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THE HEATS OF FORMATION OF URANIUM HYDRIDE
URANIUM DEUTERIDE AND URANIUM TRITIDE
AT 25°C

by

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ABSTRACT

The heats of formation of uranium hydride, deuteride and tritide were measured at 25°C by reacting finely divided uranium with hydrogen gas in an adiabatic calorimeter. It was found that the heat of formation became progressively more negative as deuterium and then tritium were substituted for hydrogen. The values obtained for UH_3 , UD_3 and UT_3 are $-30,352 \pm 30$ cal/mole, $-31,021 \pm 30$ cal/mole and $-31,141 \pm 50$ cal/mole, respectively.

INTRODUCTION

From measurements of the dissociation pressures of UH_3 and UD_3 , Spedding et al.¹ obtained the value $-30,800$ cal/mole for the heat of formation of both compounds. Flotow and Abraham² have also measured the dissociation pressures of the two compounds over the same temperature range, 300°C to 400°C, and from their data calculated the heats to be $-31,800$ cal/mole. A single calorimetric determination by Spedding et al.¹ at room temperature gave the value $-30,400$ cal/mole for the heat of formation of UH_3 . The very slow approach to equilibrium and the marked hysteresis observed while making the dissociation pressure measurements cast some doubt on their being true equilibrium values and could easily account for the 1000 calorie discrepancy. It was of some interest then to measure the heats of formation directly in order to obtain more accurate data that would aid in understanding the uranium hydrogen system. Also, with the availability of tritium it would be possible to determine by direct measurement the effect of substituting deuterium or tritium for hydrogen in UH_3 .

¹Spedding, et al., *Nucleonics*, 4, 10 (1949).

²H. E. Flotow and B. M. Abraham, unpublished results.

The reaction

is well suited for a direct calorimetric investigation, since uranium can be made to react rapidly and quantitatively with hydrogen at room temperature. Also, there is no evidence for the existence of solid solutions of uranium in uranium hydride or of hydrogen in uranium hydride so that the final state of the system is clearly defined.* The present investigation is concerned with the direct calorimetric measurement of the heat of reaction of hydrogen and its isotopes with powdered uranium metal at 25°C.

Apparatus - Figure 1 is a schematic diagram of the adiabatic calorimeter that was constructed to carry out this research. The apparatus consists of the calorimeter in the center, the adiabatic shield that surrounds the calorimeter and the vacuum jacket or submarine. The entire assembly was immersed in a constant temperature water bath that was controlled to $\pm 0.05^\circ\text{C}$.

The calorimeter was a gold-plated copper cylinder, one inch in diameter and 1.2 in. in length; an expanded view is shown in Figure 2. A 100-ohm heater of B. and S. gauge No. 36 glass-covered Nichrome wire was wound bifilarly in the square thread cut into the calorimeter body (Figure 2). The last two turns were made with B. and S. gauge No. 34 glass-covered copper wire which had been silver soldered to the heater. Two coats of Formvar insulating varnish were applied to the heater in order to bond it to the calorimeter and to improve the thermal contact between them. The internal diameter of the shell shown in Figure 2 was made 0.002 in. smaller than the major diameter of the thread. After heating the shell to 250°C and cooling the calorimeter body in liquid nitrogen, the two pieces were quickly fitted together in a jig. This method of construction resulted in excellent thermal contact between the parts and eliminated radiation losses from the heater. The sample chamber (0.20 in. diameter by 0.60 in. long) was sealed with the closure fittings shown in Figure 2. This closure remained vacuum tight even after 25 cyclings between room temperature and 270°C. The calorimeter was suspended at the center of the shield by a thin walled (0.009 in.) Monel tube that in turn suspended the shield from the submarine, see Figure 1. This tube also served as the pumping lead and the gas inlet to the calorimeter. The temperature of the calorimeter was measured with a chromel-alumel thermocouple inserted in a small hole in the shell and held in place with a set screw. The other junction was immersed in an ice bath.

*The possible effect on our results of the two crystallographic phases of UH_3 will be brought out in the discussion.

Figure 1. Schematic Diagram of the Calorimetric Apparatus

Figure 2. An Expanded View of the Calorimeter

The adiabatic shield was assembled from two hemispheres, each of 0.040 in. thick gold-plated copper, that were held together with small machine screws, as shown in Figure 1. The resulting sphere was 3.0 in. in diameter and weighed 130 g, approximately the same weight as the calorimeter. In order to control the temperature of the shield, separate heaters of B. and S. gauge No. 32 advance wire were wound on each hemisphere, and chromel-alumel difference thermocouples were provided between each hemisphere and the calorimeter. One junction of each difference couple was thermally connected to the shield with a small machine screw but was electrically insulated from the shield with Formvar varnish; the other junction was inserted in a small hole in the calorimeter shell and held in place with a set screw. Excellent thermal contact existed between the two hemispheres as shown by the rapidity with which the temperature equalized after one hemisphere had been heated.

The submarine was a brass cylinder 5.0 in. in internal diameter and 5.75 in. deep. A vacuum-tight closure was made at the top with an "O" ring. The thin-walled Monel tube was joined to a 1/8-in. copper tube at the top of the submarine by silver soldering both tubes to a boss projecting through the lid. The copper tube was then wound in a flat spiral that was soldered to the lid so that the incoming gas would equilibrate to the bath temperature before it entered the calorimeter.

All of the lead wires coming from the calorimeter were passed through a small hole in the shield, wound once around the outside surface of the shield and after making thermal contact with the submarine lid were finally brought out through a vacuum seal. The electrical circuits for controlling the adiabatic shield, for measuring the e.m.f. of the calorimeter thermocouple and for measuring the electrical energy supplied to the calorimeter heater were those used in this Laboratory for low temperature heat capacity measurements and have been described elsewhere.³

EXPERIMENTAL

Before the shield was assembled around the calorimeter, a one-gram piece of uranium metal (99.99 % uranium) was inserted into the sample chamber. This quantity of uranium was enough to react with 141 cc of hydrogen gas although only 100 cc were actually used in heat of reaction runs. Excess metal was used so that the rate of reaction in the calorimeter would always be faster than the rate at which gas was supplied to the uranium. By this expedient the heating rate from a heat of reaction run could be made to match that used during the calibration of the calorimeter. After the apparatus was assembled, but prior to making measurements, the uranium in the calorimeter was completely converted

³ E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, J. Chem. Phys., 21, 419 (1953).

to hydride by admitting hydrogen gas at one atmosphere pressure while the calorimeter was maintained at 200°C. The hydride was then decomposed by raising the temperature to 270°C and pumping off the evolved gas. The finely powdered uranium that results from this process reacts very rapidly with hydrogen at room temperature. By decomposing the hydride as above after each heat of reaction measurement, it was possible to use the same sample of uranium for the complete series of measurements.

In order to obtain calibration curves, heat capacity measurements were made of the calorimeter plus uranium and of the calorimeter plus uranium hydride from 10°C to 44°C. The difference between the two curves was 0.2 %, the latter being the higher. During each run a heating rate of 1°/min was chosen for convenient operation of the adiabatic shield, and a temperature rise of 8°C was chosen to match the expected rise from 100 cc (STP) of hydrogen gas. In both heat capacity and heat of reaction runs the temperature differential between the shield and calorimeter was controlled to within $\pm 0.002^\circ$ except for a short period at the beginning and end of the energy input. The method of operation made it unnecessary to calibrate the thermocouples; however, it was essential that they be absolutely reproducible. In order to test this, check heat capacity measurements were made between heat of reaction runs, and they were found to agree with the initial calibration to within the precision of the measurements, namely, $\pm 0.03\%$.

The H_2 , D_2 and T_2 gas samples were stored on a vacuum line as UH_3 , UD_3 and UT_3 , respectively, in order to prevent isotopic as well as foreign gas contamination of the samples. A measured quantity of pure gas was obtained by thermally decomposing the uranium hydride and collecting the liberated gas in a 200 cc glass bulb which was calibrated to ± 0.05 cc. The pressure of the gas was measured to ± 0.02 mm of mercury with a Wild cathetometer. The calibrated volume was maintained at a uniform temperature measured to $\pm 0.02^\circ C$ with a calibrated thermometer certified by the National Bureau of Standards. After applying meniscus corrections, the pressure readings were corrected to standard mm of mercury at $0^\circ C$.⁴ The local acceleration of gravity was taken as 980.278 cm/sec^2 and the ice point as $273.16^\circ K$. The moles of gas in the calibrated volume were computed using the virial corrections given by Woolley, Scott and Brickwedde⁵ and using the value $22,414.6 \text{ cm}^3$ as the molar volume of an ideal gas at standard conditions.⁴

⁴F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, J. Am. Chem. Soc. 74, 2699 (1952).

⁵H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Research NBS 41, 396 (1948) RP 1932.

The measured volume of gas was then pumped from the standard volume into a mercury pusher, illustrated in Figure 3. In order to obtain the desired rate of reaction, the hydrogen was admitted to the uranium in the calorimeter through a capillary leak at such a rate that 99 % of the reaction took place in about 8 min. Approximately 10 min. more were required for completion of the reaction and attainment of temperature equilibrium in the calorimeter. It was necessary to modify the procedure slightly for the measurements with tritium because of the radioactive decay. Although the decay product, He^3 , was removed from the sample before each experiment, sufficient He^3 was produced during the period of the measurements to form a diffusion barrier. As a result the last one or two per cent of T_2 reacted very slowly, and consequently the final drift rate correction, which was already large because of the decay energy, was uncertain. To avoid this difficulty, the T_2 gas was admitted to the calorimeter as before but the reaction was stopped by closing a stopcock to the calorimeter after about 97 % of the sample had reacted. The volume of the residual gas was measured to determine the net quantity reacted. The modified technique was tested with hydrogen and gave the same results as obtained previously.

Since the calorimeter was operated adiabatically the drift rate was essentially zero. The drift taken before and after an energy input or reaction with hydrogen and deuterium never exceeded 0.007 microvolts/min. or about $1.8 \times 10^{-4} \text{ }^\circ/\text{min.}$, which was the limit of sensitivity of the circuits; the drift rate with tritium in the calorimeter exceeded this number by a factor of fifty because of the energy released by beta decay. The total temperature rise was about 320 microvolts or about 8° . The heat of formation, ΔH_f , of one mole of uranium hydride was calculated from the equation:

$$\Delta H_f = - \frac{1.5(C \times \Delta\theta + q)}{M}$$

where C is the average value of the heat capacity in calories/microvolt at the average temperature, $\Delta\theta$ is the temperature change in microvolts, M is the number of moles of hydrogen used in the reaction, and q is the heat absorbed from the calorimeter by the hydrogen gas as it warmed from the bath temperature to the calorimeter temperature. A typical value of q was 0.2 cal which is small compared with the magnitude of the product $(C \times \Delta\theta)$, namely, 90 cal. The factor 1.5 converts the heat from one mole of hydrogen to one mole of hydride. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules.⁴

The isotopic compositions of the D_2 and T_2 gas samples were determined mass spectrometrically; the results are given in Table I. A correction of 9 cal/mole was added to the measured ΔH_f of UT_3 due to the hydrogen and deuterium in the T_2 sample. Because of the higher purities of the H_2 and D_2 samples similar corrections to the measured heats of formation of UH_3 and UD_3 were not necessary.

Figure 3. Schematic Diagram of the Vacuum Line

Table I
ISOTOPIC COMPOSITION OF D₂ AND T₂ SAMPLES

Isotope	Atom % H	Atom % D	Atom % T
D ₂	0.18	99.82	-
T ₂	1.4	1.4	97.2

RESULTS AND DISCUSSION

The values obtained for the heats of formation are given in Table II. The value reported here for UH₃ agrees very well with the calorimetric value ($-30,400 \pm 400$ cal/mole) reported by Spedding et al.¹ The estimated uncertainties in the heats of formation of UH₃ and UD₃ were based mainly on errors in determination of the hydrogen gas volume. A somewhat larger error was assigned to the measurements with tritium because two volume measurements were involved and because of the higher final drift rate.

Table II
HEATS OF FORMATION OF UH₃, UD₃ AND UT₃ AT 25°C

Experiment Number	$-\Delta H_f$ (cal/mole)		
	UH ₃	UD ₃	UT ₃
1	30,346	31,014	31,170
2	30,362	31,039	31,114
3	30,347	31,011	31,140
Mean	30,352	31,021	31,141
Estimated error	± 30	± 30	± 50

As can be seen from the table, the heats of formation become progressively more negative as deuterium and then tritium are substituted for hydrogen in UH₃, a result not indicated by the dissociation pressure measurements. Although Kopp's rule can give a rough value for the heat capacity of UH₃ at room temperature, it is of little help in trying to compare the high temperature values of the heats with the calorimetric ones, since neither the temperature coefficient of C_p nor

the change in C_p on isotopic substitution can be estimated. An error of two or three calories per degree in the estimate of ΔC_p for the reaction completely vitiates an attempted comparison.

As was mentioned above, UH_3 exists in two crystalline modifications, the common beta phase and a new alpha phase.^{6,7} The former is produced as a single phase above 200°C whereas the latter is formed in variable amounts when uranium reacts with hydrogen at or below room temperature. If there is an appreciable heat of transition, then the results reported here would be in error by some fraction of this heat. X-ray analysis of the product from a typical calorimetric run showed that the solid consisted of 25 % alpha phase and 75 % beta phase. Attempts to prepare the pure alpha phase have resulted in a product containing only 50 % alpha even when the reaction chamber was maintained at -80°C. According to the work of Mulford, et al.,⁶ the transition of alpha to beta uranium hydride appears to be irreversible. Bigeleisen and Kant⁸ have measured the exchange equilibria for HD with UH_3 . From their data the difference in the heat of formation of UH_3 and UD_3 are calculated to be -641 ± 50 calories per mole which is in excellent agreement with the measured value of -669 ± 45 , from Table I. Since they made no attempt to dissipate the heat during the preparation of their hydride samples, the product would be practically pure beta form. We conclude that the values of the heats of formation reported here represent the heat of formation of beta UH_3 within the precision given.

It should be mentioned that the heats reported here involved the reaction of hydrogen with finely divided uranium and, as pointed out by Giaque⁹ and Jura and Garland,¹⁰ the heat capacity and the enthalpy of the powder may differ appreciably from that of the massive metal. Work is now in progress to determine the total surface energy of the uranium powder so that reference state for the metal in the above reactions may be the macro crystalline state.

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⁶R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen, J. Am. Chem. Soc., 76, 297 (1954).

⁷R. Caillat, H. Coriou, and P. Perio, Compt. rend., 237, 812 (1953).

⁸J. Bigeleisen and A. Kant, J. Am. Chem. Soc., in press.

⁹W. F. Giaque, J. Am. Chem. Soc., 71, 3192 (1949).

¹⁰G. Jura and C. W. Garland, J. Am. Chem. Soc., 74, 6033 (1952).