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**ISOTHERMS FOR THE U-UH₃-H₂ SYSTEM
AT TEMPERATURES OF 700°-1050°C
AND PRESSURES TO 137.9 MPa**

John F. Lakner

July 15, 1975

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ISOTHERMS FOR THE U-UH₃-H₂ SYSTEM AT TEMPERATURES OF 700°-1050°C AND PRESSURES TO 137.9 MPa

Abstract

A new pressure system utilizing a heated internal pressure vessel was used to obtain pressure vs. composition isotherms for the U-H system over the range 700° - 1050°C at pressures up to 137.9 MP (1361 atm). The experimentally-determined "plateau" pressures are compared with

values extrapolated from lower temperatures and pressures previously obtained by other workers. The current investigation shows that, in contrast to the work of Chevalier, et al., the U-H system retains broad two-phase plateaus at temperatures as high as 1050°C.

Introduction

The literature presents considerable data on the equilibrium H₂ pressures of the U-UH₃-H₂ system below temperatures of 450° C.^{1,2,3,4} In these investigations, glass-quartz systems were used, since the dissociation pressures were less than 1 atm. Several investigations extended the studies to 650°C^{5,6,7} using a metal apparatus to contain the greater pressures. Recently, there have been experiments involving the U-H system to temperatures of 846°C.^{8,9} Most studies were made by desorbing UH₃. In the majority of cases however, no analysis was presented for the uranium used.

This report describes absorption experiments that extend the data to significantly higher pressures and temperatures: 137.9 MPa (1361 atm) and 1050°C. The system that was developed for this work is, in principle, capable of pressures to 344.7 MPa (3402 atm) and temperatures of 1200°C.

Experiments that determine the critical point, the temperature above which only one phase exists, remain to be done. In addition, a study of the effects of O₂ on the phase diagram may resolve some of the discrepancies found in the literature.³

Experimental Apparatus

An apparatus capable of clean operation at high pressure and temperature was developed, without which this work would not have been possible.

This section discusses the apparatus and instrumentation, and describes a

cartridge-type heater and a cascade pressure system.

PRESSURE SYSTEM

The cascade pressure system consists of a sample container, itself a pressure

vessel, and an external pressure vessel.* The gas pressure inside the sample container is balanced with gas pressure in the external vessel. This system allows a sample to be treated in a clean environment; i.e., the sample is not exposed to the furnace or other extraneous environment. The inner vessel can be loaded separately under Ar using dry-box procedures. The small volume of the inner vessel permits smaller volumes of gas to be used, increasing the sensitivity of the experiment.

*The external pressure vessel and trunion were designed and fabricated by Harwood Engineering Co.

Overall views of the external support vessel are shown in Figs. 1 and 2. The pressure manifold is shown in Fig. 3. Figure 4 shows the flow diagram. The cylindrical space available inside the vessel measures 7.62 cm diam and 51.2 cm in length. The body is constructed of AISI 316 steel. Within the body are two concentric liners fabricated of TYPE 316 stainless steel. The innermost liner is circumferentially grooved (grooves are criss-crossed) to permit escape of any outward-diffusing gas. In this way, only the 316 stainless steel is exposed to H_2 and never the 4340 steel. The two vessel closures are machined from A-286 steel (Fig. 5). The

Fig. 1. Hydrogen pressure vessel in operating position. External pressure system is on left, sample end on right. (Harwood Engineering Co. vessel and trunion.)

Fig. 2. Hydrogen pressure vessel in leading position. Electrical leads and thermocouple compensators are shown on left. (Harwood Engineering Co. vessel and trunion.)

Fig. 3. Instrumentation, gas manifold, sample charging system and sample desorption volumes.

Fig. 4. Schematic diagram for dual pressure system. P/T - pressure transducer; T/C - thermocouple; P/S - power supply; DPT - differential pressure transducer; DVM - digital voltmeter.

closure seal consist of a bronze wedge ring; a lead ring (square in cross-section); a Viton^{*} spring-loaded Bal Seal⁺; a removal ring, (square in cross section); and a Spirolox retainer ring. All metal rings were coated with Teflon^{**} to reduce

friction in assembly and disassembly and to prevent scoring of the vessel bore, which was honed to an 8 μ in. finish.

Electrical leads (with bayonet-type disconnects) and furnace control thermocouples enter the closure through BeCu cones. These cones are insulated from the closure with BN coated with 2902 epoxy.⁺⁺ The leads are shown on the left side of Figs. 1 and 2. On the left are also a H₂ gas port and a pressure transducer which monitors the external pressure. The closure on the right has attached to it a

* Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.

⁺ Bal Seal Engineering Co., Series 506/2,622/GWO,199.

^{**} TFE coating #6070, Crown Industrial Prod. Co.

⁺⁺ Tra-Con, Inc.

Fig. 5. Furnace (LLL design) and pressure vessel closures.

sample vessel (shown elsewhere), sample thermocouples, a H_2 inlet, a pressure transducer, and plumbing. The entire system rests on a trunion so that loading may be done vertically. In actual operation, the vessel is positioned horizontally to reduce internal convection currents. Cooling of the vessel wall is accomplished with an external water jacket.

The external pressure is obtained by pumping purified dry H_2 (purified by passing through molecular sieve and liquid N_2 traps) from a 37.9 MPa (375 atm) bottle. The H_2 in the inner vessel was also purified as described above.

The charging system for H_2 absorption work is shown in Fig. 3, just below the glass view port. To the left of the charging system is shown a series of gas bottles that would be used to withdraw measured amounts of gas from a hydrided sample in desorption experiments.

HEATER

An expanded view of the cartridge heater is shown in Fig. 5. This view shows the bayonet-type of connectors for a 2-zone furnace, while Fig. 6 shows the connectors on a 3-zone heater assembly.

Fig. 6. Terminals for a 3-zone furnace and 3 thermocouples. (LLL design.)

Figure 7 shows the windings for a 3-zone furnace. The windings are made of 0.038-cm diam KW Mo wire. The furnace core is Alundum*, with dimensions of 1.9 cm i.d. $\times$ 2.54 cm o.d., 0.079 cm groove depth, 0.079 groove width, and 16 turns per 2.54 cm. The Alundum wall is 0.3 cm thick. Each Mo heater winding has 2 Ω resistance at ambient temperature; power density is ~ 145 W/in.² at maximum operating temperature. The voltage drop across each turn is 9V.

* Norton Co. RA 4139 Alundum

Thermocouples for heater control are inserted in alumina tubes and laid across the windings. Norton RA 4139 cement insulates the windings and thermocouples. Figure 8 shows how connections are made to the inside terminals of the cartridge heater. The entire sub-assembly is then encased in two additional tubes of alumina, and a slurry of Al_2O_3 poured in the void spaces between insulated winding and the adjacent tube. A 316 stainless steel tube with two alumina end-pieces (Coors AD 85) houses the completed assembly. Lead

Fig. 7. Molybdenum windings on furnace core. Wire is 0.038 cm diam. Metal rod supports the core during windings.

plating is used on the outer surface of the stainless steel tube to avoid scratching the vessel bore when the cartridge is inserted. A special tool, shown at the bottom of Fig. 5, is used to insert the cartridge.

Heater terminals are machined from Berylco 25 BeCu. Thermocouple connectors depend on the type of couple used. They may be Cr/Al, Geminol P/N., or W5Re/W26Re.

The cartridge heater design allows removal of the furnace for repair without removing the pressure vessel closure into which it fits. With water cooling, the temperature of the uppermost surface of the outer vessel does not rise above 40°C when the sample temperature is at 1000°C and 137.9 MPa (1361 atm). At no time did the lead plate on the cartridge melt. For operation at these conditions, the power consumption for each heater was 1100*, 920, and 1368 W. A heater like the one described was cycled through 11 runs before failure occurred in the center winding. The heaters are operated above their nominal power rating. This accounts for the shorter lifetime.

HEATER CONTROLS

Controls for each winding consisted of a Leeds and Northrup strip-chart recorder with current adjusting controller and a saturable-core reactor. As in the case of Pt wound furnaces, these windings need to be brought up to temperature slowly (~200°C/hr) until sufficient resistance is obtained in the wire, or burn-out may result from excessive loading. In addition, the control couples must not contact cold H₂ as it enters the vessel, or the temperature control system will not respond properly.

SAMPLE CONTAINER

An expanded view of the sample container, serving also as a pressure vessel, is shown in Fig. 9. It measures 1.8 cm o.d. by 1.15 cm i.d. The vessel was machined from Mo bar stock.* The end of the tube is sealed into its fitting with either a flat copper washer or a copper lens-ring. Both are silver plated. The tube

* Winding nearest terminal.

* Climet Molybdenum

Fig. 8. Assembled furnace core with terminal connections. Surface of windings is covered with Alundum cement.

Fig. 9. Expanded view of sample container.

can now be sealed into the pressure vessel closure via the 59° cone shown on the end of the fitting.

The seal does not become heated, so there is no expansion and contraction and therefore leaks are avoided. A fine thread in the fitting also aids in maintaining the seal. The Mo tube has been exposed to instantaneous overpressures of 60 atm at 930°C without failure.

All plumbing associated with the sample vessel is reduced in volume with spacers or by inserting 316 stainless steel wire.

CRUCIBLES

Figure 10 shows the location of a Mo crucible with reference to the inner pressure vessel. A cylindrical piece of U lies to the left of the crucible. In Fig. 11, in addition to a Mo crucible, are shown a Lucalox,* W, and a BeO crucible. The BeO has been found to be quite satisfactory where liquid regions begin to be

*General Electric Co. Al_2O_3 .

Fig. 10. Crucible, sample, spacers, and Mo tube. Seals on closure are, left to right, wedge ring, lead ring, Bal seal, bronze ring, and retainer ring.

formed. A closed-end Mo protection tube is inserted into the crucible where cylindrical crucibles are used. This tube then houses the thermocouple, either bare or sheathed, and so prevents contaminating the hydride. In the W and BeO crucibles, a hole has been drilled horizontally in the crucible to accommodate a thermocouple. The hole can be seen in Fig. 11 at the lower end of the BeO crucible. In the other case, a closed-end Mo tube is not used, and the bare wire thermocouple is inserted directly into the crucible. The Mo and Lucalox crucibles are 1.1 cm diam $\times$ 3.175 cm long. The W and BeO crucibles are 4.3 cm long and 1.1 cm in diam.

The metal and Be cylinders extending from the closure in Fig. 10 are spacers which reduce the volume of the system, thus making it more sensitive to the detection of pressure differences. A small stainless steel frit in the closure is used to minimize gas surges and to pre-

vent particulate matter from entering other parts of the system.

THERMOCOUPLES

A high temperature, high pressure H_2 environment affects thermocouple wire in two ways. Changes in calibration occur due to pressure. Should there be any moisture or O_2 present, corrosion occurs; the degree of deterioration depending primarily on temperature. The best behavior is found in W-Re and Geminol thermocouples, although Cr-Al was also used when temperatures were not severe.

Four thermocouple designs are shown in Fig. 12. Types 1 and 2 are bare-wire thermocouples and types 3 and 4 are used for metal-MgO sheathed thermocouples. In types 1 and 2, 0.036 cm diam wire is threaded into 0.0397 cm holes in a 0.158 cm diam alumina insulator. In type 1, the wire is also threaded through 16° BeCu cones

Fig. 11. Crucibles. (From left to right: Mo, Lucalox, W, and BeO).

Fig. 12. Thermocouple assemblies. Types 1 and 2 are bare wire; types 3 and 4 are sheathed.

and brazed in place. The cone insulators are pyrophyllite or BN. The small cones with their insulators are then placed in a larger 59° metal cone and thence into a fitting which is subsequently held in position by the gland nut (Fig. 12). This sealing arrangement is good for the pressure rating of the fitting used.

Type 2 is a design using a 1.43-cm o.d. pressure tube to house the flat gaskets. It is satisfactory to 4140 atm. However, in this design, we have introduced four wires instead of two wires as used in a Pressure Products design. The gaskets are Teflon and Micarta. The fitting above the gaskets is designed not to rotate in the 1.43 cm diam tube as it is pushed onto the gaskets by gland nut rotation. Thus, there is no rotation of the gaskets which tends to shear off the thermocouple wires. A four-hole alumina insulator is used for the bare wire insulation.

Types 3 and 4 are commercially available metal-sheathed (MgO insulated) thermocouples. The ones shown are 0.0794 cm and 0.159 cm diam. They are brazed into a standard 59° cone high pressure fitting. Hydrogen will permeate through stainless steel at elevated pressures and temperatures. Conditions at which the leak occurs under pressure and temperature are not reproducible. We have had 0.0794 cm diam sheaths withstand temperatures of 950°C at pressures of 89.6 MPa while others would leak at 800°C and at 70.9 MPa in 10 hours of operation. Sheath materials are also available in Mo and W. The seal must be made as shown for Type 3 or 4. The bare wire Geminol P/N couple has been the most versatile to temperatures

of 1250°C in reducing atmospheres. After 212 hours of exposure at 954°C, the change in emf is only 0.13 mv. The hot junction can be made with an oxy-acetylene torch. The calibration is listed in Appendix A. The mv output is less than that of Chromel-Alumel. The W5Re-W 26Re couple is also excellent for use in H₂ atmospheres but the hot junction must be made in an inert atmosphere and it is brittle.

INSTRUMENTATION

The instrumentation is shown in Figs. 1 and 3. Pressures were measured using Taber Teledyne pressure transducers. The pressure-sensing diaphragm is welded to the body. They were periodically compared with Bourdon gages (accurate to within 0.1% of range) but the primary calibration was performed with a Ruska Instrument Corporation dead-weight gauge. The gauge has an overall accuracy of 0.01%. The output of pressure transducers was displayed on digital voltmeters.

Each thermocouple was supplied with its own temperature compensation device (made by Consolidated Ohmic Devices). The temperatures were also displayed on digital voltmeters, either 4 or 5-1/2 digit display.

Leak detection was performed with a portable gas leak detector, (Uson Corp., Model 510B) whose working sensitivity to H₂ is 10⁻³ cc/sec. This is equivalent to about 32.8 cc gas loss/24 hr.

Volumes of the charging section and of the internal pressure vessel were determined to ~1% by expansion of He from a series of calibrated steel vessels.

Procedure

GAS ANALYSIS

The charge gas was analyzed and found to contain the following species (all values are in ppm); Ar < 1, O $\frac{1}{2}$, N₂ 8, CH₄ < 1, CO < 1, CO₂ < 1, H₂O 2, and THC < 1.

SAMPLE PREPARATION

The U specimens used in these experiments were machined from a block of extra-high purity U metal. The elemental analysis is shown in Table I and was obtained by spark-source mass-spectroscopy. Note that the specimen analysis show O₂ and N₂ to be especially low. O₂ and N₂ analyses were obtained by neutron-activation analysis; H₂ by vacuum fusion.

A total of 105 ppm (0.01%) of the sample consisted of elements which could not combine with H₂ so that if each available U atom combined with three H₂ atoms, the apparent maximum H to U ratio would be only 2.99.

Uranium samples were machined as hollow cylinders so that a maximum surface area was exposed for hydriding. Use of cylindrical shapes also allowed pressures to be uniform throughout the crucible when expansion of the hydride occurred. The U cylinder occupied 70% of the free-volume of the crucible. Samples (7-8 g) were prepared for hydriding by degreasing in solvent, then cleaning in nitric acid and water. Further cleaning and drying was done with washings in reagent grade ethanol and acetone. Weighing and loading into crucibles, which were previously vacuum degassed at 1000°C, was performed

under dry Ar. The Mo tube with its loaded crucible was attached to the vessel closure, the gland nut torqued, and the entire assembly transferred to the main pressure vessel. A gas line with a valve (0.159 i.d.) already under vacuum was attached to the sample container after removal of a protective plug. The hook-up time (<1 min) and the small bore of the sample container precluded air contamination. Subsequent analysis shows that O₂ levels were low. After evacuating the glove-box Ar from the inner pressure vessel, the pressure vessel was back-filled with high pressure He, checked for leaks, and then evacuated with the temperature set at 200°C. Hydrogen was then introduced in measured amounts, and the sample allowed to cool. In this way, the stoichiometry of a U hydride could be determined on each activation cycle. To fully activate the sample, it was heated to 600°C while hydrogen was evacuated and then added again.

This cycle was repeated four times before the actual experiment began. Failure to activate the sample results in a displaced isotherm on the Pressure Composition Isotherm (P-C-T) diagram, indicating lower H₂ content.

ABSORPTION EXPERIMENTS

All pressure-composition isotherms were obtained by absorbing H in U. With the inner pressure vessel under vacuum and U sample in place, the temperature was raised to a desired value and a quantity of H₂ was added to the external pressure

TABLE I.

Analysis^a obtained on extra-high-purity U metal.

Weight Percent U-235, 0.1634

All impurity results are in ppm on a uranium basis.

Element	Results-ppm	Element	Results-ppm
Ag	< 1	Mo	< 0.5
Al	8	Na	1
As	<10	Nb	< 0.3
Au	< 1	Ni	3
B	< 0.1	P	<50
Ba	<10	Pb	2
Be	< 0.1	Rb	<10
Bi	< 0.3	Sb	< 1
C	15	Si	13
Ca	<10	Sn	< 2
Cd	< 0.2	Ta	< 0.3
Co	< 1	Ti	< 0.3
Cr	< 2	Tl	< 1
Cu	3	V	< 0.3
Fe	13	W	< 0.3
Ge	< 0.3	Zn	10
In	< 0.3	Zr	< 0.3
K	< 4	H	3
Li	< 1	N	4
Mg	8	O	5
Mn	4		

^aElemental analysis was obtained by emission spectroscopy, spark source mass spectroscopy and vacuum fusion.

vessel which would equal the expected pressure in the inner vessel by the addition of the first aliquot of H_2 . Some H_2 was then admitted to the inner vessel from the calibrated charging system. A pressure transducer reading indicated the amount of H_2 added. The temperature at the first heater dropped slightly as cold H_2 was added, so the system was then allowed to equilibrate until a

uniform temperature again appeared. We recorded pressure and temperature if no further changes occurred in an additional 30 min interval. Then, another aliquot of H_2 was added and the sample allowed to reach a new equilibrium. This procedure was repeated until the desired final pressure was reached at the temperature of interest.

The procedure for locating P-C isotherms amounts to successive calculations of how the H_2 is distributed between the hydride and the gas phase during each step of the experiment. The experiment is further complicated by the fact that gas exists at temperatures varying between room temperature and the temperature of the sample. In other words, the gas simultaneously occupies a hot volume and a cold volume. In addition, the expansion of the sample due to changes in density on hydriding (U metal $\rho = 19.07$; UH_3 , $\rho = 11.4$) can produce errors in the P-C-T diagram at high-gas densities because solid expansion reduces the internal free-gas-volume. Corrections must be made for this.

The method for determining the P-C isotherm involves the following steps.* First, a mock sample of Mo (or Au for lower temperatures) is placed in the crucible in lieu of the U. A constant temperature run is made in which H_2 is added in aliquots and the pressure recorded. A plot is made of n_g moles of H_2 added vs. pressure. However, this plot contains no allowance for the expansion of the various hydride compositions to be encountered in the actual run, so corrections are made as explained below.

An actual run is now made with U at the same temperature and n_t aliquots of H_2 added are plotted vs. pressure. Thus,

*The equation of state for H_2 has not been measured directly at both high temperatures and pressures. Northrup⁸ has used another method.

$(n_t - n_g)$ at a particular pressure represents the number of moles of H_2 absorbed. A rough plot is obtained in this way. Corrections are made to n_g at the "plateau" extremes due to expansion of the particular UH_x composition. In other words, because the hydride expands, decreasing the free-gas volume of the internal vessel, fewer moles $(n_g - \Delta n)$, are needed to maintain a pressure than if there were no expansion in the UH_x .

The correction may be made as explained in the following paragraph, or by determining a calibration curve which uses a mock sample equal to the volume of UH_x for the particular UH_x being considered.

$$\text{If } V_1 = n_1 Z_1 RT / P_1,$$

where

Z_1 = compressibility

V_1 = free volume at P_1 with a Mo mock sample

P_1 = pressure with n_1 moles of H_2

n_1 = moles H_2 needed to maintain P_1 in the hot-cold system,

Then when U is added to the system, the V_1 is changed by some amount, ΔV , due to the formation of a UH_x and with the new volume $(V_1 - \Delta V)$, fewer moles of n_1 are required to maintain the same pressure. Therefore,

$$V_1 = n_1 Z_1 RT / P_1$$

$$(V_1 - \Delta V) = n_2 Z_1 RT / P_1$$

where n_2 is the new number of moles of H_2 required to maintain the same pressure.

$$n_2 = [n_1 - n_1 (\Delta V / V)]$$

and n_2 becomes the new n_g . See Appendix B for a numerical calculation.

The number of moles of H_2 added were calculated using a program executed on a

CDC 7600. These code calculations are accurate to better than $\pm 0.1\%$ (2σ) for pressures to 110.3 MPa (1089 atm) over a

temperature range of 0–100°C. It should be noted that the H_2 gas for charging is always at room temperature.

Results and Discussion

The pressure-composition isotherms to 1050°C and to pressures of 137.9 MPa (1361 atm) are shown in Fig. 13. To our knowledge, this is the first report describing the phase-diagram at temperatures above 846°C. Future work will determine whether absorption and desorption isotherms are identical, although Libowitz⁷ claims that no hysteresis exists above 450°C in the U-H system. The shapes of the isotherms are consistent with the following interpretation.

When U is heated, it absorbs H_2 forming a single solid phase of H_2 dissolved in U. This process continues until the appearance of two-solid phases in equilibrium with H_2 and dependent on temperature. They consist of β -uranium hydride and α -uranium metal saturated with H_2 . The "plateau" region thus formed is nearly independent of H_2 content over a long range and the pressure remains almost constant. With the further addition of H_2 , a single solid solution (U in stoichiometric hydride) forms, represented by the rapidly ascending portions of the isotherms. In Fig. 13, if the recorded values do not represent true equilibria, they at least represent apparent equilibria of sufficient stability to be physically significant.

The stoichiometry approaches UH_3 at the lower temperatures but very high pressures would be needed to get $UH_{3.0}$ at

higher temperatures. As seen from the figure, the trend of experimental points indicates that the deviation from stoichiometry at the experimental pressures is appreciable at higher temperatures. According to Libowitz, the non-stoichiometric behavior of U hydride is due to H_2 vacancies rather than interstitial U and higher temperatures which accommodate more vacancies.¹¹ Condon¹² presents an alternate model in which he considers the effect of O_2 contamination on the position of isothermal lines. In our experiments, the O_2 levels increased from 5 ppm in the as-received metal up to 146–310 ppm in the hydridized samples. The H_2 content varied from 15–35 ppm.

In the region where the plateaus turn upwards, we have noticed that the upturn is not as abrupt as might be expected. Slowness in attaining equilibrium may be a contributing factor, but this is only a guess. It is speculated that at 1050°C the single phase region on the H_2 rich side would begin at a H/U ratio of ~ 2.23 . At 1000°C the H/U ratio is 2.35.

In our work to date, we have not reached the "critical point" where the two plateau edges (U-rich and hydride-rich sides) must coincide. Condon¹² has stated that if the hydride remained solid, a critical point may not be achieved below 1800°C. In contrast to the above, Chevalier, et al.,¹³ describes a critical

Fig. 13. Pressure-composition-temperature diagram for the U-UH₃-H₂ system, absorption isotherms.

point of only 830°C. This critical point is also inconsistent with reported temperatures as high as 1400°C, and with the two-phase equilibrium pressures observed by Mallett and Trzeciak.¹⁴ It is possible that Chevalier's sample reacted with some

other material in the open-furnace environment and failed to consume H₂ at the higher temperature. We have observed incipient fusion at 1050°C in post mortem examination of the sample. Earlier work showed that melting occurred at about ... temperature.¹⁵

In Fig. 13, we observed that a slope occurs in the plateau pressures. It varies from a small total ΔP of 0.55 MPa (5.4 atm) in the 700°C isotherm to a ΔP of 6.89 MPa (68 atm) at 1000°C. Sloping plateaus have also been observed by Northrup,^{8,16} Several attempts have been made to explain the causes for a slope. McQuillan,¹⁷ in his work with Ti hydrides, attributes it to impurities. The plateau pressures of the Th dihydride measured by Nottorf¹⁸ and Mallett and Campbell¹⁹ are also not constant, but increase with increasing H content. Libowitz²⁰ has shown that the existence of thermal gradients along the sample during the P-C-T measurements will lead to such a sloping plateau. We have also performed experiments deliberately varying the temperature flat-zone and found large slopes when this was done. If a reason has to be given at this time for our sloping plateau, it is probably small and undetected temperature gradients and not impurities, since we used very pure U in our work. However, we cannot exclude the possibility that if a sufficient number of points were taken along the plateau more than one slope might result indicating some phase change.

Two isochores are plotted in Fig. 14. One is for a U hydride composition of $UH_{0.5}$ and the other is for $UH_{2.0}$. Using the integrated form of the van't-Hoff equation,²¹

$$\ln P_{H_2} = (\text{atm}) = \frac{2}{3R} \left(\frac{\Delta H_p}{T} - \Delta S_f \right)$$

for each composition we obtain a value of -26.4 Kcal/mole for the enthalpy (ΔH_p)* formation of $UH_{0.5}$ and -26.6 Kcal/mole

for $UH_{2.0}$. Extrapolating these values leads to -27.3 Kcal/mole for the apparent enthalpy of UH_3 for the temperature range 700°C - 1050°C. At lower temperatures (260-650°C), a value of $\Delta H = -30.6$ Kcal/mole (average value) was obtained by previous investigators. The ΔS values calculated from our data were -39.13 and -39.6 Kcal/°K/mole H_2 respectively.

Table II compares data extrapolated from previous data at lower pressures and temperatures with our current investigation. Impurities affect the location of a plateau²² in that they raise the dissociation pressure. It should be noted that the values tabulated from previous work are for desorption experiments.

A comparison was made of Northrup's and our data at the H-rich plateau terminus for comparable temperatures. The comparison is shown in Table III.

Our UH_x values are slightly lower by -2-3% depending on the temperature selected. The variations in the data may be due to differences in experimental and calculational technique.

HYDRIDED SAMPLE EXAMINATION

Two samples of hydrided U were reclaimed for post-mortem examination. Figure 15 shows a sample which had been hydrided at 950°C to a stoichiometry of $UH_{2.53}$ and then cooled for 1 hr under high pressure H_2 until the pressure reached 43.9 atm at room temperature. The final composition was analyzed as $UH_{2.987}$ and the structure is seen to be porous. Figure 16 shows a sample treated at 1050°C to a composition

* ΔH_p = plateau ΔH .

Fig. 14. Van't Hoff isochore for compositions $\text{UH}_{0.5}$ and $\text{UH}_{2.0}$. Extrapolat on to 402°C yields a dissociation pressure of 1 atm.

TABLE II.

Comparison of thermodynamic properties for Uranium Hydride

Investigator	Temperature range-°C	Enthalpy-Kcal/mole	Pressure atm			
			800°	900°	1000°	1050°
Spedding ¹	260-430	-30.8	160.7	181.1	765.5	1041.1
Flotow & Abraham ²	300-420	-30.45	93.6	217.75	411.68	544.37
Wicke & Otto ⁴	200-430	-30.5	148.8	326.6	666.8	898.2
Mogard & Cabane ⁵	500-650	-30.7	139.5	319.8	639.6	843.8
Libowitz & Gibb ⁷	450-650	-30.3	141.5	323.2	643.0	850.6
Northrup ⁸	450-800	-30.6 ^a	139.7 ^b	323.2	639.6	847.2
This Work (Absorption Only)	700-1050	-27.3	127.6 ^b	270.1 ^b	535.5 ^b	748.5 ^b
			(Average values across "plateau.")			

^aNorthrup⁸ reports an extrapolated value of -28.96 at 425°C.^bIndicates experimental value; all others are extrapolations.

TABLE III.

Comparison of Sandia Labs and LLL data at single-phase boundary region.

Temperature °C	UH _x Sandia	UH _x LLL	ΔX
846	2.7	2.62 estimated	0.08
801	2.72	2.67	0.05
700	2.8	2.73	0.07

(Note: The UH_x values were obtained from comparable isotherms of the respective plotted data.)

Fig. 15. Sample of uranium hydride, cooled under H_2 , after treatment to $950^\circ C$. Composition at $950^\circ C$ was $UH_{2.53}$. Final stoichiometry $UH_{2.987}$.

Fig. 16. Sample of uranium hydride, cooled under H_2 , after treatment to $1050^\circ C$. Composition at $1050^\circ C$ was $UH_{0.8}$. Final stoichiometry $UH_{2.72}$.

of $\text{UH}_{0.8}$.^{*} It was also cooled under high pressure H_2 until the pressure stabilized at 227 atm at room temperature. The final composition was $\text{UH}_{2.72}$. This sample indicates that incipient fusion had occurred. This was shown by the lack of porosity, rounding of particles, and the reflection of the contour of the BeO crucible. Figures 17 and 18 are polished specimens of the above two samples. Polishing was accomplished with 1 μ (particle size) diamond dust in kerosene. The white stringers are U metal in a matrix of hydride.

It appears from the final stoichiometry and the photomicrographs that

* The 1050°C isotherm on the P-C-T diagram was run on a different sample of U.

slightly more free U is present in the 1050°C sample, although there was sufficient H_2 to completely hydride it. In the 950°C sample, the amount of free U is ~1% as determined by a Quantimet 720 image analyzer. In the 1050°C sample, it is ~2.2%. It is thought that H_2 did not penetrate the surrounding hydride to the metal stringers in the relatively short cooling time. The H/U ratio of 2.72 in the 1050° sample could be due to accidentally sampling an unusually metal-rich region. The location of white stringers in the micrograph suggests original U grain boundaries. In the fabrication of U hydride composites under isostatic pressures, one probably needs to hold the system at a constant temperature for an appreciable time for H_2 to diffuse throughout the entire mass.

Summary

- Isotherms for the U- UH_3 - UH_2 system have been determined from 700°C to 1050°C. At the high temperature, it seems that the start of the single phase region on the hydrogen-rich side would begin at H/U ~2.23. At 1000°C, it is at a H/U = 2.35. Incipient fusion has been seen at ~1050°C. We believe that the phase diagram can be extended to at least 1200°C and 345 MPa (3402 atm) H_2 pressure in the present apparatus. Apparently the so-called "critical point" may be at lower temperature than previously believed.

- The use of an internal pressure vessel made of Mo, heated externally, and supported externally with H_2 gas is possibly the cleanest apparatus for high temperature pressure work used to date. Both absorption and desorption experiments may be performed with it.

- A method has been used whereby calculation of the density of H_2 in a variable temperature system has been avoided. This involves the use of calibration curves, and making appropriate corrections for the UH_x expansion.

Fig. 17. Sample treated at 950°C to a stoichiometry of $\text{UH}_{2.53}$. Cooled under high pressure H_2 . The dark areas are voids. Final composition $\text{UH}_{2.987}$. Magnified 500X. Oxygen analysis on two sections showed 146 ppm and 210 ppm. Nitrogen analysis showed 20 ppm and 35 ppm, respectively.

Fig. 18. Sample treated at 1050°C to a stoichiometry of $\text{UH}_{0.6}$. Cooled under high pressure H_2 . Polished mechanically with 1 diamond power. Cooled in one hour. Final composition $\text{UH}_{2.72}$. Magnified 500X.

Fig. 19. Sample area adjacent to that in Fig. 18. O_2 is 310 ppm; N_2 is 15 ppm.

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Appendix A

Geminol P and N thermocouple*
emf in mV reference junction at 32°F

°F ⁺	0	10	20	30	40	50	60	70	80	90	Change per °F
0		-.79	-.16	-.027	.10	.24	.37	.50	.63	.77	.0133
100	.90	1.04	1.17	1.31	1.44	1.58	1.72	1.85	1.99	2.12	.0136
200	2.26	2.40	2.54	2.68	2.82	2.96	3.10	3.24	3.38	3.52	.0140
300	3.66	3.80	3.94	4.08	4.22	4.37	4.51	4.65	4.79	4.93	.0141
400	5.07	5.22	5.37	5.52	5.67	5.82	5.97	6.12	6.27	6.42	.0150
500	6.57	6.73	6.89	7.05	7.21	7.37	7.52	7.68	7.84	8.02	.0159
600	8.18	8.36	8.52	8.69	8.85	9.02	9.19	9.35	9.52	9.68	.0166
700	9.84	10.01	10.18	10.36	10.53	10.70	10.87	11.04	11.22	11.39	.0172
800	11.56	11.74	11.92	12.10	12.28	12.46	12.63	12.81	12.99	13.17	.0179
900	13.35	13.54	13.72	13.91	14.09	14.28	14.46	14.65	14.83	15.02	.0185
1000	15.20	15.39	15.58	15.77	15.96	16.16	16.35	16.54	16.73	16.92	.0191
1100	17.11	17.30	17.50	17.69	17.89	18.08	18.27	18.47	18.66	18.86	.0194
1200	19.05	19.25	19.45	19.65	19.85	20.06	20.26	20.46	20.66	20.86	.0201
1300	21.06	21.26	21.47	21.67	21.88	22.08	22.28	22.49	22.69	22.90	.0204
1400	23.10	23.31	23.52	23.73	23.94	24.15	24.36	24.57	24.78	24.99	.0210
1500	25.20	25.41	25.62	25.83	26.04	26.25	26.46	26.67	26.88	27.09	.0210
1600	27.30	27.52	27.73	27.95	28.16	28.38	28.60	28.81	29.03	29.24	.0216
1700	29.46	29.68	29.90	30.12	30.34	30.56	30.77	30.99	31.21	31.43	.0219
1800	31.65	31.87	32.09	32.31	32.53	32.76	32.98	33.20	33.42	33.64	.0221
1900	33.86	34.08	34.30	34.53	34.75	34.97	35.19	35.41	35.64	35.86	.0222
2000	36.08	36.30	36.53	36.75	36.98	37.20	37.42	37.65	37.87	38.10	.0224
2100	38.32	38.54	38.76	38.99	39.21	39.43	39.65	39.87	40.10	40.32	.0222
2200	40.51	40.76	40.98	41.21	41.43	41.65	41.87	42.09	42.32	42.54	.0222
2300	42.76										

* Driver Harris Co. The positive leg consists of a 20% Cr, 1% Co balance Ni alloy. The negative leg consists of 3% Si in Ni. The negative leg is magnetic. Accuracy of the thermocouple is $\pm 4^\circ\text{F}$ in the range 0-500°F, and $\pm 3/4\%$ above 500°F.

Appendix B

Calculations to correct the placement of the P-X curve:

$$7.8571 \text{ g U}$$

$$n_2 = n_1 - n_1(\Delta V/V_1)$$

where

$$n_2 = \text{moles of gas when } \text{UH}_x \text{ forms}$$

$$n_1 = \text{moles of gas when U present}$$

$$\Delta V = \text{change in free-gas vol.}$$

$$V_1 = \text{original volume, } 11.67 \text{ cc}$$

$$U_D = 19.07 \text{ g/cc}$$

$$\text{UH}_{2.635} = 11.67 \text{ g/cc}$$

$$7.8665/19.07 = 0.4125 \text{ cc U}$$

$$(2.635 + 238.07) = 240.705$$

$$240.705/238.07(7.8665) = 7.9536 \text{ g UH}_{2.635}$$

$$7.9536/11.67 = 0.68154 \text{ cc UH}_{2.635}$$

$$0.68154 - 0.4125 = 0.26904 \text{ cc less volume}$$

$$n_2 = 0.0295 \text{ (from } n_x$$

vs P Plot) -

$$\frac{0.0295 (0.26904)}{11.67}$$

$$n_2 = 0.02882 = \text{new } n_x$$

to be subtracted

from n_T to get

moles absorbed at

the particular

pressure.

$$n_T - n_2 = (0.07303 - 0.02882)$$

= moles absorbed,

then

$$\frac{(\text{moles H}_2 \text{ absorbed}) 2 \text{ atoms/mole}}{\text{Moles U metal}} = \text{UH}_x$$

TAL/grw