TABLE V

POSSIBLE NEPTUNIUM ION SPECIES TAKING PART IN DISPROPORTIONATION REACTION

	Possible ions of Neptunium		H^+ power	H_2O power
Np^{+4}	NpO_2^+	NpO_2^{++}	4	−2
Np^{+4}	$NpOOH^{+2}$	NpO_2^{++}	2	−2
Np^{+4}	NpO^{+3}, $Np(OH)_2^{+3}$	NpO_2^{++}	0	0, −2
Np^{+4}	$NpOH^{+4}$	NpO_2^{++}	−2	0
Np^{+4}	NpO_2^+	$NpOOH^{+3}$	5	−2
Np^{+4}	$NpOOH^{+2}$	$NpOOH^{+3}$	3	−2
Np^{+4}	$Np(OH)_2^{+3}$, NpO^{+3}	$NpOOH^{+3}$	1	0
Np^{+4}	$NpOH^{+4}$	$NpOOH^{+3}$	−1	0
Np^{+4}	$Np(OH)_2^{+3}$	$Np(OH)_2^{+4}$	2	−2
Np^{+4}	$Np(OH)^{+4}$	$Np(OH)_2^{+4}$	0	0

ion was more susceptible to reaction with hydrogen ion than the neptunium(V) ion. This would appear unlikely in view of the greater formal charge on the neptunium(VI) atom. Furthermore, from the previous discussion, the possibility of ions having fewer than two OH^- groups can also be excluded insofar as both neptunium(V) and neptunium(VI) are concerned. The fact that the disproportionation reaction occurs also eliminates those ion species giving a zero or inverse hydrogen ion function for the reaction. With these restrictions in mind reference can be made to the data on the disproportionation reaction summarized in Table IV. The constant for the reaction can be written in the form

$$K_1' = \frac{[Np(IV)][Np(VI)]}{[Np(V)]^2[H^+]^x} = K_1 \frac{\gamma_H^x + \gamma_{Np(V)}^2}{\gamma_{Np(VI)}\, \gamma_{Np(IV)}\, [a_{H_2O}]^y} \quad (4)$$

In the absence of any quantitative data on the activity coefficients of any of the neptunium ions, an approximate calculation of the hydrogen ion power on the assumption that the activity coefficient ratio $\gamma_{Np(V)}^2/(\gamma_{Np(VI)}\gamma_{Np(IV)})$ is unity, neglecting the water activity term, and using the mean activity coefficients of perchloric acid from the data of Robinson and Baker[21] for the hydrogen ion activity gives an approximately third power hydrogen ion dependence between the 1.0 *M* and 5.34 *M* acid solutions. Although this might be interpreted as indicating the formulas $NpOOH^{+2}$ and $NpOOH^{+3}$ for the neptunium(V) and (VI) ions, respectively, in view of the rather drastic assumptions involved this cannot be taken as conclusive. Further investigations of the disproportionation reaction at constant ionic strength are contemplated to settle the question.

[21] R. A. Robinson and O. J. Baker, *Trans. Royal Soc. New Zealand*, **76**, 250 (1946).

CHICAGO, ILL.

RECEIVED SEPTEMBER 14, 1950

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

The Titanium–Hydrogen System and Titanium Hydride. II. Studies at High Pressure

BY THOMAS R. P. GIBB, JR., JAMES J. MCSHARRY AND ROBERT W. BRAGDON

The equilibrium pressure of hydrogen over the metallic titanium–hydrogen system has been measured as a function of the hydrogen content of the solid phase. Measurements have been made over the range 175 to 1000° at pressures ranging up to 5,000 cm. and the results plotted as log *P vs.* reciprocal of absolute temperature. A series of straight lines is obtained whose slope increases with decreasing hydrogen content. From these slopes the differential heats of dissociation are calculated. A family of isotherms shows plateaus at compositions approaching TiH_2 indicating presence of a novel phase.

In the first paper of this series[1] it was shown that titanium hydride has an unexpectedly high dissociation pressure. Moreover, the equilibrium pressures above various hydrogen-rich compositions in the Ti–H system were found to exceed the feasible limits of conventional equipment at temperatures of the order of a few hundred degrees. Accordingly a special apparatus was constructed and a technique devised for study of the system over a wide range of conditions. The work reported in this paper includes (1) the design of a special apparatus for investigation up to 1000 p.s.i. at temperatures up to 1000°, (2) a presentation of the results obtained, (3) a discussion of the theoretical implications thereof, and (4) calculation of the heat of dissociation and allied thermodynamic quantities.

Method.—The procedure employed for measurement of dissociation pressure is relatively simple: Titanium hydride, either formed *in situ* or previously, is contained in three bombs D (Fig. 1) attached by capillary tubing to a manifold consisting of recording pressure gages B, B′, B″, C, a calibrated reservoir J, and a hydrogen-purifying train GG′. All volumes are measured by a pressure-drop method employing a manometer–reservoir system A.

Measurement of dissociation pressure is made as follows: a quantity of purified hydrogen at moderately high pressure is admitted to the evacuated and previously purged system. The bombs of hydride are then heated slowly and the pressure developed plotted as a function of temperature as in Fig. 2. The lower left-hand portions of each curve represent thermal expansion. These portions are close to linear except in the vicinity of 140° where there is a barely perceptible dip of unknown origin. The time required at any temperature or pressure for attainment of equilibrium varies from a few minutes to an hour or more depending on these variables and also on the composition and previous thermal history of the sample. The intersection of the nearly linear thermal expansion curve with the steeper portion is taken as the point at which the solid phase just starts to dissociate. This point is assumed to represent the dissociation pressure of TiH_2. From the curved portions of the plots shown in Fig. 2, the equilibrium pressure for various compositions may be ascertained. The exact composition represented by any point on this curve is calculated from the known volume and pressure, *i.e.*, the amount of gaseous hydrogen present in excess of that introduced originally is calculated and subtracted from the amount of hydrogen originally present in the stoichiometric hydride to give the composition of the solid phase at the temperature and pressure in question. Since any point on the curved portions of Fig. 2 represents an equilibrium state, the result of the above calculation gives a composition of the Ti-H_2 system at equilibrium with the hydrogen above it at the temperature and pressure chosen.

In the higher pressure and temperature regions, one

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[1] Thomas R. P. Gibb, Jr., and Henry W. Kruschwitz, Jr., THIS JOURNAL, **72**, 5365 (1950).

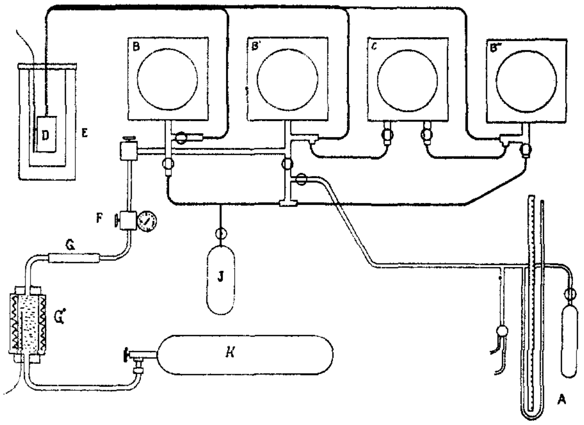

Fig. 1.—Apparatus: (D) bomb containing hydride, (E) furnace (BB'B''C), recording pressure gages, (F) precision gage, (GG') hydrogen purifying train, (H) hydrogen cylinder, (J) calibrated reservoir, (A) standard volume and manometer for calibrating volume of system.

might expect the calculated composition to be affected most seriously by diffusion losses. These, however, were shown to be only slightly greater than the gage error by retracing the entire pressure–temperature curve during cooling. The retraced curves were less than 10 p.s.i. lower than the original curves over the range 360–600° and were substantially parallel thereto, thus demonstrating the absence of hysteresis or serious loss by diffusion.

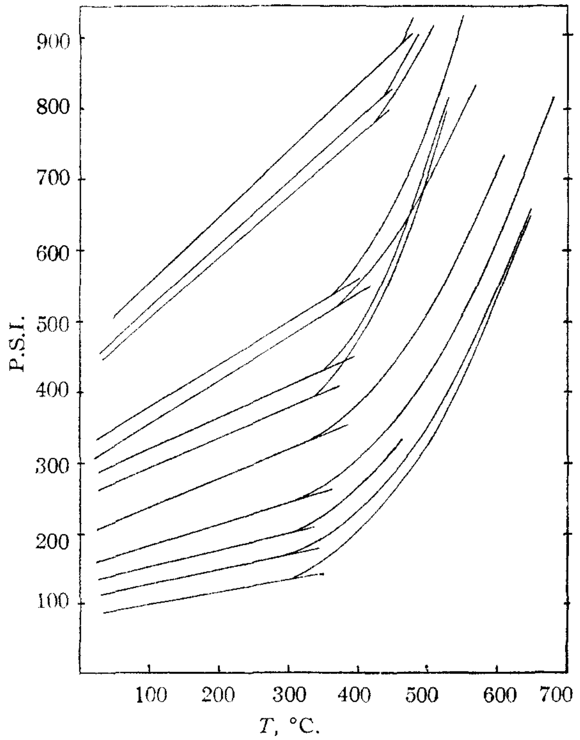

Fig. 2.—Pressure–temperature curves showing intersection of linear thermal expansion curves with dissociation curves. Ordinate is pressure in p.s.i. developed in bomb at temperature T° (from recording pressure gage). Numbering from the top, curves 1, 2, 3, 5, 8, 9, and 11 are for 50.5 g. of TiH_2 in free volume 120 cc.; curve 4 is for 105.4 g. in 100.7 cc.; curves 6 and 7 for 120.0 g. in 94.2 cc.; and curves 10 and 12 for 50.3 g. in 120 cc. free volume.

Linear plots of these dissociation pressures at various percentages of theoretical composition are shown in Fig. 3. All appear to be straight lines which on extrapolation intersect the 100% or TiH_2 curve at more or less regular intervals. The 50 and 70% lines are from data obtained with the low-pressure equipment[1] and confirm the agreement of the two methods. The data from both methods are plotted as a series of isotherms in Fig. 4. The points used in plotting these isotherms were for the most part obtained graphically from an enlarged plot of Fig. 3. Intermediate points and those at temperatures of 500° or less were calculated from the curves of Fig. 2 and from data given in the first article of this series. Calculated points and those derived graphically checked fairly well with the exception of a single calculated point on the 700° curve. The logarithmic ordinate is necessary for graphical presentation in view of the wide pressure range covered. This scale also emphasizes the near plateaus in the middle portion of the upper three isotherms and the sharp inflections in the high-pressure, high-hydrogen-content regions.

Discussion

Johnson, Stubbs, *et al.*,[2] have reported that the slope of the log *P vs.* 1/*T* plot for calcium hydride depends on composition in much the same manner as indicated in Fig. 3. They studied two compositions over a rather limited range and noted that the respective curves intersected (on extrapolation) at 1000° which they suggest may represent the lowest temperature at which a single liquid phase exists. They also give isotherms for the calcium–hydrogen system over a low range of pressures which show plateaus at intermediate compositions interpreted as due to the presence of saturated solutions of calcium and calcium hydride in each other. From Fig. 3 it is evident that for the $Ti–H_2$ system, the intersection of the curves of constant composition with the 100% curve occurs at temperatures well below the sintering temperature of any components of the system; thus a liquid phase is not involved. Rather the data show a single solid phase to exist at these intersections which necessarily has the composition of stoichiometric TiH_2. The relation of phases (so called) is best shown in Fig. 4 where the points representing 100% composition are at the extreme right. Following the 800° isotherm toward the left, it is seen that there is a plateau between 90 and 100%, which presumably represents a mutually saturated system containing stoichiometric TiH_2, hereinafter called the γ-phase and the previously reported β-phase. The pressure–composition region in which these phases coexist is triangular and sharply defined by the intersections of the (dotted) plateaus and the ascending portions of the isotherms. It appears that the γ-phase is not stable below approximately 400°, and indeed it is obtained only as a metastable or transitory phase by cooling, as reported in the first article of this series. This is at variance with the theory of Smith[3] in the case of the zirconium–hydrogen system, where the novel phases reported earlier by Hägg are considered to be distortions of the α- and β-phases. Continuing to follow the 800° isotherm to the left, there is a fairly well-marked region between 90 and 80% where a single phase, probably the β-phase is present, followed by a plateau between 80 and 60% where again two phases must be present. These are thought to

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[2] W. C. Johnson, M. F. Stubbs, A. E. Sidwell and A. Pechukas, THIS JOURNAL, **61**, 318 (1939).

[3] D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1948, p. 166.

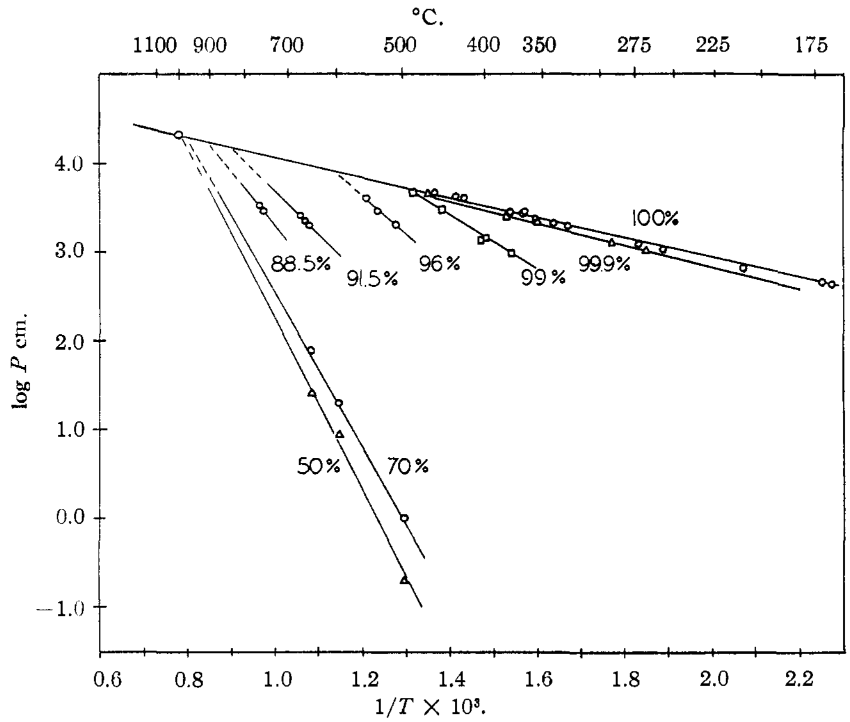

Fig. 3.—Relation of log dissociation pressure in cm. to reciprocal of absolute temperature × 10³ as a function of composition. The curves are labeled according to the per cent. theoretical hydrogen content (TiH_2 = 100%). The uppermost point at extreme left is calculated from ΔF.

be the α- and β-phases from our earlier X-ray diffraction studies (*q.v.*, the β-phase in one mixture was found to have a composition of roughly 75%). Below 60% there is another single phase region corresponding to the α-phase discussed in our preceding paper. The other isotherms are generally similar and the central plateaus, unlike those of palladium, seem to be shorter or at least less well defined at lower temperatures. While hysteresis may be present, particularly at 500° and 600°, it could not be observed. Quite possibly hysteresis is absent above a limiting temperature (*ca.* 650°) or below a limiting pressure (*ca.* 8.0 cm.) as in the case of the palladium–hydrogen system.

The foregoing classical interpretation of phase relationships in the titanium–hydrogen system leaves many questions unanswered. Hydrogen penetrates titanium quite uniformly, as revealed by photomicrographs, and the coexisting phases referred to above must be well dispersed in each other and not segregated macroscopically as in a typical alloy. This is borne out by observation of appreciable line broadening in X-ray diffraction patterns. The effect of a very large interphase surface may, as suggested by Lacher,[4] affect the equilibrium pressure. In addition the sum of the hydrogen sites occupied and the potential hydrogen sites is not equal to the maximum composition as was found in Lacher's study of the palladium–hydrogen system. This may be due, however, to the considerable change of lattice constant and type with composition which is much more marked than in the latter system. Presumably the hydrogen atoms are confined to the tetrahedral lattice holes (which are filled at the composition TiH_2) since the octahedral holes are probably too large for single hydrogen atoms.

There are three other interpretations of the apparent phase changes in the titanium–hydrogen system. The first parallels that of Lacher,[4] who treats the problem statistically and interprets the univariant portions of the palladium–hydrogen system as regions where at constant pressure hydrogen is taken up by cluster formation in the lattice. On this basis the hydrogen in the lattice must be substantially un-ionized (contrary to Lacher's assumption) and the central plateaus of Fig. 4 are then attributed to formation of hydrogen clusters. (It seems likely, however, that the plateaus would be better defined at lower temperatures if actual clustering takes place.) A similar interpretation is given by Barrer,[5] who develops an equation relating equilibrium pressure to (a)

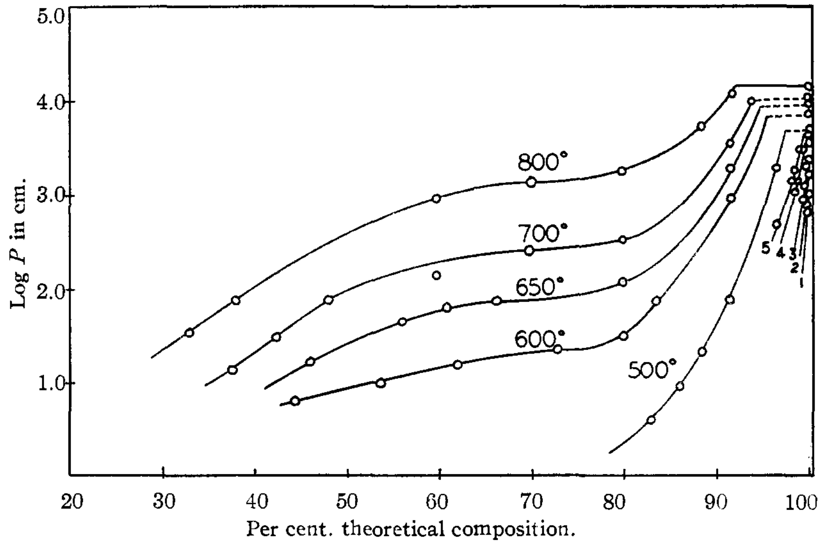

Fig. 4.—Isotherms at high pressure; the temperature is shown in °C. For the right-hand numbered isotherms the temperatures are: (1) 250°, (2) 300°, (3) 350°, (4) 400°, (5) 450°.

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[4] J. R. Lacher, *Proc. Royal Soc.* (*London*), **A161**, 525 (1937).

[5] R. M. Barrer, *Discussions Faraday Soc.*, No. 4, 68 (1948).

fraction of occupied sorption sites (b) oscillation frequency of the hydrogen therein and (c) the least energy required to remove a hydrogen atom from the solid phase. It is beyond the scope of this paper to attempt an interpretation in these terms, but it is interesting to note that to make the hydrogen oscillator fully mobile involves an entropy change of 16 cal./°C. which is not far from the difference between the entropy of dissociation of $TiH_{<2}$ and TiH_2 (see below). The third interpretation assumes instead of hydrogen clustering a transition from what might be called normal interstitial hydrogen to a hydrogen bridge structure in which it is possible that part of the hydrogen atoms bear a fractional positive charge. Such a structure is related to the hydrogen bridge structure proposed by Rundle[6] for uranium hydride (see also Pauling[7]) and also to the proposed structure of diborane.[8] On this basis the titanium–hydrogen system tends at increasing concentration of hydrogen to form a three-dimensional structure in which hydrogen atoms carrying a fractional positive charge act as bridges between titanium atoms. While some support is lent to this theory by analogy with the bridge structure of uranium hydride (whose interatomic distances UU and UH are in keeping with Pauling's theory of resonating covalent bonds), the only additional evidence lies in the fact that hydrogen dissolved in solid palladium migrates in part to the cathode under an applied potential.[9] The titanium–hydrogen system has not been investigated in this manner nor has the magnetic susceptibility been determined as a function of hydrogen concentration. Fitzwilliam, *et al.*,[10] have shown that the magnetic susceptibility of the zirconium–hydrogen system falls rapidly to a low constant value as the hydrogen content increases to 100%, *i.e.*, to ZrH_2. The single composition, $TiH_{1.2}$, studied had a higher susceptibility than pure titanium. (Presence of either H_2^+ or H_2^- would presumably give a paramagnetic composition.) A hydrogen bridge structure might also explain hysteresis as due to the slight energy required by the transformation of a hydrogen bridge atom to a normal interstitial atom.

Thermodynamic Properties.—The slopes of the curves of Fig. 3 permit calculation of the heat of sorption or heat of dissociation of both stoichiometric hydride and various lower compositions by the method of Lewis and Randall.[11] If the value of ΔC_p is taken as unity below 500° and slightly less than unity above 650° (compare (11) p. 473), the integration constant I in equation (1)

$$\Delta F = \Delta H_0 - \Gamma T \ln T - {}^1/_2\, \Delta\Gamma_1 T^2 + \ldots IT \quad (1)$$

does not vary significantly and then the thermodynamic constants shown in Table I may be calculated. Case I refers to the dissociation of stoichiometric titanium hydride whereby a negligible amount of hydrogen is released. Case II refers to the dissociation of $TiH_{1.93}$ and is applicable to compositions between the rough limits $TiH_{1.75} - TiH_{1.93}$.

TABLE I

	Case I	Case II
Heat of dissociation ΔH at 25°, cal./mole H_2	5168	19,150
Heat of dissociation ΔH_0 cal./mole H_2	4870	18,850
Free energy of dissociation ΔF at 25°, 1 atm.	709	10,030
Entropy of dissociation ΔS e.u. 25°	14.9	32.3

The dissociation constants are given respectively by the equations

Case I

$$\log_{10} K_{\mathrm{I}} = (4870 - 2.3T \log_{10} T - 8.27T)/(-4.58T)$$

Case II

$$\log_{10} K_{\mathrm{II}} = (18{,}850 - 2.3T \log_{10} T - 23.9T)/(-4.58T)$$

where the pressure is expressed in atmospheres and the temperature in °A. In each equation the numerator is the free energy of dissociation at temperature T.

The striking change in equilibrium pressure with composition is reflected in these equations by the more than threefold difference in the heat of dissociation. Also remarkable is the low temperature at which an appreciable dissociation pressure develops. The difference in the two entropies of dissociation is 17.3 cal./degree. If one attempts to apply Lacher's equation relating heat of sorption (negative heat of dissociation) to composition, it is evident that the titanium–hydrogen system does not fulfill the requirement of the equation that the lattice may not be greatly altered by sorption of hydrogen. It is obvious that any relation between temperature, pressure, and composition must be fairly complex with at least two additional variables.

Experimental

The considerable difficulty of retaining hydrogen in a reaction vessel at high pressures and temperatures is well known. Hydrogen diffuses rapidly through most of the refractory metals at red heat and in the studies reported here, loss of hydrogen would vitiate the results in view of the sensitive dependence of dissociation pressure on composition. A further difficulty lies in the known reactivity of titanium hydride toward many metals and most ceramics at elevated temperatures. Fortunately an earlier investigation in this Laboratory of hydrogen permeability of metals had shown that suitably treated 316 and 347 stainless steels are satisfactorily impervious to hydrogen. These alloys are found to be substantially unaffected by titanium metal up to 1000°, and the more impervious alloy, 347, was accordingly selected for construction of the high-pressure apparatus. The problem of closures is equally serious since all mechanical closures tried leaked badly at red heat. After trial of various methods of welding closures, it was found that an atomic hydrogen weld was far superior to other types. The selected containers used in the studies reported below were found to be satisfactory in all respects and withstood months of high temperature operation without failure.

Apparatus.—A schematic drawing of the equipment used is shown in Fig. 1. The bombs are of 347 stainless steel 1.583″ i.d., 1.897″ o.d., and 4.2″ long. The end plates are 0.6″ thick and welded by atomic hydrogen. An 18″ stem of 0.25″ o.d. stainless steel, capillary tubing is welded in a hole in one end and soldered to a $^1/_8$″ o.d. copper capillary tube. These bombs are conditioned by prolonged treatment with hydrogen at 800°. The metal portions of the manifold are connected by soldering or by stainless steel compression fittings. The pressure gages are Brown Instrument Co. 0–1000 p.s.i. recording gages which were calibrated to ±1% by a standard, dead-weight gage. Chromel–alumel thermocouples were used and were calibrated

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(6) R. E. Rundle, THIS JOURNAL, **69**, 1719 (1947).

(7) L. Pauling, *ibid.*, **70**, 1660 (1948).

(8) K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(9) B. Duhm, *Z. Physik*, **94**, 434 (1935); **96**, 801 (1936).

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

(11) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 472.

in a comparison furnace *vs.* a Bureau of Standards thermocouple through the courtesy of Mr. H. A. Brown, of this company. The temperature of the bomb furnace was recorded by a Brown Instrument Co. thermocouple potentiometer. Reservoir A and the attached manometer were used for volume calibration of the system at various temperatures. Both hydrogen and argon were used as calibrating gases. Reservoir J was used to admit known volumes of purified hydrogen to the system at high pressures.

Materials.—"Water-pumped" electrolytic hydrogen from a single selected cylinder was purified by passage over incandescent zirconium in the high-pressure getter system G'G which quantitatively removed oxygen, moisture, nitrogen and carbonaceous impurities. Extreme precautions must be taken to purify even the best available hydrogen. Samples of titanium from both the Bureau of Mines and the du Pont Co. were used. The 99.02% metal was heated slowly to 350° in a vacuum furnace protected by titanium getters and allowed to degas. (Higher temperatures fix the adsorbed gases otherwise evolved.) When a vacuum of 0.1 micron was obtained, the temperature was raised very slowly to 1000° and held for 1.5 hr. Hydrogen purified by passage over (a) palladium catalyst, (b) Drierite, (c) a mixture of titanium sponge and zirconium powder at 850° was admitted and the temperature reduced over 9 hr. to 375°, then over 16 hr. to 25°. Considerable amounts of volatile metals including magnesium and silicon were lost during evacuation and the resulting hydride samples analyzed 94.4% Ti, 3.99-4.00% H, 0.01-0.03% N, 0.03-0.08% C, 0.01-0.08% Si, 0.1% Mg, and less than 0.1% Mn, Ca, Cu. In all cases spectrographic analysis showed other metallic impurities to be substantially absent. Chloride, sulfur, and oxygen were not determined. (The chemical analysis for Ti cited above was somewhat lower than that obtained by quantitative hydrogen absorption.) The brittle hydride was ground in an argon- or nitrogen-filled dry box and loaded into the previously treated bombs through the capillary stem. The bombs were degassed at 100° and flushed repeatedly with purified hydrogen before used. Analysis after several months of use showed no change beyond the limits of analytical error except for a pick-up of fractional percentages of chromium, manganese, and iron from the bombs. The argon and nitrogen gases used were of guaranteed purity 99.99%. The argon was found to be moist, however, and was dried by passage over Drierite.

Acknowledgment.—The experimental work reported herein was supported by the NEPA Project, Oak Ridge, Tennessee. The authors wish to express their appreciation for this support and for helpful advice given by Drs. K. Anderson, V. P. Calkins and A. J. Miller, of the NEPA Laboratory, and by Drs. P. P. Alexander, M. D. Banus, and Mr. H. W. Kruschwitz, Jr., of this company. In particular they wish to acknowledge the help of Mr. Eugene V. Mingotti, of the Middlesex Welding Co., Somerville, Mass., who developed the closure techniques employed.

Beverly, Mass. Received July 28, 1950

[Contribution from the Coates Chemical Laboratories, Louisiana State University]

The Anodic Oxidation of Thallous Ion on the Rotating Platinum Microelectrode

By Paul Delahay and G. L. Stiehl[1]

Thallous ion is irreversibly oxidized to thallic hydroxide on a rotating platinum microelectrode. The corresponding anodic wave can be observed above *p*H 7.85. At lower *p*H the evolution of oxygen interferes. The overvoltage decreases as the *p*H increases. Half-wave and decomposition potentials are compared with potentials calculated from thermodynamic data.

The anodic oxidation of thallous ion in acid solutions has been reported by Grube and Hermann[2] but this reaction has not been investigated in neutral or alkaline solution as far as we know. The application of the rotating microelectrode to the study of this reaction is reported in the present paper.

Experimental

Since the oxidation of thallous ion occurs at rather highly positive potentials, the dropping mercury electrode cannot be used. Good waves were obtained with the rotating microelectrode described by Laitinen and Kolthoff.[3] Waves were recorded with a "Sargent" manual polarograph model III. A polarographic cell with a mercury pool and the H-cell designed by Lingane and Laitinen[4] were used. Before determining a wave the microelectrode was cleaned in concentrated sulfuric acid to dissolve any thallic hydroxide which might have been deposited in a previous experiment. Distorted waves were observed when the microelectrode was not thoroughly cleaned. The values of the *p*H below 10 were measured with a Beckman model G instrument. Values above *p*H 10 were calculated. Dissolved oxygen did not interfere.

Description of Wave and Discussion of Results

Anodic waves obtained in various media from *p*H 7.85 to pH 13.7 are shown in Fig. 1. Waves are arbitrarily shifted along the vertical axis in this diagram. No distinct wave could be observed below *p*H 7.85 because of the simultaneous evolution of oxygen. Waves are shifted toward more positive potentials as the *p*H decreases. This can be expected from the dependence of the equilibrium potential on *p*H according to the formula

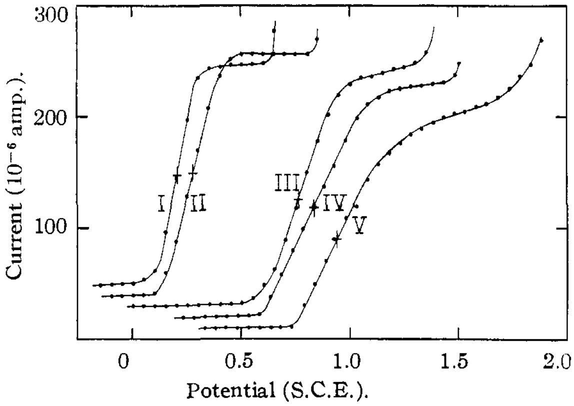

Fig. 1.—Anodic waves of 10^{-3} molar Tl^+ solutions at various *p*H: I, *p*H 13.7, NaOH 0.5 *N;* II, *p*H 13.0, NaOH 0.1 *N;* III, *p*H 11.0, NH_4OH and $(NH_4)_2SO_4$ buffer in KNO_3 0.1 *N;* IV, *p*H 9.20, borate buffer; V, *p*H 7.85 phosphate buffer.

$$E = 1.19 - 0.0886pH - 0.0295 \log a_{Tl^+} \quad (1)$$

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[1] This paper is part of a dissertation to be submitted to the Graduate School of Louisiana State University by G. L. Stiehl in partial fulfillment of the requirements for the degree of Master of Science.

[2] Grube and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Laitinen and Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

[4] Lingane and Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).