[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Heats of Formation of Uranium Hydride, Uranium Deuteride and Uranium Tritide at 25°[1]

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The heats of formation of uranium hydride, deuteride and tritide were measured at 25° by treating finely divided uranium with hydrogen gas in an adiabatic calorimeter. The values obtained for UH_3, UD_3 and UT_3 are −30,352 ± 30, −31,021 ± 30 and −31,141 ± 50 cal./mole, respectively.

Introduction

From measurements of the dissociation pressures of UH_3 and UD_3, Spedding, *et al.*,[2] obtained the value −30,800 cal./mole for the heat of formation of both compounds. Flotow and Abraham[3] have also measured the dissociation pressures of the two compounds over the same temperature range, 300 to 400°, and from their data calculated the heats to be −31,800 cal./mole. A single calorimetric determination by Spedding, *et al.*,[2] 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 casts some doubt on their being true equilibrium values and could easily account for the 1000 cal. 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 it was possible to determine by direct measurement the effect of substituting deuterium or tritium for hydrogen in UH_3.

The reaction $U_{(powder)} + 3/2H_2 \rightarrow UH_{3(powder)}$ 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°.

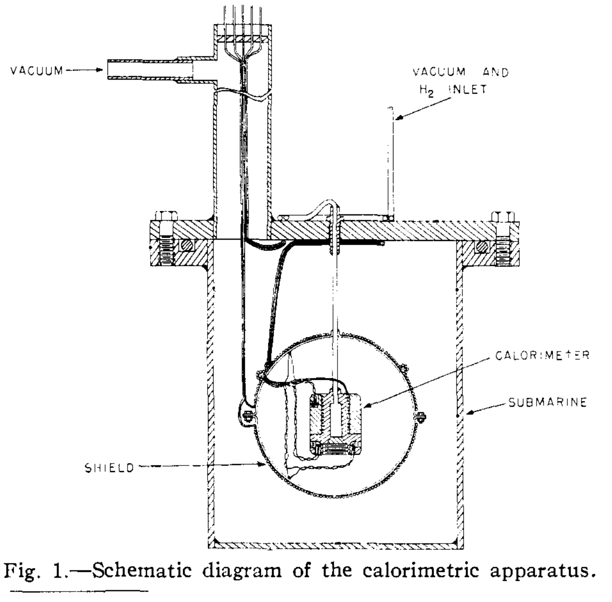

Fig. 1.—Schematic diagram of the calorimetric apparatus.

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 ±0.05°.

The calorimeter was a gold plated copper cylinder 2.5 cm. in diameter and 3.0 cm. long. A 100 ohm heater of B. and S. gage No. 36 glass covered Nichrome wire was wound bifilarly in a square thread (major diameter 1.25 cm.) cut into the calorimeter body. A copper shell was shrunk over the thread to make a cylinder of uniform exterior diameter. The sample chamber (0.5 cm. in diameter by 1.5 cm. long) was sealed by forcing a plug having a 60° taper into a hole having a 59° taper. This closure remained vacuum tight even after 25 cyclings between room temperature and 270°. The calorimeter was suspended at the center of the shield by a thin walled 0.023 cm. Monel tube that in turn suspended the shield from the submarine. 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 adiabatic shield was assembled from two hemispheres, each of 0.10 cm. thick gold plated copper, that were held together with small machine screws, as shown in Fig. 1. The resulting sphere was 7.6 cm. 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. gage 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.

The submarine was a brass cylinder 12.7 cm. in internal diameter and 14.6 cm. deep. A vacuum tight closure was made at the top with an "O" ring. The thin-walled Monel tube was joined to a 0.32 cm. 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 attain the bath temperature before it entered the calorimeter.

All of the lead wires coming from the calorimeter were brought into thermal contact with the shield and with the submarine lid before being brought out through a vacuum seal. The thermocouple e.m.f.'s were measured with a White double potentiometer. The circuits for the adiabatic shield control and for energy measurements are those used in this Laboratory for low temperature heat capacities and have been described elsewhere.[4]

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, March 16, 1953.

[2] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, **4**, 10 (1949).

[3] H. E. Flotow and B. M. Abraham, unpublished results.

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

Reagents.—The uranium used in this work was produced by electrolysis in a molten salt-bath. Chemical and spectrographic analysis of the metal indicated a total impurity content of 156 p.p.m. which was distributed as follows: K, 50 p.p.m.; Li, 50 p.p.m.; C, 18 p.p.m.; O, 15 p.p.m.; Si, 12 p.p.m.; N, 5 p.p.m.; Cr, 3 p.p.m.; Fe, 2 p.p.m.; Cu, 1 p.p.m.

The hydrogen gas was ordinary tank gas that had been purified by forming uranium hydride and then liberating pure hydrogen by thermal decomposition at 350°.

The deuterium was obtained from the Stewart Oxygen Co. A mass spectrometric analysis of the gas showed the presence of 0.18 atom % hydrogen; no correction was made for this contaminant.

The tritium was obtained through the kindness of Dr. E. Robinson of the Los Alamos Scientific Laboratory. Analysis of this gas showed the presence of 1.4 atom % hydrogen and 1.4 atom % deuterium, for which a correction of 9 cal./mole was added to the measured heat.

The gases were stored as UH_3, UD_3 and UT_3 in order to avoid isotopic as well as foreign gas contamination.

Experimental

A one-gram piece of uranium metal was inserted into the sample chamber and the calorimeter was then assembled. Prior to making measurements the uranium was completely converted to the hydride, which was then decomposed to recover the metal. The finely divided uranium that results from this process reacts very rapidly with hydrogen at room temperature.

Heat capacity measurements were made of the calorimeter plus uranium and of the calorimeter plus uranium hydride from 10 to 44° in order to obtain calibration curves. 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° 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 ±0.002° 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 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, ±0.03%.

A measured quantity of pure gas was obtained for the measurements 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 which was measured to ±0.02° with a calibrated thermometer certified by the National Bureau of Standards. After applying meniscus corrections, the pressure readings were corrected to standard gravity (980.665 $cm./sec.^2$) and 0°. The local acceleration of gravity was taken as 980.278 $cm./sec.^2$ and the ice point as 273.16°K. The moles of gas in the calibrated volume were computed with the aid of the virial corrections given by Woolley, Scott and Brickwedde[5] and the value 22,414.6 $cm.^3$ as the molar volume of an ideal gas at standard conditions.[6]

The measured volume of gas was transferred quantitatively with a Toepler pump from the standard volume into a mercury pusher. In order to obtain a heating rate similar to that used during the calibration, the gas was admitted to the calorimeter through a capillary leak. The pressure on the inlet side of the leak was maintained constant by slowly raising the mercury in the pusher. After approximately 99% of the gas had reacted a by-pass was opened and the pressure then fell rapidly to a micron, as read on a Pirani gage.

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 measurements to form a diffusion barrier. As a result, the last 1 or 2% of T_2 reacted very slowly. This was particularly objectionable because the calorimeter was continually warming due to the energy released from β-decay. 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, and drift corrections did not have to be made except when working with tritium.

The heat of formation ΔH_f of one mole of uranium hydride was calculated from the equation

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

where C is the average value of the heat capacity in cal./μV at the average temperature. $\Delta\theta$ is the temperature change in μV, 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 $C\Delta\theta$, 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.[6]

Results and Discussion

The values obtained for the heats of formation are given in Table I. The value reported here for UH_3 agrees very well with the calorimetric value (−30,400 ± 400 cal./mole) reported by Spedding, *et al.*[2] The estimated uncertainties in the heats of formation of UH_3 and UD_3 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 I

HEATS OF FORMATION OF UH_3, UD_3 AND UT_3 AT 25°

Expt. no.	$-\Delta H_f$ (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
Est. 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 UH_3, a result not indicated by the dissociation pressure measurements. The nature of the equilibrium reaction $U + 3/2\ H_2 \leftrightarrows UH_3$ is such that the uranium metal and the uranium hydride are always obtained as microcrystalline powders. It is appropriate, therefore, that the reference state for the solids be the powder as was the case for the results given in Table I.

Recently a new allotropic form of UH_3 has been discovered.[7,8] The common β-form is produced as a single phase above 200° whereas the new phase, alpha, is formed in variable amounts when uranium reacts with hydrogen at or below room

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

(6) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, THIS JOURNAL, **74**, 2699 (1952).

(7) R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen, *ibid.*, **76**, 297 (1954).

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

temperature. X-Ray analysis of the product from a typical calorimetric run showed that the solid consisted of 25% α-phase and 75% β-phase. Attempts to prepare the pure α-phase resulted in a product containing only 50% alpha even when the reaction chamber was maintained at −80°.

If there were an appreciable heat of transition between alpha and beta then the results reported here would differ from the heat of formation of the beta form by about 25% of the heat of transition. However, the recent work of Bigeleisen and Kant[9] on the exchange equilibria of HD with UH_3 indicates that the difference in the heat of formation of UH_3 and UD_3 is −641 ± 50 cal./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, their uranium hydride would be practically pure β-form. We conclude that the heat of transition of alpha to beta is small and that the heats reported here represent the heats of formation of beta UH_3 within the precision given.

Acknowledgment.—We wish to thank Dr. D. W. Osborne for assistance with the calorimetric techniques and Dr. Stanley Siegel for the X-ray analysis of our samples. We also wish to thank Dr. J. Bigeleisen for helpful discussions. This work was performed under the auspices of the U.S. Atomic Energy Commission.

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[9] J. Bigeleisen and A. Kant, THIS JOURNAL, **76**, 5957 (1954).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

The Solubility of Uranium Trioxide, $UO_3 \cdot H_2O$, in Solutions of Sodium Hydroxide and Perchloric Acid at 25°[1]

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The solubility of uranium trioxide has been studied in perchloric acid and in sodium hydroxide solutions at 25°. The oxide reacts predominantly as a basic oxide, the chief reaction being $UO_3 \cdot H_2O + 2H^+ = UO_2^{++} + 2H_2O$ in concentrated acid. K_6 for this reaction is 1.1×10^6, and $\Delta F^0 = -8100$ cal./mole. $K_{sp} = K_6 K_w^2 = 1.1 \times 10^{-22}$ for the reaction $UO_3 \cdot H_2O = UO_2^{++} + 2OH^-$. The presence in dilute solutions of polymerized ions is indicated.

The purpose of this investigation was to obtain information regarding the reactions of uranium trioxide with respect to acid and base, to determine the possible ionic species involved in such reactions, and to evaluate free energies and equilibrium constants for such reactions.

$UO_3 \cdot H_2O$ is treated here as amphoteric oxide, but the results of this work indicate that it reacts more as a base than as an acid.

Procedure

The general procedure is similar to that described by Garrett and Heiks.[2] An all-glass apparatus was used.

Water.—Conductivity water was prepared in a Barnstead conductivity still, degassed by boiling with nitrogen bubbling through it, and then stored under nitrogen.

Perchloric Acid Solutions.—Approximately one molar acid solutions were prepared from 70% G. F. Smith purified perchloric acid with degassed conductivity water, and then stored under nitrogen. Standard acid solutions were also prepared with conductivity water and standardized against standard sodium hydroxide solution.

Sodium Hydroxide Solutions.—Approximately one molar solutions of base were prepared under nitrogen by dissolving Baker and Adamson reagent pellets with degassed conductivity water in a paraffined flask. Barium hydroxide solution was added in amount just sufficient to precipitate any carbonate. The solutions were then stored under nitrogen. Standard base solutions were also prepared with conductivity water and standardized against potassium acid phthalate using phenolphthalein indicator.

Uranyl Acetate Solutions.—Baker and Adamson uranyl acetate reagent grade was dissolved in degassed conductivity water and stored under nitrogen.

Colorimetric Reagents.—A standard uranium solution was prepared by dissolving stoichiometric $UO_3 \cdot H_2O$ (prepared by hydrolysis of the uranyl acetate) in perchloric acid. Aliquot portions of this solution were used to prepare the color standards. A 10% sodium hydroxide solution was prepared from Baker and Adamson reagent pellets and distilled water. A 20% sodium carbonate solution was prepared with Baker and Adamson anhydrous reagent and distilled water. Baker and Adamson 30% hydrogen peroxide was used in preparing colorimetric solutions.

Uranium Trioxide.—Pure $UO_3 \cdot H_2O$ was prepared by hydrolysis of uranyl acetate solution by prolonged boiling, followed by fifteen to twenty 500-ml. washings with distilled water and five 500-ml. washings with conductivity water. A small amount of sodium chloride was then added to the precipitate, and the washing with conductivity water continued. A negative sodium flame test indicated complete washing. Weighed samples of $UO_3 \cdot H_2O$ prepared in the manner described and dried over drierite were ignited to U_3O_8, and the uranium content was found to be 78.2, 78.2 and 78.3%; calcd., 78.3%. Also, the solid phase from some acid samples was washed, dried and ignited. On drying over drierite for 24 hours, the uranium content was 77.5, 77.8 and 78.1%. The solid phase from basic samples contained associated sodium.[3]

Equilibration.—Pairs of 100-ml. samples of the oxide in acid or base were collected in 125-ml. florence flasks under nitrogen at each concentration. One of each pair was agitated in a 35° thermostat for at least seven days, and then allowed to settle in the 25° thermostat for three to five days before analysis. The other member of each pair was immediately agitated for at least seven days in the 25° thermostat and allowed to settle for three to five days.

Determination of *p*H ($-\log a_{H^+}$).—The flask necks were broken while enclosed in a rubber membrane and samples were taken using a Beckman 290-78 hypodermic type glass electrode. Measurements were made with a Beckman Model G meter which was calibrated at *p*H 4 with 0.05 *M* potassium acid phthalate buffer, at *p*H 7 with Beckman 3581 buffer, and at *p*H 10 with boric acid–sodium hydroxide buffer.

Uranium Analysis.—The uranium analysis was made with a Beckman Model B spectrophotometer using the

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[1] From a dissertation submitted by Mr. Herman Leider in partial fulfillment of the requirements for the Doctor of Philosophy degree at Wayne University.

[2] A. B. Garrett and R. E. Heiks, THIS JOURNAL, **63**, 562 (1941).

[3] C. A. Wamser, J. Belle, E. Bernsohn and B. Williamson, *ibid.*, **74** 1020 (1952).