cobalt, the above metals were found to react completely with molten sodium hydroxide. The rate of reaction was dependent upon the availability of unreacted metal. These metals, therefore, were studied briefly to establish their valence state in the reaction products. Simultaneously, the absence of a "steady-state" and hydrogen inhibition was established.

The procedure used was a modified material balance technique in which a small weighed quantity of the metal reacted completely with an excess of sodium hydroxide contained in a nickel tube. The hydrogen yielded by the reaction was then balanced against the original weight of metal (after a chemical check of the residue to ensure complete reaction) and thus interpreted into which oxide of the metal could have resulted from the reaction.

The following equations summarize the results. The temperatures shown are approximate points of significant reaction

$$2Fe + 6NaOH \xrightarrow{600^\circ} Fe_2O_3 + 3Na_2O + 3H_2 \tag{13}$$

$$2Cr + 6NaOH \xrightarrow{650^\circ} Cr_2O_3 + 3Na_2O + 3H_2 \tag{14}$$

$$Ti + 4NaOH \xrightarrow{325^\circ} TiO_2 + 2Na_2O + 2H_2 \tag{15}$$

$$2Ta + 10NaOH \xrightarrow{600^\circ} Ta_2O_5 + 5Na_2O + 5H_2 \tag{16}$$

$$Be + 2NaOH \xrightarrow{650^\circ} BeO + Na_2O + H_2 \tag{17}$$

$$Mn + 4NaOH \xrightarrow{600^\circ} MnO_2 + 2Na_2O + 2H_2 \tag{18}$$

None of the runs resulting in the establishment of the above equations gave metallic sodium or water vapor as reaction products. They were, however, short time experiments. Prolonged exposure to hydrogen may result in the production of some water and sodium.

All of the solid products on the right in the above equations react with water, yielding hydroxides or hydrated oxides. In the case of tantalum, the hydrolysis product is completely soluble. In the case of chromium, when leached in air, part of the residue forms a soluble chromate.

Ferrous alloys (304 SS, 310 SS, 36% Ni-64% Fe alloy, and 64% Ni-17% Cr-17% Fe alloy) react as might be predicted from all of the foregoing. The iron and chromium fractions react completely as shown by their individual equations, while the nickel portion appears to remain unattacked, probably by reason of the protective effect of the produced hydrogen. The over-all effect on the alloy, however, is one of complete destruction. The mechanism of attack is one of severe penetration in contrast to the more or less uniform removal from the surface of nickel, copper and gold.

Meager data on the reaction of NaOH with silver indicates a similarity to gold. One exception is the fact that silver tubes become quite porous to molten NaOH after a few fusions.

Cobalt was investigated by a single test which showed "steady-state" pressures of hydrogen and water vapor identical to those shown for nickel. Its further reactions are assumed to be identical.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY,[1] GENERAL ELECTRIC COMPANY]

The Titanium-Hydrogen System[2]

BY R. M. HAAG AND F. J. SHIPKO

RECEIVED APRIL 23, 1956

The equilibrium pressure of hydrogen over titanium-hydrogen has been measured at 300, 400 and 500°. Similar measurements have been made of titanium-deuterium and titanium-tritium. At 500° no isotope effect was observed.

The titanium-hydrogen system is one of several metal-hydrogen systems which have been studied both from the practical standpoint because of the high hydrogen occlusion obtained and from the academic viewpoint because of the light which may be shed on the properties of metal systems. The high hydrogen concentrations (approximately 450 cc. (STP) H_2/g. titanium) obtainable in this system make it ideal for many storage applications. Among these are the following: 1. Separation of hydrogen and its isotopes from other gases; 2. Transfer of large quantities of gas in a small volume at low pressure; 3. Preparation of materials with high hydrogen density.

In the titanium-hydrogen system, as in the similar systems zirconium-hydrogen and hafnium-hydrogen, the occluded gas has apparently less metallic character than in the possibly unique palladium-hydrogen system, but more than in the uranium-hydrogen and thorium-hydrogen systems.

The dissociation pressures of the hydrides are the most convenient functions and have been extensively studied. Kirschfeld and Sieverts[3] and recently McQuillan[4] have studied the Ti-H system at pressures from 1 to 760 mm., and at temperatures below 1000°. Gibb, *et al.*,[5] have made measurements above 500° and at high as well as low pressures. No results have been reported, however, for the micron pressure region which includes low concentrations at 500° and nearly the entire range at 400 and 300°.

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[1] The Knolls Atomic Power Laboratory is operated by the General Electric Company for the Atomic Energy Commission. The work reported here was carried out under Contract No. W-31-109 Eng. 52.

[2] Presented before the Physical and Inorganic Division of the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

[3] L. Kirschfeld and A. Sieverts, *Z. physik. Chem.*, **A145**, 227 (1929).

[4] A. D. McQuillan, *Proc. Roy. Soc.* (*London*), **204A**, 309 (1950).

[5] T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, THIS JOURNAL, **73**, 1751 (1951).

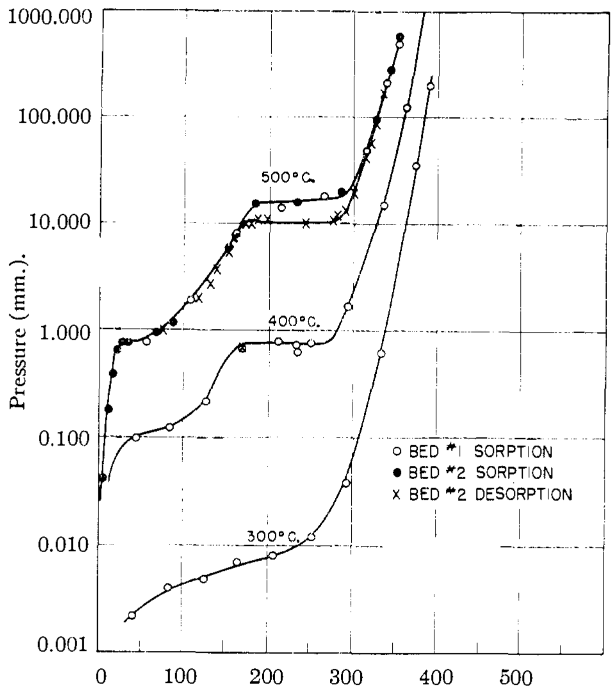

Fig. 1.—Equilibrium pressure *vs.* hydrogen concentration (titanium powder).

Experimental

The vacuum system that was used consisted of a manifold to which was attached a mercury manometer, McLeod gage, one-liter bulb and a sample bulb. The one-liter bulb which had been calibrated with water was used for the volume calibration of the rest of the system. The McLeod gage had a range of 0.1 to 2000 μ. The mercury manometer was read with a cathetometer to 0.1 mm. A U-tube trap between the stopcock and the quartz bulb was held at −80° with a Dry Ice–trichloroethylene bath to protect the sample against contamination by mercury and hydrocarbons from the stopcock grease. The sample bulb was held at temperature by a resistance heated oven.

Temperatures were measured with a chromel–alumel thermocouple located in the sample bulb and connected to a Speedomax recorder. The thermocouple used was calibrated at the melting points of tin, lead and zinc and showed no error greater than 2°. Therefore no corrections were made.

The hydrogen and deuterium used were obtained from Matheson Company and Stuart Oxygen Company, respectively. The gas was purified by the formation and decomposition of uranium hydride (or deuteride) and stored in the same form.

Pressure measurements were made on both takeup and evolution. In a typical experiment, hydrogen was evolved into the manifold alone or the manifold plus the one-liter bulb from the uranium bed. When a predetermined pressure was reached, the uranium bed was shut off and the pressure read on the manometer. The titanium bed which had previously been brought to the temperature of the experiment was then opened to the manifold. Although the reaction was quite rapid, the system was allowed to remain a few degrees above the desired temperature for about 16 hr. after which it was cooled at a rate of about 1° per hr. for six hr. From the temperature–pressure curve so obtained, the value of the dissociation pressure at the desired temperature was obtained by interpolation. Successive increments of hydrogen were added to the system by repeating the above process. Upon completion of a sorption isotherm in this manner, the desorption isotherm was obtained by isolating the titanum bed, sorbing on the uranium bed the gas contained in the manifold and one-liter bulb, isolating the uranium bed, opening the titanium bed and allowing the system to come to equilibrium. As before, from 16 to 24 hr. were allowed for equilibration.

The accuracy of the concentration values given below is dependent upon the measurement of the sample weight (±0.1%), of the volume of the system (±0.2%), of the pressure (±0.2 mm. on the manometer or 1–10% on the McLeod depending upon the value of the pressure measured), and of the temperature of the gas (±0.5°). Since the added gas had generally an initial pressure of roughly 100 mm., we have an uncertainty of 0.2% in the pressure, 0.2% in the volume, 0.15% in the temperature and 0.1% in quantity of titanium giving an uncertainty in the concentration of 0.33%. Since, in general, about 10 or 15 measurements were made consecutively we would expect an uncertainty in concentration at the highest concentration of roughly 1%, corresponding to 5 cc. (STP) H_2/g. titanium. We actually observed errors of closure after cycles of sorption and desorption averaging 1.3% with titanium powder and only 0.21% with the better-behaved titanium foil. The highest value with foil was 0.3% (1.9 cc. in 650 cc. after 31 operations) while one was as low as 0.04% (0.3 cc. in 722 cc. after 10 operations), indicating that the estimates above are conservative. The precision of the equilibrium pressure measurements depends on the measurement of pressure (see above) and of the sample temperature (±1°). At 400° and at most concentrations the latter gives an error of 3%. On the upper plateau at 500° the pressure is about 10 mm. which can be measured to 0.2 mm. or 2%. Thus the relative error of this measurement should be approximately 4%. We find standard deviations from the mean of approximately 3.5% for seven points on the hydrogen curve and 3% for four points on the deuterium curve. The accuracy of measurement of the equilibrium pressure is influenced by a temperature uncertainty of possibly 2° or 6% in the pressure which together with the 2% uncertainty in the measured pressure gives a total uncertainty of roughly 6.5% or 0.6 mm.

Preliminary measurements were made on titanium metal formed by the decomposition of titanium hydride powder (Metal Hydrides, Inc., Beverly, Mass.). This material

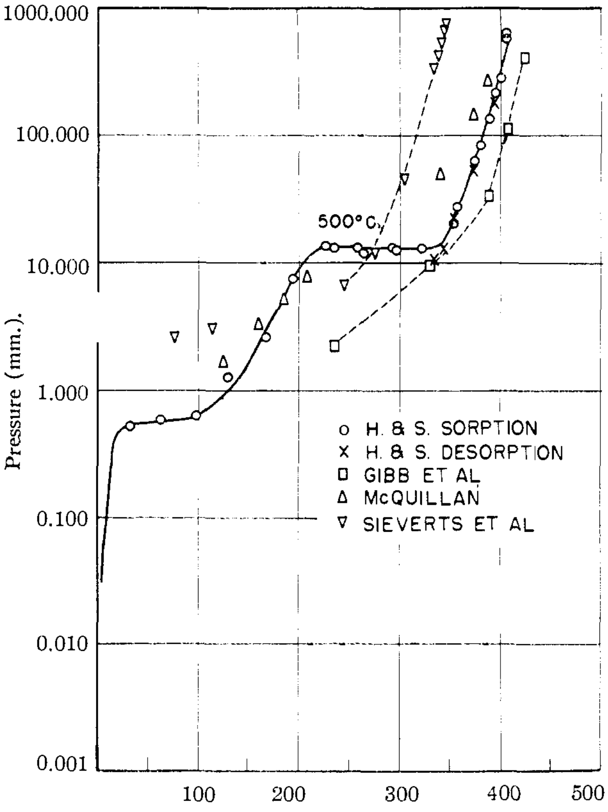

Fig. 2.—Equilibrium pressure *vs.* hydrogen concentration (titanium foil).

contained approximately 1% aluminum, 0.2% silicon and traces of magnesium, lead, manganese, iron, antimony, platinum and copper. The hydrogen content of the powder as received was measured by evolving the hydrogen at 600° into an uranium bed from which it was subsequently removed and measured. It was found that this material contained 412 cc. H_2 (STP)/g. titanium or 88% of the theoretical composition. Measurements were made at 300 and 400° of the sorption isotherm and at 500° of both the sorption and desorption isotherms. No measurements were made on desorption at 300 and 400° because of the very small amounts of gas removable per cycle. These results are shown in Fig. 1.

The 500° isotherm was repeated using massive metal (0.002 in. foil). This material (Kroll Process) contained approximately 0.2–0.3% iron and 0.2% silicon as the major impurities together with traces of manganese, magnesium and aluminum. Before use the foil was degreased in boiling trichloroethylene, rinsed in acetone and transferred to the same bulb. The bulb was evacuated and the sample degassed at room temperature for approximately one week after which the temperature was raised over a period of eight hours to 500° and held there for 16 hours. The final rate of degassing was approximately 7 × 10^{-5} cc. (STP)/hr. Following this, the 500° isotherm was traced as shown in Fig. 2. Using the same metal, the titanium–deuterium system was studied at 300, 400 and 500° with the results shown in Fig. 3.

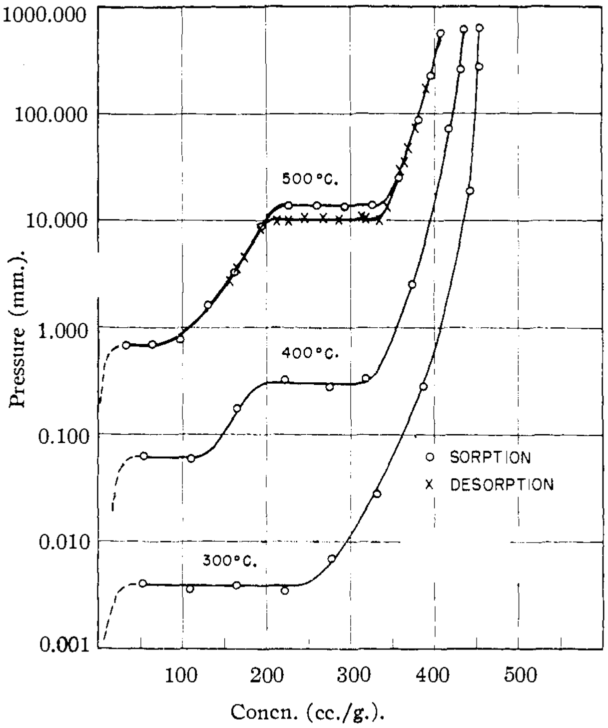

Fig. 3.—Equilibrium pressure *vs.* deuterium concentration (titanium foil).

Preliminary isotherms at 400 and 500° were obtained for the tritium–titanium system (Fig. 4). The tritium used had a composition of roughly 65% T_2, 35% H_2. No measurements were made at 300° because the He^3 formed during a run at this temperature would exceed the equilibrium pressure of the tritium at most concentrations. In general not more than three points were determined consecutively. Between these groups of points, the titanium bed was completely degassed to remove any He^3 formed during the interval. Before each introduction of gas, the uranium storage bed was cycled to remove the He^3 formed there since the preceding operation. In general the uncertainty of these measurements is somewhat higher than that proposed for hydrogen and deuterium and here we used an uncalibrated thermocouple and introduced the gas at lower pressures.

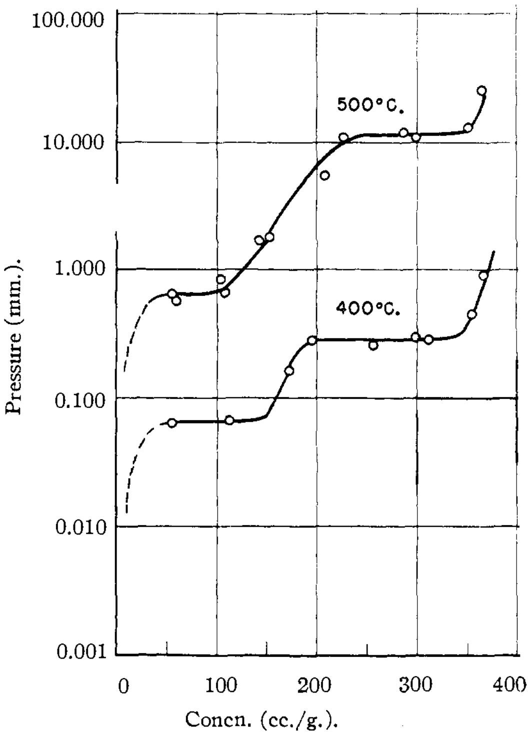

Fig. 4.—Equilibrium pressure *vs.* tritium concentration (titanium foil).

Results

Comparison of Figs. 1 and 2 shows that the powdered titanium had a hydrogen capacity 15% lower than that of the massive metal. Although no single reason for this lower capacity has been determined, we can eliminate some possible sources. We cannot ascribe this discrepancy to surface effects since the available area seems much too small. Although no direct area measurements were made, electron micrographs showed a particle size distribution in which approximately 97 weight % of the particles had a diameter of approximately one μ or more. Thus we have for these particles only 0.1% surface titanium and a total of at least 97% bulk titanium. This assumes, of course, no rifting which cannot be proven unless and until adsorption studies are made. Furthermore, web thicknesses of the order of 15 atom diameters would be required to give the observed effect if rifting did occur. Neither can this be ascribed to the formation of TiO_2 or Ti_3N_4 since chemical assay showed greater than 99.5% titanium metal in the powder (exclusive of the aluminum impurity). Hall, Martin and Rees[6] have shown in the zirconium–hydrogen systems that the presence of oxygen reduces the occlusive capacity of the metal only to the extent that the compound ZrO_2 is formed. Bumps, *et al.*,[7] have indicated the existence of the compound TiAl. The aluminum impurity formed here (one weight % or two atom %) combined with two atom % of titanium would cause a decrease of capacity only one-fourth that observed, assuming the compound to be

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[6] M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

[7] E. S. Bumps, H. D. Kessler and M. Hanson, *J. Metals*, **4**, 609 (1952).

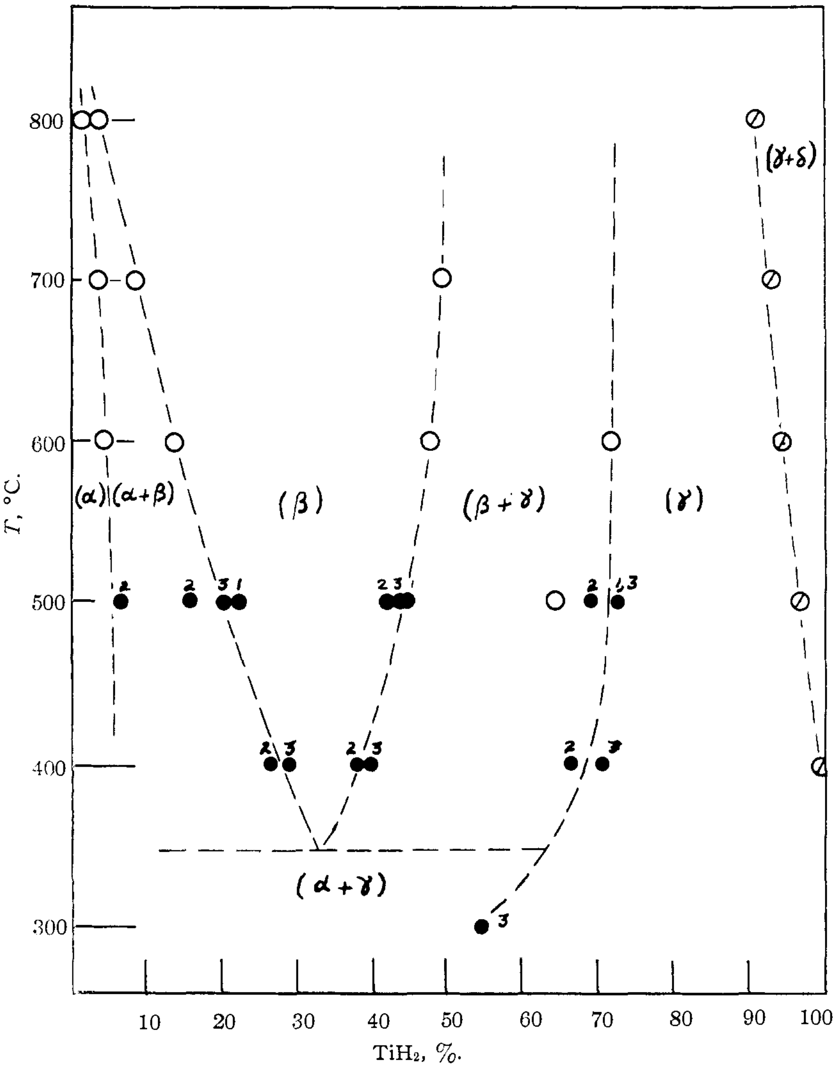

Fig. 5.—Phase relations in the titanium–hydrogen system: ●, H and S (1 = H_2–Ti foil, 2 = H_2–Ti powder, 3 = D_2–Ti foil); O, McQuillan; ⊖, Gibb, *et al.*

non-occluding. At the present time we can only say that the cause of this lower capacity may be found in the behavior of the ternary system Ti–Al–H. McQuillan[8] has compared Kroll-process and iodide-process titanium and has found in the less pure former metal some distortion of the isotherm as compared with the latter, mainly in the lower concentration ranges.

In Fig. 2 our data are compared with those of previous workers. The results of Sieverts[3] with the much less pure material available then are, at the higher concentrations, very similar to those obtained here with powder. His data, however, do not show any plateau. The data of Gibb,[5] *et al.* (obtained with metal of somewhat higher purity) are taken from their Fig. 4 except for the 234 and 330 cc./g. points which are taken from their Fig. 3. They assume in each case that their original material is the stoichiometric hydride TiH_2, and calculate concentration by difference. Thus any lack of saturation would lead to a calculated value of the concentration higher than that actually present. The results of McQuillan are very similar to ours except for a slightly narrower upper plateau and a higher pressure on that plateau. Their plateau is approximately 30% higher equivalent to a temperature difference of 7°.

The deuterium data given in Fig. 3 show no isotopic effect at 500°. The comparison at 300 and 400° is inconclusive since for hydrogen we have only the data obtained with the powdered titanium. Similarly, the tritium–hydrogen mixture shows, within the limit of experimental error, no deviation from pure hydrogen.

Discussion

McQuillan,[4] in his study of the titanium–hydrogen system at elevated temperatures ($T >$ 500°) has found three phases which he has called α, β and γ. The α-titanium hydride phase constitutes a solution of hydrogen in the parent hexagonal close-packed lattice of a α-titanium metal and hence has the structure of that lattice. The β-titanium hydride is likewise smoothly formed from the modification of the metal. Hagg[9] and Gibb, *et al.*, have investigated the γ-phase (their β) and found it to be face-centered cubic. Gibb has also found at high temperature a fourth phase of the undetermined structure which he calls γ. This is possibly the compound TiH_2 which we will call the δ-phase. The constitutional diagram of the system as shown by the present work and that cited above is given in Fig. 5. In Table I we compare the nomenclature used by other workers with that used here.

TABLE I

COMPARISON OF STRUCTURE AND NOMENCLATURE

Hagg	α		β	
Sieverts, *et al.*	α	α	β	
McQuillan	α	β	γ	
Gibb, *et al.*	α	α	β	γ
This work	α	β	γ	δ
Structure	HCP	BCC	FCC	?

The reactions in the various areas of the phase diagram may be represented by the equations

$$dn\ H_2(g) + Ti(s) \longrightarrow TiH_{2dn}(s) \quad (1)$$

$$dn\ H_2(g) + TiH_x(s) \longrightarrow TiH_{x+2dn}(s) \quad (2)$$

$$dn\ H_2(g) + \frac{2dn}{y' - x'}\ TiH_{x'} \longrightarrow \frac{2dn}{y' - x'}\ TiH_{y'} \quad (3)$$

The infinitesimal heat change d ΔH then is equal to $(\partial \Delta H/\partial n_2)_{T,\,n_1} dn_2$ or $\Delta \bar{H}_2\ dn_2$. But this is

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(8) A. D. McQuillan, *J. Inst. Metals*, **79**, 371 (1951).

(9) G. Hagg, *Z. physik. Chem.*, **B11**, 433 (1930).

just $R\ (\partial \ln p/\partial 1/T)\ dn_2$. The observed change of equilibrium pressure with temperature gives then a quantity which may be called the partial (or differential) relative molal heat content. This differs slightly from the quantity L_2 used in most solution work in that the change in heat content is measured against the gas in equilibrium with the solution rather than against a gas at some fixed pressure. To indicate this difference we will continue to use the notation ΔH, thus $\Delta \bar{H}_2$ as above and $\Phi\Delta H_2 = \Delta H/n_2$. In the region covered by this work ($p < 1$ atm.) the correction is well within the experimental error. At the higher pressures studied by Gibb the correction may be appreciable.

In Fig. 6 we have plotted the average value between 400 and 500° of $\Delta \bar{H}_2$ for the $\alpha + \beta$, β, and $\beta + \gamma$ regions. In each of the two phase regions the value is of course constant and in the β-region[4] is constant within experimental error. In the γ-region we have plotted $\Delta \bar{H}_2$ averaged between the same temperatures for a number of concentrations. In this region McQuillan[4] has shown at higher temperatures that $\Delta \bar{H}_2$ is dependent both upon temperature and concentration so that these averaged values may not correspond to the same temperature. From these data and McQuillan's value of -21.6 kcal./mole for the α-phase we have computed ΔH and $\phi\Delta H_2$ as shown in the same figure.

Sieverts and Gotta[10] have measured the heat of combustion of $TiH_{1.73}$ and obtained at room temperature the value $\Delta H = -31.1$ kcal./mole for the heat of formation of the hydride. Assuming Kopps law we find $C_p = 0.865\ (6.8 - 2.3 \times 2) = 1.90$. Then at 450° we obtain $\Delta H = -30.3$ kcal./mole which is in fair agreement with our value of -28.7 kcal./mole. Until heat capacity measurements of the hydrides are reported we can make no better comparison of the two methods of measurement.

Rees[11] has recently constructed a model of two component interstitial solid solutions in which all non-metal atoms occupy interstitial sites in a parent metal lattice. These interstitial sites may be of varying types and the total number of one type may be dependent upon the number of another type which have already been filled. He further assumes that the energy of an atom in an interstitial site relative to that of a free atom is independent of (1) changes of symmetry of the parent lattice, and (2) changes of cell dimensions and temperature, and that interaction energies are independent of these factors and of concentration. From this model he deduces pressure–temperature–composition relationships which he tests against his zirconium–hydrogen data.[12]

Unfortunately this model and its results do not reproduce the observed properties of the titanium–hydrogen system. We do not observe loops in the phase diagram characteristic of critical phenomena. Across an α-β or a β-γ phase boundary we go in the first case from an HCP to a BCC structure and in the latter case from a BCC to a FCC structure. These structural changes with their accompanying change in number and quality of interstitial sites surely violate the postulates of the model in the worst way.

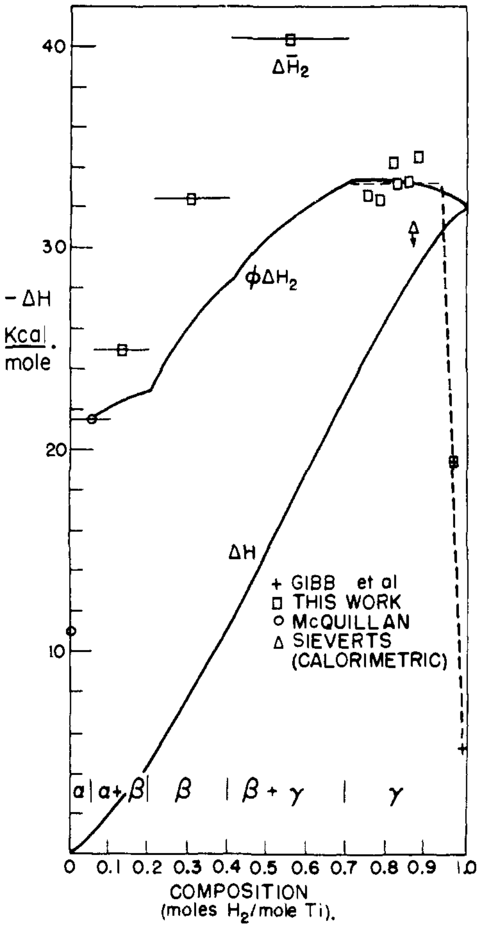

Fig. 6.—Reaction heats at 450°.

We make one reservation in our denial of the validity of this treatment. Below about 325° where the two phases, α and γ, are possible we may construct on the phase diagram part of a critical solution loop. Here in passing from an HCP to a FCC lattice the structural changes are really very minor and obtainable by slight rotations of the hexagonal close packed layers of the parent metal lattice. The metal–solute interaction energies should be only very slightly dependent upon structure. Each dissolved hydrogen occupies in each case a tetrahedral hole. Solute–solute interactions may be expected to be slightly different in the two cases, since in the HCP lattice solute pairs occur with closer spacing than in the FCC lattice.

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[10] A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, **199**, 384 (1931).

[11] A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 335 (1954).

[12] S. L. H. Martin and A. L. G. Rees, *ibid.*, **50**, 343 (1954).