will give the differential heat of solution, if the heat of fusion is known.

From the limiting slope of our curve we determined $\Delta\bar{H}$ to be about 9700 cal./mole. It is known that the heat of fusion for copper at its melting point (1356° *K.*) is 3120 cal./mole.[9] If we assume this heat of fusion to be independent of temperature, we get a value of 6580 cal./mole for the differential heat of solution at high dilution. In a similar manner, if we assume the entropy of fusion, which at the melting point is 2.30 cal./degree mole, to be independent of temperature, we find from the intercept $x \cong 6.5$ that the excess partial molal entropy is about 1.4 cal./degree mole. If data for the specific heat of the undercooled liquid copper had been available, we might have been able to improve these values by taking into account the dependence of the heat and entropy of fusion on temperature. In the absence of such data, we are only able to estimate the direction of this correction. It is well known that, at the melting point, the specific heat, C_p, of the liquid metal is normally somewhat larger than for the corresponding solid.[10] If we assume ΔC_p to have the same sign at lower temperatures, this will lead to higher values for the calculated differential heat of solution and also for the excess partial molal entropy.

Acknowledgments.—The authors are indebted to Mr. L. J. Howell for the spectrographic work done for this investigation. The authors also wish to thank Drs. T. Rosenqvist and N. H. Nachtrieb for valuable suggestions and comments.

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CHICAGO, ILL. RECEIVED APRIL 18, 1951

[CONTRIBUTION FROM THE BATTELLE MEMORIAL INSTITUTE]

The Dissociation Pressures of Thorium Dihydride in the Thorium–Thorium Dihydride System[1a]

BY MANLEY W. MALLETT[1b] AND IVOR E. CAMPBELL[1b]

Dissociation pressures have been measured in the thorium–hydrogen system for the range of compositions up to approximately $ThH_{1.90}$ at temperatures from 650–875°. The system resembles the Pd–H system in that the observed dissociation pressures are dependent on the solid-phase composition throughout the system.

Introduction

The reaction of thorium with hydrogen reported first by Winkler[2] in 1891, has been studied by numerous investigators.[2–6] Systematic pressure–composition studies of the Th–H system were made by Sieverts and co-workers,[7–9] using metal 96% pure and contaminated chiefly with thorium oxide.

The data of Sieverts and co-workers show that the Th–H system is similar to the Pd–H system, the most extensively investigated of the metal–hydrogen systems. They found the ability of thorium to absorb hydrogen to depend on the condition of the specimen, and noted hysteresis effects similar to those obtained with Pd–H.

No reference has been found in the literature to dissociation pressure studies in which pure metal was used. Since previous workers have noted that the absorption and desorption of hydrogen in the Th–H system are strongly influenced by the previous history of the metal, it was thought desirable to determine the dissociation pressure of the thorium–thorium hydride system, using the purest metal available.

Apparatus.—The hydride preparation and the pressure determinations were carried out in a modified Sieverts apparatus.

The thorium sample was contained in a double-walled, clear-silica reaction vessel which was connected to a full-length, open-end mercury manometer by a Picein wax seal. The system was evacuated with a Cenco Hyvac pump pumping through a Dry Ice–alcohol trap used to remove condensable vapors. An automatic Toepler pump was used to remove hydrogen from the system for measurement and analysis. A McLeod gage was used to check the tightness of the system and the degree of initial evacuation.

Hydrogen additions were measured with a 50-ml. gas buret graduated in 0.1-ml. divisions. Readings were estimated to the nearest 0.03 ml. Sample temperatures were measured with Pt, Pt-Rh (10%) thermocouple in conjunction with a Leeds and Northrup precision potentiometer. The thermocouple was calibrated at the gold point and tested for homogeneity before and after each run.

The heat input to the furnace was so adjusted that temperature fluctuations were only ±2°. All equilibrium pressures were read when the reaction bulb was at the exact temperature recorded, however, and it is believed that the probable error in sample temperature is less than ±1°, since equilibria were reached very rapidly in each case.

Pressures were estimated, with the aid of a magnifying lens, to ±0.3 mm. All readings were corrected for the thermal expansion of mercury. The fluctuation in pressure after reaching equilibrium was less than ±1.0 mm., and this probably represents the over-all precision of the pressure values. Atmospheric pressure was measured with a Taylor aneroid barometer, calibrated periodically against a mercury barometer.

The reaction bulb was heated by a heavily insulated platinum-wound tubular furnace 1.5 inch inside diameter and 18 inches long. A Foxboro controller was used to maintain the furnace at the desired temperature.

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[1] (a) This work was carried out under sponsorship of the Manhattan Engineering District and the Atomic Energy Commission, Contract No. W-7405-eng-72. (b) Battelle Memorial Institute, Columbus, Ohio.

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TABLE I

EQUILIBRIUM PRESSURES IN MM. *versus* TEMPERATURE AT VARIOUS COMPOSITIONS OF ThH_x

Temp., °C.	Ratio of hydrogen atoms to thorium atoms 0.05	0.10	0.30	0.50	0.90	1.30	1.50	1.65	1.80
650	4.0	13.0	15.0	16.0	16.2	18.0	19.0	22.0	55.0
675	..	...	23.0	25.0	26.0	28.0	30.0	32.5	90.0
700	7.5	23.5	37.0	39.0	41.5	46.0	48.0	57.5	151.0
725	..	...	60.0	61.0	65.0	71.0	75.0	83.0	247.0
750	12.5	42.0	85.0	90.0	98.0	109.0	115.0	135.0	390.0
775	..	...	128.0	134.0	151.0	166.0	175.0	200.0	600.0
800	21.0	69.0	185.0	195.0	217.0	240.0	254.0	283.0	...
825	..	...	266.0	285.0	311.0	338.0	352.0	427.0	...
850	32.0	106.0	368.0	392.0	434.0	476.0	497.0	605.0	...
875	..	...	501.0	537.0	600.0	664.0	707.5	837.0	...
900	49.0	162.5	623.0	692.0	779.0	950.0	1075.0	1175.0	...

Reagents.—Commercial hydrogen, purified by passing over hot copper shreds at 700° and drying with anhydrous magnesium perchlorate, was used in forming the thorium hydride. The hydrogen used in the jacket of the reaction bulb was not purified.

With the exception of five experimental points, all of the data were obtained with a single sample of thorium obtained from the Westinghouse Electric Corporation. The estimated purity of the sample was about 99.8%, the chief impurities being oxygen (0.16%) and carbon (0.04%). Spectrographic analysis showed the presence of the following impurities: Fe, 0.01%; Mo $<$ 0.01%; and Ti $<$ 0.01%. The percentages of all other metallic impurities were in the third decimal place or lower. The sample was used in the form of fine chips, freshly cut on a shaper from a clean bar of metal. Two points were obtained from a second sample of this metal.

Three points were obtained with a sample taken from a bar of metal obtained from the Iowa State College. The estimated purity of this specimen was about 99.7%, the chief impurities being carbon (0.2%), oxygen (0.03%), aluminum (0.03%), iron (0.03%) and silicon (0.02%). Other metallic impurities were low and were approximately the same as for the Westinghouse material.

Experimental Procedure.—The surface of the bar of thorium was cut away with a shaper, using a clean tool free of oil and grease. After a fresh surface was produced, sufficient chips were cut to furnish the desired sample which was weighed (2.989 g.) and then introduced into the silica reaction vessel without further treatment.

The reaction bulb was then sealed to the system and evacuated to 0.001 mm. Pumping was continued while the furnace was heated to 400°. Sufficient hydrogen was then added to form ThH_2. The hydrogen reacted as rapidly as additions could be made, the total time required for addition of the hydrogen being less than 15 minutes. Hydrogen, at a pressure approximately equal to that in the reaction bulb, was maintained in the surrounding jacket at all times.

After obtaining dissociation data at one approximate composition, the H:Th atom ratio was adjusted to the desired value in the range $ThH_{0.05}$ to $ThH_{1.88}$ and other equilibrium pressures were measured. Pressures for each composition were taken at 25° intervals from 650 to 875°. Three compositions above $ThH_{1.70}$ were studied first, then the composition was lowered to $ThH_{1.10}$ and later to $ThH_{0.05}$ in eight successive steps. Finally the composition was raised to approximately $ThH_{1.30}$, $ThH_{1.45}$ and $ThH_{1.65}$. The equilibrium points at one approximate composition were taken at increasingly higher temperatures, and the following composition was studied by lowering the temperature step-wise. Each basic composition changed slightly with temperature because the amount of hydrogen in the gas phase changed with the dissociation pressure.

An over-all check on the accuracy of the measurements of hydrogen additions was made by removing all of the residual hydrogen from the metal with the Toepler pump at the end of one typical run. A total of 290.0 ml. (S.T.P.) of hydrogen was initially added to the system. On removing the hydrogen in 12 intervals over a period of 10 days, 290.1 ml. (S.T.P.) of hydrogen was collected.

The gas volume in the system was determined from the volume of argon required to fill the free volume of the system at the temperatures used in measuring equilibrium pressures.

The composition of the solid phase was determined from the weight of the thorium sample and the volume of hydrogen (S.T.P.) sorbed by the metal. To obtain the volume of sorbed hydrogen, the measured volume of hydrogen added to the system was corrected for the volume of hydrogen remaining in the gas phase within the reaction system.

The measured dissociation pressure at each temperature was plotted against the calculated solid-phase compositions to give a series of pressure–composition isotherms (Fig. 1). From the isotherms, the dissociation pressures at constant compositions were obtained (Table I). These values were used in plotting log P against $1/T$ for the various compositions (Fig. 2).

Discussion

The experimental data plotted as pressure–composition isotherms (Fig. 1) were obtained from two runs on the Westinghouse metal and a third run on the Iowa State metal. The data from the three runs agree within the probable limits of experimental error.

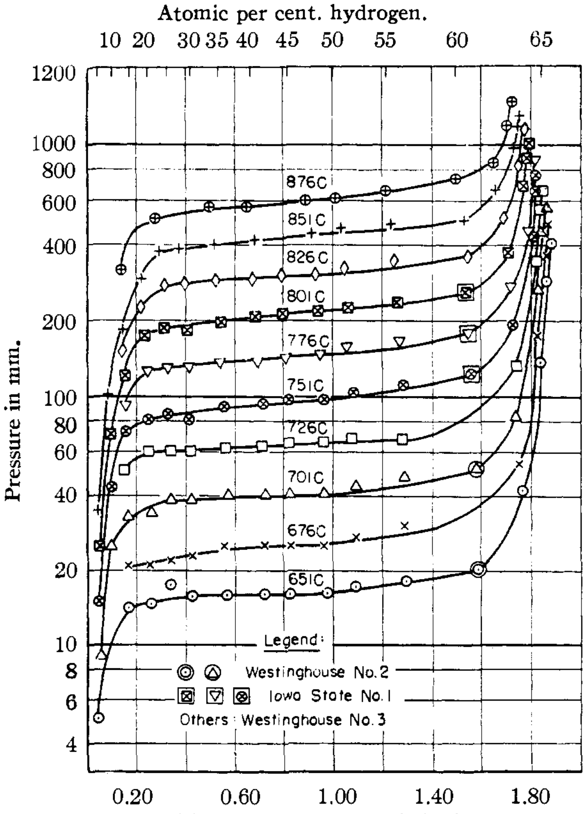

Fig. 1.—Log p *versus* composition isotherms for the system thorium–ThH_2–H_2.

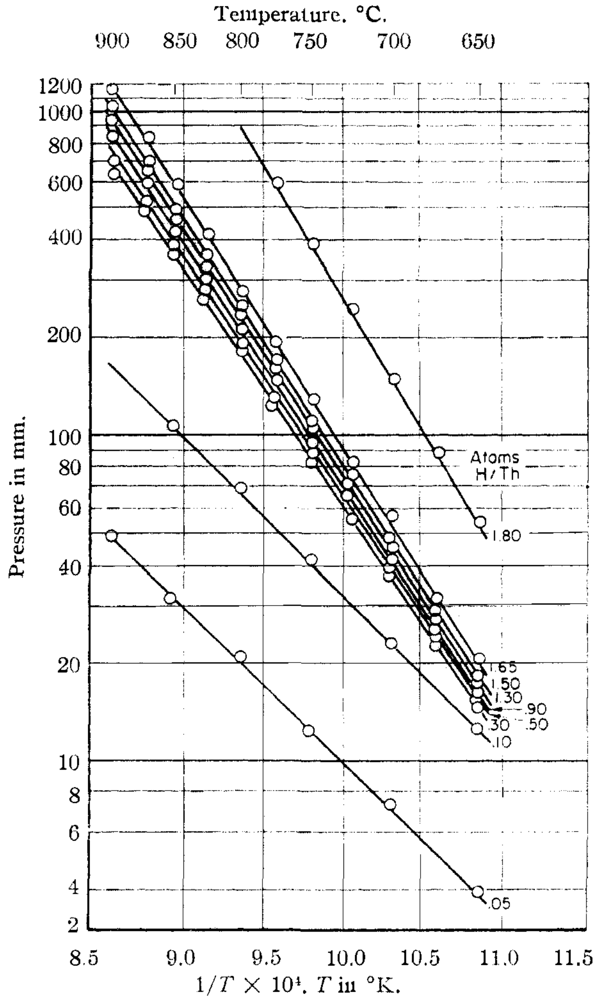

Fig. 2.—Log *p versus* $1/T$ for the system thorium–ThH_2–H_2, with various compositions.

The efficiency of the hydrogen recovery showed that no loss of hydrogen took place by diffusion through the wall of the silica bulb at high temperatures, when the double-walled vessel was used. In preliminary runs in which the jacket was not used, however, loss of hydrogen was observed at the higher temperatures.

The isotherms shown in Fig. 1 resemble those for the Pd–H, Ti–H, Zr–H, PuH_2–H[10] and other systems involving the exothermic occlusion of hydrogen by metals.[11] In the range of rapidly increasing pressure at low hydrogen concentrations, the amount of sorbed hydrogen is proportional to the square root of the "equilibrium" hydrogen pressure, and this region represents the range of solid solution of atomic hydrogen in thorium. The solubility increases from about 13 atomic per cent. at 650° to about 23 atomic per cent. at 900°.

The central portion of the isotherms is relatively flat. However, there is a slight but definite increase in pressure with increased hydrogen concentrations, and the slope of the isotherms increases as the temperature is increased. In addition, the range encompassed by the flat portion of the isotherm decreases as the temperature increases. If one assumes that the pressure represents true equilibrium conditions, then in accordance with the phase rule, this region must be a single-phase region. No X-ray data are available on this system at high temperatures, but X-ray diffraction at room temperature of a sample of the composition $ThH_{1.0}$ has shown the presence of two phases identified as thorium and thorium dihydride.

TABLE II

EQUILIBRIUM DATA FOR THE DISSOCIATION OF THORIUM HYDRIDES

Atomic ratio H:Th	$\log_{10} P$(mm.)	ΔH, kcal./mole	ΔS_{1073} cal./mole/ °K.
0.05	$-4720/T + 5.71$	+21.6	+12.9
.10	$-4760/T + 6.26$	+21.8	+15.5
.30	$-7220/T + 8.99$	+33.0	+27.9
.50	$-7550/T + 9.34$	+34.5	+29.4
.90	$-7550/T + 9.36$	+34.5	+29.5
1.30	$-7460/T + 9.33$	+34.1	+29.4
1.50	$-7480/T + 9.36$	+34.2	+29.6
1.65	$-7480/T + 9.44$	+34.2	+29.9
1.80	$-8060/T + 10.47$	+36.9	+34.4

Although there is some question as to the exact explanation for this behavior in metal–hydrogen systems, it is generally assumed that this is a two-phase region and that the apparent dependence of pressure on composition is due to failure to obtain true equilibrium. The failure to achieve equilibrium has been explained by D. P. Smith who has advanced the "rift" theory.[11]

According to the "rift" theory, true equilibrium is obtained only at internal phase boundaries, and the external pressure, being dependent on concentration gradients, is not equal to the true equilibrium pressure. In the present work no gross hysteresis effects between absorption and desorption isotherms, as noted by Sieverts and more recently by Spedding, *et al.*,[12] were observed. The pressures could be reproduced upon repeated removal and addition of hydrogen.

Representative equations for the logarithm of the dissociation pressures of thorium hydride at various compositions are given in Table II along with calculated heats and entropies of dissociation. The dissociation in each case is considered to be to a product with a hydrogen concentration lower than that of the reactant solid by an almost infinitesimal amount. The reported energies are for the production of one mole of hydrogen by this reaction. Although the energy values are the same as would be calculated from the equation $ThH_2 \rightarrow Th + H_2$, the former concept is thought to give a truer picture for systems in which the heat of reaction varies with composition. It will be noted that the heat of dissociation is constant at 34.3 ± 0.2 kilocalories per mole over the range of compositions from $ThH_{0.5}$ to $ThH_{1.65}$.

COLUMBUS 1, OHIO RECEIVED APRIL 16, 1951

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