would be $\{X\}\ \{O_2\}\ \{B_2H_6\}$, and could be explained on the basis of a rapid reversible reaction between any two of the above three species followed by a slower chain branching step involving the third.

However, in the light of present knowledge of this reaction, the mechanism outlined in equations 2 to 4 is to be preferred.

Regardless of whether the mechanism involves third order terms or not, from the magnitudes of the coefficient ratios of Equation 1 it can be seen that oxygen is about 1.5 times as effective a chain stopper as hydrogen, and is five times as effective as nitrogen. Further, since there is no correlation with the relative collision frequencies, these effects are probably partially chemical in nature rather than pure energy transfer as in the hydrogen–oxygen reaction.[9]

It should be emphasized that the mechanism proposed above should be considered tentative only. However, in common with most reaction schemes, it explains in a fairly satisfactory manner most of the proved facts. Much more work obviously must be done with such a complex and labile system before a definitive mechanism can be proposed.

Summary

The first and second pressure limits of explosion of B_2H_6–O_2 mixtures have been investigated. The effects of temperature, composition and vessel size have been studied.

The first limit showed little effect of temperature (135–250°) and composition (10% B_2H_6–50% B_2H_6) occurring around 10–15 mm. total pressure. It was concluded that both chain branching and chain breaking processes occur at the wall.

The second limit of the stoichiometric mixture was studied as a function of temperature. The influence of diluent gases on the second limit was studied at 180°, and showed a marked effect. The limit could be expressed by an equation of the type $aP_{B_2H_6} + bP_{O_2} + \sum_i c_iP_i + k = 0$. It was concluded that here both chain branching and breaking took place in the gas phase.

SCHENECTADY 5, N. Y. RECEIVED MAY 5, 1950

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[9] Frost and Alyea, THIS JOURNAL, **55**, 3227 (1933); Hinshelwood, *et al.*, *Trans. Faraday Soc.*, **24**, 559 (1928); Hinshelwood, *et al.*, *Proc. Roy. Soc.* (*London*), **122A**, 610 (1929); **124A**, 219 (1929).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES, INC.]

The Titanium–Hydrogen System and Titanium Hydride. I. Low-Pressure Studies

BY THOMAS R. P. GIBB, JR., AND HENRY W. KRUSCHWITZ, JR.

The titanium–hydrogen system has been investigated by several workers whose results are unfortunately somewhat at variance with one another. The only systematic study of *p–t* relations is that of Kirschfeld and Sieverts[1,2,3] who report isotherms and isobars over a wide range of temperatures but only for pressures less than 800 mm. It is evident from the fact that the stoichiometric composition, TiH_2, was not closely approached under otherwise favorable conditions that these workers did not use sufficiently pure titanium or hydrogen. The density and lattice constants of various compositions are reported by Biltz[4] and by Hägg[5] whose results are not completely concordant, and the density by Sieverts.[3] Fitzwilliam[6] studied magnetic susceptibility as a function of composition, and Gulbransen and Andrew[7] have found the rate of absorption of hydrogen by titanium to be complex and not easily interpreted. The heat of formation of $TiH_{1.73}$ was measured calorimetrically by Sieverts and Gotta[8] who obtained a value of 31.1 kcal. for the heat of formation. McQuillan,[9] who studied the effect of hydrogen lowering on the α–β transformation temperature of titanium (860–900°), has calculated the heat of solution of hydrogen in the α and β forms of titanium and finds an anomalous positive value in the vicinity of the transformation temperature. Smith[10] compares the titanium- and palladium-hydrogen systems and adduces evidence for their basic similarity. An excellent theoretical interpretation of metal–hydrogen equilibria is given by Barrer,[11] who refers briefly to the Ti–H system.

Discussion

The unique ability of hydrogen to form alloy-like compositions with a number of metals has prompted several investigations of the properties and structures of such systems. Unfortunately early investigators failed for the most part to recognize that traces of impurities in the metal, or more seriously in the hydrogen, inhibit the dissolution of hydrogen.

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[1] H. Huber, L. Kirschfeld and A. Sievets, *Ber.*, **59B**, 2891 (1926).

[2] L. Kirschfeld and A. Sieverts, *Z. physik. Chem.*, **145**, 227 (1929); *Z. Elektrochem.*, **36**, 123 (1930).

[3] A. Sieverts, *Z. metallkunde. Chem.*, **21**, 37 (1929).

[4] W. Biltz, *Z. anorg. allgem. Chem.*, **174**, 42 (1928).

[5] G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1931).

[6] J. Fitzwilliam, A. Kaufmann and C. Squire, *J. Chem. Phys.*, **9**, 678 (1941).

[7] E. Gulbransen and K. Andrew, *J. Metals*, **1**, No. 10, Trans. 741 (1949).

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

[9] A. D. McQuillan, *Nature*, **164**, 24 (1949).

[10] D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Illinois, 1948.

[11] R. M. Barrer, *Discussion Faraday Soc.*, No. 4, 68–81 (1948).

In the work reported here, an attempt has been made to evaluate and eliminate those factors which have caused previous difficulties. By employing titanium of high commercial purity and by taking unusual precautions to purify the hydrogen used, it is possible to prepare a stoichiometric compound, TiH_2. This compound is apparently metallic in that it is hard, lustrous in massive form and a fairly good conductor of electricity and of heat. The observed brittleness is probably due in part to the presence of pores, microcracks and larger fissures, which in turn are caused by the 17.2% volume expansion attendant on the solid state conversion of the metal to the hydride.

Whether this limiting composition is properly called a compound is debatable. There is unequivocal evidence, for example, that its composition and gross properties are definite and reproducible, and that its X-ray diffraction pattern contains moderately strong lines not hitherto reported in the titanium–hydrogen system. These novel lines are two in number (d = 2.076, 1.801 Å.) and are observable only for freshly prepared material whose X-ray spectrum consists otherwise of the lines reported by Hägg for pure β-phase. The novel lines are found to disappear gradually as the hydride is stored over a period of a few weeks in air, although the hydrogen content shows a loss which, if significant, is so slight (0.01% by weight) as to be well within the analytical error. That a phase entirely distinct from the hexagonal β-phase exists in compositions closely approaching TiH_2 is also confirmed by the observed leveling off of isotherms in this composition region.[12] Short plateaus would be permissible according to the phase rule only if two phases were present.

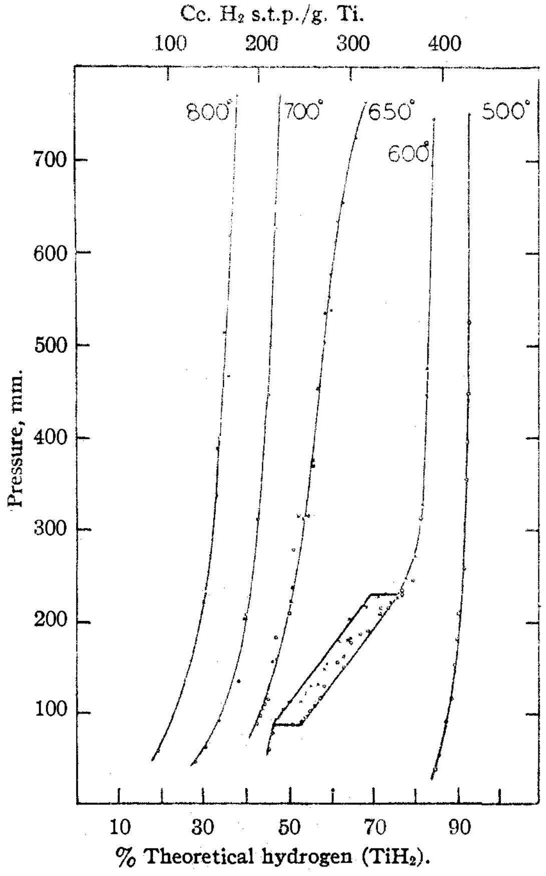

Fig. 1.—Isotherms of Ti–H system: equilibrium pressure in mm. *vs.* composition expressed as % maximum H-content (lower scale) or cc. H_2 per gram Ti (upper scale). The circles represent desorption, the crosses represent sorption measurements. The isotherm temperature is given in °C.

There is thus evidence that an unstable compound of stoichiometric composition and properly termed "titanium hydride" exists as a limiting phase. Since commercial "titanium hydride" is identical with the β-phase and does not contain the unstable "true" hydride, the use of the term "hydride" in this connection is somewhat ambiguous. To avoid conflict with established usage, it is perhaps wise to allow some latitude in the nomenclature of this type of compound; however, in this article the term "hydride" is understood to refer to the stoichiometric compound irrespective of the structure (for a definition see (13)).

Pressure–Temperature–Composition Curves.—The isotherms shown in Fig. 1 are qualitatively similar to those reported by Sieverts but are displaced almost uniformly to the right, *i. e.*, toward higher hydrogen content. From occasional trials with impure metal or more frequently, inadequately purified hydrogen, we have discovered that traces of impurities have a marked effect on the equilibrium pressure and on the rate of attainment of equilibrium. Traces of nitrogen, oxygen and possibly other elements retard attainment of equilibrium and generally displace it in the direction of lower hydrogen content. Thus the difference between Sieverts' results and those reported herein are probably due to the higher purity metal and hydrogen employed in this work.

The effect of hydrogen purity on the rate of hydriding is referred to by Burke and Smith for the U–H system.[14] We have found that pure, partially hydrided titanium and specially purified hydrogen react rapidly even at 20° and that equilibrium at any temperature or pressure in the range cited is attained rapidly although not always at a reproducible rate. Variations in rate are not interpretable solely in terms of purity but depend on the previous thermal history of the sample and to a large extent on the amount of hydrogen remaining in it. The effect of the history of the sample is not reflected in the *equilibrium* pressure except in the case of the 600° isotherm where a typical hysteresis loop was found. Figure 2 shows an expanded graph of this loop. Although

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(12) T. R. P. Gibb, Jr., and J. J. McSharry, unpublished.

(13) T. R. P. Gibb, Jr., *J. Electrochem. Soc.*, **93**, 199 (1948).

(14) J. R. Burke and C. S. Smith, THIS JOURNAL, **69**, 2500 (1947).

the roughly rectangular shape, indicated in Fig. 1, is typical of other metal–hydrogen systems, the hysteresis in this case is more subtle since the points shown which do not conform exactly to a rectangular shape (Fig. 1) are largely reproducible. The outline of the loop is, therefore, irregular and a complex mechanism is implied.

Smith's ingenious theory of rifts[10] does not fully explain all details of the hysteresis which unquestionably involves more than one factor. Very possibly the proximity to the α–β transformation temperature, which is lowered by the presence of hydrogen, is significant, and the rifts or lattice fissures are due to some such transformation which does not occur at lower temperatures and which occurs smoothly and continuously at higher temperatures. The tendency of hydrogen to stabilize an expanded lattice is well known.

Lacher[15] has suggested that in the palladium–hydrogen system hysteresis is due to a supersaturation of one solid phase by hydrogen, and that true equilibria are attained in the loop despite the apparent violation of the phase rule. Lacher attributes this to the effect of the enormous interphase surface on the magnitude of the dissociation pressure of one (or both) phases. Thus a finely dispersed, new phase would show a greater dissociation pressure than when present in bulk. Presumably the free energy of the system, *including* the contribution of the surface, is at a minimum at each point in the hysteresis loop.

Barrer[11] offers a third explanation of hysteresis in which sorption sites *recently* vacated by hydrogen are considered to affect the equilibrium pressure during evolution in much the same way as occupied sites. Thus the system would appear univariant over the limited region where this behavior is shown (see plateaus in the 600° isotherm of Fig. 1). Moreover the possibility is raised that hydrogen cluster formation at certain compositions might account for the system becoming univariant.

Irrespective of the mechanism, it is interesting that the loop shown in Fig. 2 is much smaller than that found by Sieverts for the 640° isotherm, indicating that traces of impurities may affect the size and shape. The absence of any hysteresis in the 650° isotherm is also noteworthy because of the proximity to Sieverts' 640° loop. Sieverts does not give any isotherms in the range 650–750°. The lower portion of Fig. 1 undoubtedly consists of a family of horizontal isotherms which bend sharply upward to meet the curves shown. Spedding[16] and Johns[17] have studied these lower regions in the case of the U–H and Pu–H systems, respectively, and find the isotherms substantially horizontal, indicating the presence of two solid phases.

Because of the differences between our results and those of previous workers, the accuracy of our experimental data and the reliability of the techniques used require brief comment. We have been able to take different samples of titanium, subject them to hydrogen treatment following various thermal cycles and still obtain isotherms actually superposable on those shown in Fig. 1. Moreover, several isotherms have been determined repeatedly both up and down a wide pressure range and also found superposable on those shown. On the other hand, we have found some samples containing oxygen and other impurities to behave qualitatively according to Sieverts' earlier data. We have also found that the hydrogen content and rate of attainment of equilibrium at a given pressure depend to a large extent on what must be exceedingly small traces of impurities in the hydrogen gas used. Furthermore the effect of these gaseous impurities depends on whether they are brought in contact with the original metal or previously formed hydride. In the latter case the effect is smaller and may even be in the opposite direction.

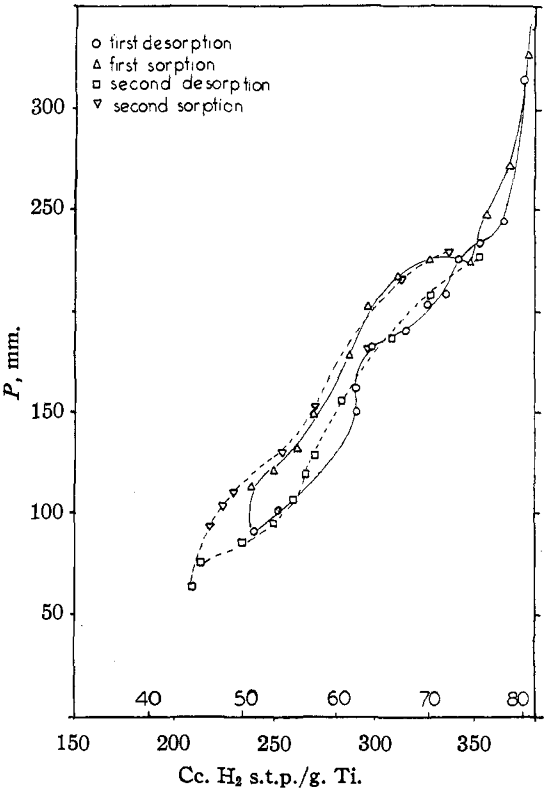

Fig. 2.—An enlarged portion of the Ti–H isotherm at 600° showing reproducibility of data in the hysteresis region. Sorption measurements are denoted by circles and squares; desorption measurements are denoted by upward and downward pointing triangles, respectively. The connecting lines are shown simply to clarify the relation of the four sets of observations.

Density and Lattice Constants.—The relationship we have found between density and

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(15) J. R. Lacher, *Proc. Roy. Soc.* (*London*), **A161**, 525 (1937).

(16) J. C. Warf, A. S. Newton, T. A. Butler and F. Spedding, *Nucleonics*, **4**, No. 1, 2 (1949); **4**, No. 2, 17 (1949).

(17) I. B. Johns, MDDC 717, LADC 277.

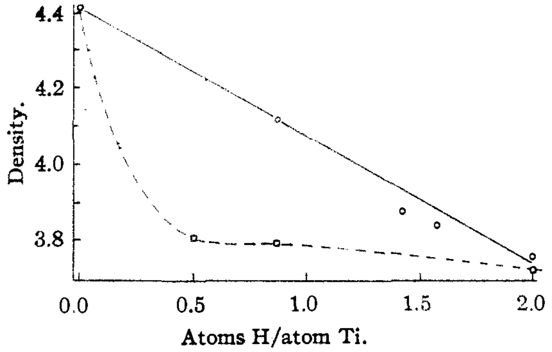

Fig. 3.—The relation of density (g./cc.) to composition (atoms H per atom Ti) in the Ti–H system. The earlier data of Biltz[18] are shown as the dotted curve.

hydrogen content is shown as the solid line in Fig. 3. The data of Biltz[18] are indicated by the dotted line. While no explanation is offered for the discrepancy, it is possible that the helium displacement method used by us[19] is less sensitive to sample porosity or inhomogeneity than the procedure used by Biltz. It is quite possible that there are minor discontinuities in the relationship, but the reproducibility from sample to sample is not good enough to warrant indicating any systematic deviation from the almost linear relation shown. X-Ray diffraction patterns of samples containing various amounts of hydrogen up to 1.95 atoms confirm only in general the work of Hägg[5] (see Table I), but the discrepancies may be attributed to differences in the purity and thermal history of the two sets of samples (Compare (10), p. 101). The lack of correlation between X-ray data and dissociation pressure measurements indicates that phase transformations may occur as the samples are cooled and prepared for diffraction analysis. Facilities were not available for X-ray study of samples at elevated temperatures. The large lattice constant for $TiH_{1.26}$ reported by Hägg does not appear to be consistent either with our results or with the density curve (Fig. 3). The density of TiH_2 as calculated from our X-ray measurement (3.96 g./cc.) does not agree with our density determined by helium displacement (3.76 g./cc.), although the density determined by Biltz (3.72 g./cc.) confirms the latter figure. However, the X-ray determination yields only the density of the β-phase.

TABLE I

LATTICE CONSTANT AS A FUNCTION OF COMPOSITION

Sample	a_0	c_0	Phase	Reference
Ti	2.95	4.69	αTi	Patterson[20]
$TiH_{0.66}$	3.11	5.02	αTi + αH	Hägg
$TiH_{0.36}$	2.95 (α) 4.395 (β)	4.68 (α)	αTi + βH[a]	[b]
$TiH_{0.95}$	4.397		βH	Hägg[5]
$TiH_{1.26}$	4.460		βH	Hägg[5]
$TiH_{1.65}$	4.40		βH	[b]
TiH_2	4.45		βH + TiH_2	[b]

[a] Note: From the spacing of the β-phase, the composition is roughly $TiH_{1.60}$. [b] X-Ray diffraction studies were carried out by Dr. H. T. Evans, Jr., of M. I. T.

When hydrogen diffuses into pure α-titanium, apparently an α-solute phase forms as soon as a small concentration is attained. The two phases co-exist either until the titanium is exhausted when the α-H-phase is the only solid phase or until the β-phase appears. As the hydrogen absorption continues, the β-phase increases at the expense of the α-phase until the latter disappears. The system is then all β-phase up to nearly stoichiometric TiH_2 when, according to our findings, a new phase starts to form as evidenced by the appearance of diffraction lines not ascribable to the β-lattice.

Experimental

Titanium.—The metal employed was obtained from the du Pont Co. and was purified by heating at 1000° in high vacuum when the principal impurities (Mg, Si) were volatilized. The nitrogen content was found to be 0.02%, acid insoluble titanium 0.04%, silica 0.07%. Spectrographic analysis revealed no appreciable contamination by other metals. The purified samples took up the theoretical volume of pure hydrogen.

Hydrogen.—A selected cylinder of oil-pumped, Linde-Air Products Co. hydrogen was used. All samples from several producers showed considerable contamination presumably by moisture, carbon monoxide, and air. After several trials by conventional methods, it was found necessary to purify the hydrogen by the following, somewhat cumbersome procedure: The gas was allowed to pass slowly over a Deoxo palladium catalyst, through a tower of Drierite (J Fig. 4), through a stainless steel tube K, 40 × 3 cm. packed with a mixture of Metal Hydrides Inc. Grade R' zirconium powder with sufficient titanium sponge to reduce the resistance to flow. This

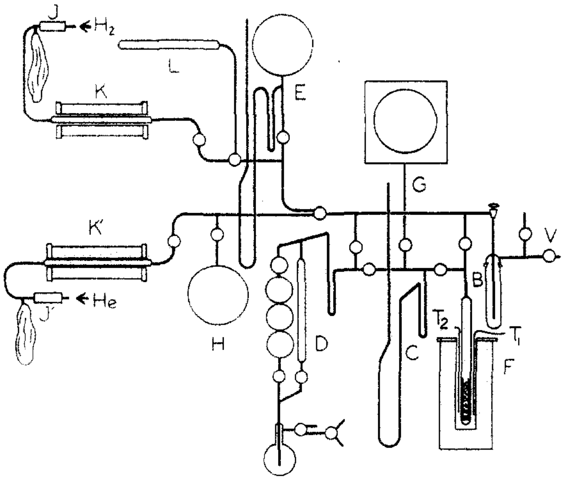

Fig. 4.—Diagram of equipment used for low pressure studies of the Ti–H system: (F) thermostatically controlled furnace with quartz tube containing sample, (G) recording pressure gage, (D) gas buret, (H) helium storage bulb, (E) hydrogen storage bulb, (K) (K') getter furnaces, (L) titanium hydride used as hydrogen reservoir.

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(18) W. Biltz, "Rauchemie der festen Stoffe," L. Voss, Leipzig, 1934.

(19) W. C. Schumb and E. S. Rittner, THIS JOURNAL, 65, 1692 (1943).

(20) R. A. Patterson, *Phys. Rev.*, 26, 56 (1925).

tube was kept at a temperature of 875°. The hydrogen thus purified was absorbed into ordinary degassed titanium contained in a heated silica tube L. After absorption and cooling, the resulting hydride was evacuated briefly at 200-300°, following which pure hydrogen was obtained as needed by heating to above 500°.

Helium.—This gas was used for volume calibration and was dried over Drierite and purified by passage through a tube containing zirconium powder heated to 875°.

Apparatus.—The dissociation measurements were made by observing the equilibrium pressure of hydrogen over a sample at a given temperature. The hydrogen content was determined by calculation from the pressure and known volume of the system. Changes in the volume of the sample due to the presence of hydrogen were found to have a negligible effect and were ignored. The equipment used is shown in Fig. 4. A weighed sample of pure titanium was placed in a 347-alloy stainless steel crucible which had previously been subjected to a blank run. The crucible was placed in the silica tube B in furnace F and degassed in high vacuum overnight at room temperature. The temperature was raised to 1000° over 17 hr. and a pressure of 0.1 μ maintained. A known volume of hydrogen at known pressure was admitted to the isolated sample from storage vessel E, the furnace allowed to cool overnight to 400° and then slowly at 25°.

After evacuation the volume of the measuring portion of the system was determined by admitting a known volume of helium from H and observing the pressure at C. The system was evacuated through V, then heated to the temperature of the desired isotherm. Known volumes of hydrogen were added or removed from the sample tube B *via* the double gas buret D. Equilibrium pressures were measured by manometer C and recorded by a Brown Instrument Co. pressure gage G. The Hoskins FA 120 furnace F was controlled to 0.5° by a reflection-galvanometer and phototube relay system connected to thermocouple T_1. The other thermocouple, T_2 (chromel-alumel), was frequently calibrated *vs.* a Bureau of Standards Pt-Pt, 10% Rh thermocouple and was used for measurement of temperature to 0.5°.

Equilibrium pressures were usually attained in a matter of minutes and could be maintained without change over a period of days. In general 45 min. was allowed after a constant pressure was noted. Diffusion losses were negligible and within experimental error over a period of weeks, as evidenced by constancy and reproducibility of readings. Contamination of the sample by mercury vapor was prevented by keeping the U-tubes adjoining the gas buret and each manometer immersed in Dry Ice-acetone.

Stoichiometric hydride TiH_2 was prepared in the above equipment, by cooling slowly to room temperature, and also in a large vacuum furnace consisting of a welded 347-alloy, stainless steel retort within a Hevi-Duty 1200° muffle furnace. Crucibles of the same alloy were broken in by trial runs. Titanium was degassed below 450° for 8-48 hr. to avoid fixation of adsorbed gases, then at 1000° for several hours in high vacuum. Hydrogen purified by passage through red hot Ti-Zr mixture was admitted and the furnace cooled over a period of 12-24 hr. A titanium getter layer was used to protect the sample from traces of oxygen and nitrogen which were always detected by slight discoloration of the getter. Hydrogen pressure was atmospheric throughout the absorption process.

Acknowledgment.—The work reported herein was sponsored by the NEPA Project. The authors wish to express their appreciation for this support and for many helpful discussions with Drs. V. P. Calkins, W. K. Anderson and J. W. Johnson, of the NEPA Group. Suggestions by Drs. A. E. Finholt, M. D. Banus and Mr. R. W. Bragdon, of this company, contributed materially to the solution of experimental difficulties. Dr. H. T. Evans, of M. I. T., carried out the X-ray studies and the interpretation thereof.

Summary

Stoichiometric titanium hydride was prepared and its density determined. The dissociation pressure was measured for the Ti–H system over the range 500–800°, 50–800 mm. and an hysteresis noted in the 600° isotherm. X-Ray diffraction patterns were observed for several compositions in the range $TiH_{0.86}$ to TiH_2 and two evanescent lines were found in the pattern of the stoichiometric hydride. A nearly linear relation of density to composition was found in this system from Ti to TiH_2. Titanium containing small quantities of interstitial hydrogen was found to react rapidly with pure hydrogen at room temperature and atmospheric pressure.

BEVERLY, MASS. RECEIVED MAY 13, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PHILADELPHIA QUARTZ COMPANY]

The System Na_2O–SiO_2–H_2O at 50, 70 and 90°*

BY C. L. BAKER, L. R. JUE AND J. H. WILLS

The only available information on phase stability in the system Na_2O–SiO_2–H_2O from 50 to 100° is the solubility curve for sodium metasilicate hydrates[1] and some data on phases separating at 60 and 100° determined by Leidenroth.[2] Leidenroth reported a compound $3Na_2O \cdot 2SiO_2 \cdot 6H_2O$ which is certainly the $3Na_2O \cdot 2SiO_2 \cdot 5H_2O$ or $Na_3HSiO_4 \cdot 2H_2O$ found at lower temperatures.[3] His data at 60° indicate that he obtained $Na_3HSiO_4 \cdot 1H_2O$ as well as the other hydrates. At 100° his data usually approach the $Na_3HSiO_4 \cdot 1H_2O$ composition rather than that of the dihydrate. Jordis[4] reported $Na_2SiO_2 \cdot 1.5H_2O$ formed at 100°.

Fairly complete isotherms at 50 and 70° are here reported. An incomplete system showing the more alkaline silicates at 90° is included. The new compounds found are $\alpha Na_2SiO_3 \cdot 6H_2O$,

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* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society 116th Meeting, Atlantic City, N. J., September, 1949.

(1) C. L. Baker and L. R. Jue, *J. Phys. Chem.*, **42**, 165 (1938).

(2) K. Leidenroth, "Ein Beitrag zur Kenntnis der Natrium Silikate," Inaugural Dissertation, Martin Luther University, Halle-Wittenberg, June 29, 1939.

(3) J. H. Wills, *J. Phys. Chem.*, **54**, 304 (1950).

(4) E. Jordis, *Chem. Ztg.*, **38**, 922 (1914).