 10^{10} \left(\frac{1}{T}\right)^3 \quad (2)$$

Cavett and Bonham⁷ determined an enthalpy of decomposition of 68.7 ± 2.2 kcal/mole for the mononitride by mass spectrometric Knudsen studies in the temperature range 1600C to 2000C. Although their studies did not yield values for nitrogen pressure, they did indicate that the gaseous species over UN in this temperature range are monatomic uranium and molecular nitrogen. The heat of formation of UN was determined by Gross et al.⁸, Neumann et al.⁹, and Hubbard¹⁰ by combustion calorimetry. They reported values for ΔH_{f298}° of -69.6 ± 0.4 , -68.46 and -70.95 kcal/mole, respectively.

Westrum¹¹ has measured the low temperature (10K to 350K) heat capacity of UN and arrived at $S_{298}^{\circ} = 14.93$ e.u. Rand and Kubaschewski¹² estimated the standard entropy of $\text{UN}_{(s)} S_{298}^{\circ}$ to be 13.0 ± 1.5 e.u.

Harrington¹³ has measured the heat capacity of UN from 0C to 1200C and reports

$$C_p = 44.33 \times 10^{-3} + 9.38 \times 10^{-6} T - 333.5 T^{-2} \text{ cal/gm-}^{\circ}\text{K}$$

Equilibrium pressures of the higher nitride phases were determined by Lapat et al.¹⁴ in the composition range $\text{UN}_{1.1}$ to $\text{UN}_{1.7}$ and the temperature range 600C to 1100C.

II. EXPERIMENTAL

A. Method

The vapor pressures reported in this work were determined by the method of Knudsen^{15, 16, 17} wherein the pressure is related to the rate of effusion from a small orifice in a crucible containing the material under investigation. The pressure is calculated by the equation

$$P = \frac{Z}{44.33 \text{ kAt}} (TM)^{1/2} \quad (3)$$

where P is the pressure of the gaseous species expressed in atmospheres; Z, the number of moles of the species effusing through an orifice with an area of A square centimeters in t seconds; k is the Clausing coefficient¹⁸ used to correct for non-ideal orifice geometry; M is the molecular weight of the effusing species, and T is the temperature in Kelvin degree

The individual pressure-temperature points were plotted as the logarithm of pressure versus reciprocal temperature and a linear least squares equation determined. The pressure data were analyzed by both second-law and third-law methods to give the values of thermodynamic variables for the process.

The second-law method involves the integrated form of the Clausius-Clapeyron equation,

$$\left[\frac{\partial(\Delta F^0/T)}{\partial T} \right]_P = \frac{-\Delta H^0}{T^2} \quad (4)$$

In the third-law method the heat of reaction at some reference temperature, θ , is obtained directly from each experimental pressure by using the following relationship:¹⁹

$$\Delta H^0_{\theta} = \left[T - R \ln K - \left(\frac{\Delta F^0_T - \Delta H^0_{\theta}}{T} \right) \right] \quad (5)$$

where K is the equilibrium constant for the reaction, $\Delta F^0_T - \Delta H^0_{\theta}/T$ is the free energy function of the products minus the free energy function of the reactants, and T is the reaction temperature in $^{\circ}\text{K}$. In this method free energy functions must be available or calculated from entropy and heat capacity data.

B. Apparatus

The Knudsen apparatus included a gas collection and measuring system since one of the products of the decomposition, N_2 , is non-condensable at room temperature. The apparatus is shown schematically in Fig. 1. The effusion cell was surrounded by a Vycor envelope fitted into a water cooled standard taper joint. Heating was accomplished with a 5 kw, 450 kilocycle induction generator. The system was evacuated using a two inch oil diffusion pump backed by a mercury diffusion pump. A Toepler pump fed the collected gas to a calibrated volume measuring system. With liquid nitrogen trapping, the ambient pressure at the cell was kept below 10^{-7} mm Hg with pressures as high as 10 mm Hg in the measuring system. Pressures in the calibrated volume were read at regular intervals with a McLeod gauge. Therefore, for a given isothermal run, using pressure-volume-temperature relationships, the rate of N_2 effusion from the cell could be determined.

Three cell materials were used; tungsten, tantalum-lined tungsten and tantalum carbide. The tungsten cells, 3/4 inch diameter by 1 5/8 inch high, contained a 1/2 inch diameter by 3/4 inch high specimen cavity. Cell covers were fabricated from 0.005 inch tungsten sheet and held in place by a snap ring. A black body hole, 1/16 inch diameter by 7/16 inch deep, was drilled into the bottom of each cell. Tantalum liners for the tungsten cells were made from 0.025 inch sheet and their dimensions were such that a snug fit was obtained. When using these liners, the cell cover (0.005 inch Ta foil) was attached by welding. The black body hole in the original tungsten cell was lengthened so that it penetrated into the specimen cavity and temperature measurements could be taken directly on the bottom of the tantalum liner.

Tantalum carbide knudsen cells were fabricated by hot pressing high density (>90% of theoretical) cylinders and using diamond grinding and drilling techniques to get the desired configuration. Overall dimensions were similar to those of the tungsten cell. In this case, the cell cover was fitted to the cell body by grinding mating champhers and diamond lapping the two pieces together. The black body holes were 1/32-inch diameter by 1/4 inch deep.

In all cases cell orifices were approximately 1/16 inch diameter and Clausing factor values for the orifice geometries ranged from 0.3 to 0.9 as calculated from the data of Dushman.¹⁸

Temperatures were measured using a disappearing filament micro optical pyrometer which was calibrated against a National Bureau of Standards certified lamp with the sight glass and first surface mirror interposed. The effect of varying the angle of incidence of the mirror was evaluated and was found to be negligible. The relative temperature profile of the cell was measured by sighting on the surface along both the radial and axial directions and was found to vary by not more than 20C. The cell temperature was very stable (± 5 C) with respect to time at a given control setting on the high frequency generator.

C. Material

The uranium mononitride used was prepared by reacting uranium hydride powder with nitrogen gas, and pressing and sintering the product. The sintered pellets, 95-98% of theoretical density were crushed into coarse chips under an inert atmosphere prior to loading into a cell. Metallographic examination of the as-sintered material revealed only a single phase structure. X-ray diffraction analysis also indicated a single phase, face-centered-cubic compound with a lattice parameter of 4.89 Å. Chemical analyses for the major impurities showed 500 to 2000 ppm oxygen and approximately 1500 ppm carbon. After the vapor pressure measurements, free uranium was identified metallographically and by X-ray diffraction. The lattice parameter of the UN phase, however, was unchanged.

D. Experimental Procedure

Prior to specimen loading, each cell was thoroughly outgassed at a temperature at least 100C higher than the maximum temperature of any experimental run. The rate of pressure increase in the gas collection system containing an empty cell was determined as a function of cell temperature. The cells were loaded with 0.6 to 3.6 grams of UN chips under an argon atmosphere and the system evacuated. Background pressures of 10^{-7} to 10^{-8} mm Hg were obtained at room temperature after bakeout. System pressures were maintained in the 10^{-5} to 10^{-6} mm Hg range at elevated temperatures.

The cell temperature was slowly raised to the desired range and after achieving isothermal conditions, the amount of gas effusing from the cell during a specified time interval was measured. The pressure increase in the calibrated volume at a given temperature was found to be linear with time. A series of runs at varying temperatures was made on each specimen before replacing it with a new cell and/or specimen. The apparatus was baked out and evacuated overnight between cell and specimen changes.

III. RESULTS AND DISCUSSION

A. Nitrogen Pressure over UN

Fifty-eight nitrogen effusion experiments were made; 32 in tantalum carbide cells, 17 in tungsten cells and 9 in tantalum lined tungsten cells over the temperature range, 1645C to 1992C. Equation (3) was used to calculate the nitrogen pressures and the pertinent data are shown in Fig. 2. The logarithm of nitrogen pressure is plotted as a function of reciprocal absolute temperature in Fig. 3 where the data are identified according to the cell material and Clausing factor. A linear least squares fit of these data is given by

$$\log_{10} P_{N_2} \text{ (atm)} = 8.279 - 2.874 \times 10^4 T^{-1} \quad (6)$$

Where T is in °K .

The nitrogen pressures are compared in Fig. 3 with those obtained by Keller⁶ who measured the decomposition temperature in the pressure range 10^{-7} to 2.5 atm. The agreement is quite good, considering that independent methods were used at fairly high temperatures. However, the slope of Keller's curve is somewhat different than that reported here.

Several data points were determined for the pressure of uranium over uranium mononitride by chemically analyzing the deposit on the Vycor tube surrounding the Knudsen cell after an isothermal run. However, because of the difficulties involved in containing the liquid uranium within the cell, these data are not considered reliable and have been omitted.

B. Second-Law Analysis

The nitrogen results were first analyzed by the second-law method. The standard state free energy change for the decomposition process

can be written

$$\Delta F_T = -RT \ln P_{N_2}^{1/2} \quad (7)$$

if the activities of $UN_{(s)}$ and $U_{(l)}$ are taken as unity. The nitrogen solubility in liquid uranium is probably very low at the low pressures observed in this study, 10^{-5} to 10^{-7} atm. Keller²⁰ has reported a solubility of UN in liquid uranium of less than 10 m/o under 1 atm nitrogen pressure in the temperature range of this investigation. One would expect the solubility to be even lower at pressures below 1 atm. Therefore, correction for nitrogen solubility in liquid uranium is not considered to be significant in relation to the scatter in the measured nitrogen pressures. Variations in cell material did not affect the scatter in nitrogen activity.

A plot of ΔF_T versus temperature yields a straight line, the slope of which is ΔS_T and whose intercept is ΔH_T . ΔC_p is assumed to be zero in the temperature range of interest. A linear least squares analysis resulted in the expression

$$\Delta F_T = 65.9 \times 10^3 - 19.0 T \quad (1918K \text{ to } 2265K) \quad (8)$$

Therefore, the average enthalpy change for reaction (1) is 65.9 kcal/mole and the average entropy change is 19.0 e.u. in the range 1645C to 1992C.

Cavett and Bonham⁷, who have studied the intensity of the nitrogen peaks over UN_(s) as a function of temperature, reported a value of 68.7 ± 2.2 kcal/mole for ΔH_T in the range 1600C to 2000C. The slope of their data and that obtained in this work agree quite well.

The standard heat of formation of UN_(s) at 298K, ΔH_{f298}^0 , was calculated from the second-law ΔH_T , heat capacity data, and the relationship:

$$\Delta H_T - \Delta H_{298} = \int_{298}^T \Delta C_p dT \quad (9)$$

Heat capacities for U_(l), U_(s), and N_{2(g)} were taken from Stull and Sinke²¹ and Harrington's¹³ data on UN_(s) extrapolated to the temperature range of this investigation. The resultant value, $\Delta H_{f298}^0 = -61.9$ kcal/mole, is considerably lower than the calorimetrically determined values.

C. Third-Law Analysis

The enthalpy change for the decomposition reaction (1) at the melting point of uranium, ΔH_{1406} , was calculated by the third-law method using equation (5). The activity of UN_(s) and U_(l) was again assumed to be equal to unity so that ΔF_T could be calculated from equation (7). (1) Free energy functions for liquid uranium and nitrogen gas were taken from Stull and Sinke²¹. The free energy functions of UN_(s) were calculated from the heat capacity data of Harrington¹³ and Westrum's¹¹ entropy value. The pertinent data are shown in Fig. 4. The resultant value $\Delta H_{1406} = 79.7 \pm 1.0$ kcal/mole, (limits represent standard deviation of mean) was combined with the heat of fusion of uranium, 3.7 kcal/mole²¹, and equation (9) used to obtain the standard heat of formation of UN_(s) at 298K. This value, $\Delta H_{f298}^0(\text{UN}_{(s)}) = -74.4 \pm 2.0$ kcal/mole, is considerably higher than the figure obtained by the second-law method. Here the indicated limits represent the combined uncertainties in the experimental and thermodynamic data. The third-law value is considered more reliable than the second-law calculation since the former method uses each experimentally determined value of the vapor pressure to evaluate an independent value of the heat of vaporization.

Fig. 5 is a comparison of the standard heat of formation of UN_(s) determined in this laboratory with the published values of other investigators. In view of the differences in the method of determination, the agreement in the data is considered good.

IV. SUMMARY

A Knudsen effusion apparatus was used to measure the partial pressure of nitrogen over uranium mononitride. The N_2 pressure was found to vary from 1.7×10^{-7} to 3.9×10^{-5} atm over the temperature range 1645C to 1992C. Based on the decomposition mechanism

the second-law analysis yields a heat of reaction of $\Delta H_{2100} = 65.9$ kcal/mole and $\Delta S_{2100} = 19.0$ e.u. in the temperature range investigated.

The standard heat of formation of $UN_{(s)}$ derived from a third-law analysis is $\Delta H_{f298}^0 = -74.4 \pm 2.0$ kcal/mole.

V. REFERENCES

1. B. A. Hayes and M. A. DeCrescente, "Thermal Conductivity and Electrical Resistivity of Uranium Mononitride," Pratt & Whitney Aircraft Report No. PWAC-481, 1965. To be submitted to the Journal of Am. Ceramic Society.
2. W. M. Olson and R. N. R. Mulford, J. Phys. Chem. 67, 952 (1963)
3. D. L. Keller, "Development of Uranium Mononitride," Quarterly Progress Report for July-Sept., 1962, Battelle Mem. Inst. Report No. BMI-X-10019, (Oct., 1962).
4. B. M. Johnson and E. W. Terry, Private communication, unpublished results.
5. P. A. Vozzella, A. D. Miller, and M. A. DeCrescente, "The Thermal Decomposition of Uranium Nitride," Pratt & Whitney Aircraft Report No. CNLM-5066 (1963). Preliminary Report Presented at the American Nuclear Society Symposium on Nuclear Materials for Space Applications, Cinn., Ohio, April 17-19, 1963.
6. D. L. Keller, "Development of Uranium Mononitride," Quarterly Progress Report for January - March, 1964, Battelle Memorial Institute Report No. BMI-X-10083, April, 1964.
7. A. D. Cavett and R. W. Bonham, National Lead Company of Ohio, Report Number NLCO-885, June 30, 1963.
8. P. Gross, C. Hayman and H. Clayton, in Thermodynamics of Nuclear Materials, IAEA, Vienna, 1962, (p. 653).
9. B. Neumann, C. Kroeger and B. Haebler, Z. Anorg. Chem. 207, 145 (1932).
10. W. N. Hubbard, "Thermochemical Studies at Argonne National Laboratory," TID-15554, 1962.
11. E. F. Westrum, Jr. "International Symposium on Compounds of Interest in Nuclear Reactor Technology", Edited by J. T. Waber, P. Chiotti, and W. N. Miner, The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers. Edwards Bros., Inc., Ann Arbor, Michigan, 1964.
12. M. H. Rand and O. Kubaschewski, "Thermochemical Properties of Uranium Compounds," United Kingdom Atomic Energy Authority document no. AERE-T-3487 (1960).
13. L. C. Harrington, "Heat Capacity and Enthalpy of Uranium Mononitride from 0C to 1200C," Pratt & Whitney Aircraft Report No. CNLM-4461.
14. P. E. Lapat, J. J. Prusak, and R. B. Holden, "Thermodynamics of the Uranium-Nitrogen System," United Nuclear Corp. Report No. UNC-5077, Jan. 15, 1964.
15. M. Knudsen, Ann. Physik 28, 75 (1909).
16. Ibid, 999 (1909).
17. Ibid, 29, 179 (1909)
18. S. Dushman, "Scientific Foundations of Vacuum Technique," 2nd Ed., John Wiley and Sons, Inc., New York, 1962.

19. J. O'M. Bockris, J. L. White, and J. D. Mackenzie, "Physicochemical Measurements at High Temperatures," Academic Press Inc., New York, 1959.
20. D. L. Keller, "Development of Uranium Mononitride", Quarterly Progress Report for April-June, 1963, Battelle Memorial Institute Report No. BMI-X-10053, July, 1963.
21. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series No. 18 (American Chemical Society, Washington, D. C., 1956).

SCHEMATIC DIAGRAM OF V. P. APPARATUS

FIG 1

FIG 2

URANIUM NITRIDE EFFUSION DATA

Run No.		Temp. (°K)	Time (sec x 10 ⁻³)	Moles of N ₂ Collected (X 10 ⁶)	N ₂ Pressure (atm x 10 ⁶)
1	A	2189	1.44	55.6	11.8
2	A	2011	3.72	8.67	0.681
3	A	2189	1.56	46.6	9.10
4	A	2011	3.30	4.10	0.363
5	A	2189	1.80	74.4	12.6
6	A	2011	3.60	8.06	0.654
7	A	2069	1.86	10.8	1.72
8	A	2127	1.02	22.0	6.48
9	A	2247	0.36	57.3	49.1
10	A	1964	3.42	5.70	0.481
11	A	2089	1.86	26.7	4.27
12	A	2058	2.16	11.0	1.51
13	A	2125	1.80	30.0	5.01
14	A	2216	1.11	71.2	19.7
15	A	2266	0.63	88.0	43.3
16	A	2033	1.80	7.12	1.16
17	A	2147	1.62	49.6	9.25
18	B	1950	0.90	0.934	0.299
19	B	2036	0.72	2.17	0.884
20	B	2097	0.96	9.12	2.83
21	B	2130	0.36	19.8	16.5
22	B	2108	1.20	24.8	6.18
23	B	2189	0.90	41.3	14.0
24	B	2019	1.32	6.51	1.44
25	B	2266	0.90	63.2	21.8
26	B	2189	0.90	29.6	10.0
27	C	2242	1.20	73.0	50.0
28	C	1908	1.80	0.617	0.261
29	C	1969	1.80	1.49	0.640
30	C	2023	1.80	3.27	1.42
31	C	2072	1.80	8.19	2.97
32	C	2131	1.20	14.1	9.40
33	C	2183	1.20	30.7	20.8
34	C	2244	1.20	73.2	50.2
35	C	1909	1.80	0.616	0.259
36	C	1967	1.80	1.43	0.611
37	C	2020	1.80	3.50	1.52
38	C	2074	1.50	7.59	4.00
39	C	2124	1.20	12.8	8.52
40	C	2161	1.20	24.5	16.5
41	C	1985	1.80	1.69	0.726
42	C	2041	1.80	4.06	1.77
43	C	2096	1.80	9.62	4.25
44	C	2150	1.20	14.6	9.77
45	C	2202	0.90	25.5	23.1
46	D	2083	1.20	6.64	2.81
47	D	2165	0.90	14.4	8.24
48	D	2204	0.90	21.9	12.7
49	D	2087	1.02	5.33	2.65
50	D	2158	1.32	18.6	7.25
51	D	2198	1.02	27.2	13.9
52	D	2130	1.02	9.19	4.62
53	D	2025	1.86	3.36	0.902
54	D	2086	1.50	5.82	1.97
55	D	2132	1.38	9.15	3.40
56	D	2186	1.20	17.5	7.57
57	D	2039	1.38	2.64	0.959
58	D	1964	1.62	1.36	0.413

FIG 3

PRESSURE OF NITROGEN OVER $UN_{(s)}$

FIG 4

THIRD LAW CALCULATIONS FOR THE REACTION

Run No.		Temp. (°K)	ΔF_T^b (kcal/mole)	$-T\Delta f_{ef}$ (kcal/mole)	ΔH_{1406} (kcal/mole)
1	A ^a	2189	24.7	55.9	80.6
2	A	2011	28.4	51.5	79.9
3	A	2189	25.2	55.9	81.2
4	A	2011	29.6	51.5	81.1
5	A	2189	24.5	55.9	80.5
6	A	2011	28.5	51.5	79.9
7	A	2069	27.3	52.9	80.2
8	A	2127	25.3	54.4	79.6
9	A	2247	22.2	57.4	79.5
10	A	1964	28.5	50.3	78.8
11	A	2089	25.7	53.4	79.1
12	A	2058	27.4	52.7	80.1
13	A	2125	25.8	54.3	80.1
14	A	2216	23.9	56.6	80.4
15	A	2266	22.6	58.0	80.7
16	A	2033	27.6	52.0	79.6
17	A	2147	24.7	54.9	79.6
18	B	1950	29.1	50.0	79.1
19	B	2036	28.2	52.1	80.3
20	B	2097	26.6	53.6	80.2
21	B	2130	23.3	54.5	77.8
22	B	2108	25.1	53.9	79.0
23	B	2189	24.3	55.9	80.2
24	B	2019	27.0	51.7	78.7
25	B	2266	24.2	57.8	82.0
26	B	2189	25.0	55.9	81.0
27	C	2242	22.1	57.2	79.3
28	C	1908	28.7	48.9	77.7
29	C	1969	27.9	50.4	78.3
30	C	2023	27.1	51.8	78.9
31	C	2072	26.2	53.0	79.2
32	C	2131	24.5	54.5	79.0
33	C	2183	23.4	55.8	79.2
34	C	2244	22.1	57.3	79.4
35	C	1909	28.8	48.9	77.7
36	C	1967	28.0	50.4	78.4
37	C	2020	26.9	51.7	78.6
38	C	2074	25.6	53.1	78.7
39	C	2124	24.6	54.3	78.9
40	C	2161	23.7	55.2	78.9
41	C	1985	27.9	50.8	78.7
42	C	2041	26.9	52.2	79.1
43	C	2096	25.8	53.6	79.4
44	C	2150	24.6	54.9	79.6
45	C	2202	23.4	56.2	79.6
46	D	2083	26.5	53.3	79.7
47	D	2165	25.2	55.3	80.5
48	D	2204	24.7	56.3	81.0
49	D	2087	26.6	53.4	80.0
50	D	2158	25.4	55.1	80.5
51	D	2198	24.4	56.1	80.6
52	D	2130	26.0	54.5	80.5
53	D	2025	28.0	51.8	79.8
54	D	2086	27.2	53.4	80.6
55	D	2132	26.7	54.5	81.2
56	D	2186	25.6	55.8	81.5
57	D	2039	28.1	52.2	80.3
58	D	1964	28.7	50.3	79.0

Average = 79.7 ± 1.0^c

a - Runs labeled A - W cell, $k = 0.926$
 Runs labeled B - Ta lined, W cell, $K = 0.926$
 Runs labeled C - TaC cell, $k = 0.337$
 Runs labeled D - TaC cell, $k = 0.527$

b - Calculated from $\Delta F \approx -RT \ln P_{N_2}^{1/2}$

c - Standard deviation of mean.

STANDARD HEAT OF FORMATION OF UN_(s)

<u>ΔH_f^0 (298°K)</u> <u>(kcal/mole)</u>	<u>Method</u>	<u>Reference</u>
-74.4 ± 2.0	Vapor Pressure	This Research
-69.6 ± 0.4	Calorimetry	Gross et al. ⁸
-68.46	Calorimetry	Neumann et al.
-70.95	Calorimetry	Hubbard ¹⁰