

Application of the Metal-Hydrogen Equilibration for Determining Thermodynamic Properties in the Ti-Cu System

M. ARITA, R. KINAKA, AND M. SOMENO

A technique has been proposed for determining thermodynamic activities in a binary alloy from measurements of the pressure of hydrogen gas equilibrated with the alloy and the hydride of one of the components. The technique is similar to a method by equilibration of oxygen gas with an alloy and the oxide of a component. With the use of this technique, activities of the components in the Ti-Cu system at 773 K have been measured. From the measured activities, the standard free energies, enthalpies, and entropies of formation for intermetallic compounds "TiCu₄", "TiCu", and "Ti₂Cu" have been determined.

VARIOUS techniques¹ have been employed for measuring thermodynamic activities in multicomponent systems. Among the indirect measurements, the method of measuring the equilibrium oxygen pressure between an alloy and the oxide of one of the components has been successful with the use of oxygen concentration cells.² The principle of this method is very simple, and it should be applicable to hydrides, nitrides, sulfides, chlorides, and so forth. This extended application, however, has been not so widely used as for oxides, firstly because no convenient *in situ* pressure measuring device like solid electrolytes with lime-doped zirconia have been successfully developed.

For the case of metal-hydrogen equilibration, another discouraging reason is that most hydrides have a large departure from stoichiometry, whose degree depends strongly on the hydrogen gas pressure. This strong dependence indicates that the chemical potential of the metal in a hydride is not a linear function of logarithmic pressure of hydrogen gas. Accordingly, a precise knowledge of the variation of the metal activity in the hydride with hydrogen gas pressure is vital for thermodynamic studies of alloys with the aid of the metal-hydrogen equilibration. Even when the metal activity is determined in an alloy equilibrated with the metal hydride, there is one more step of calculation to assign a conclusive value to the metal activity in the alloy containing no hydrogen, whose solubility is in general significantly large.

The purpose of this work is firstly to show the method of determining the activity of a component in an alloy from a measurement of the hydrogen gas pressure in equilibrium with the alloy and with a hydride of the component, and secondly to report the thermodynamic properties of the Ti-Cu binary system, which were determined by the above method.

PRINCIPLE FOR DETERMINING ACTIVITIES FROM EQUILIBRIUM HYDROGEN GAS PRESSURE

In this section is considered a binary alloy *A-B*, in which *B* forms a much more stable hydride *BH_x* than

M. ARITA and M. SOMENO are Research Associate and Professor, respectively, Department of Metallurgical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152 Japan. R. KINAKA, formerly Senior Student at Tokyo Institute of Technology, is now with Kawasaki Steel Corp., Chiba, 280 Japan.

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A does. The partial molar free energy of *B*, *G_B*, in the alloy, which is equilibrated with *BH_x* and hydrogen gas under constant pressure and temperature, equals that of *B* in *BH_x*. This equilibrated hydride contains an amount of *A* atoms, which is negligibly small because of much lower stability of the *A* hydride than the *B* hydride. Accordingly, the *B* hydride may be considered "pure". *G_B* in pure *BH_x* can separately be determined from a variation of the hydrogen concentration with the pressure of hydrogen gas in equilibrium with pure *B* metal.

The Gibbs-Duhem relation in the *B-H* system under constant temperature and pressure is $X_B dG_B + X_H dG_H = 0$, which can be rearranged to:

$$X_B d \ln a_B + X_H d \ln P_{H_2}^{1/2} = 0 \quad [1]$$

where X_i is the mole fraction of component *i*, a_B is the activity of component *B* with pure *B* placed as the standard state, and P_{H_2} is the pressure of hydrogen gas in equilibrium with the alloy. In derivation of Eq. [1], the equality, G_H in alloy = $G_{H_2}/2$ in gas, by virtue of the second law of thermodynamics and the approximation of "ideal" H_2 gas have been used. Equation [1] can be integrated to

$$\ln a_B = - \int_0^{P_{H_2}^{1/2}} \frac{X_H dP_{H_2}^{1/2}}{(1 - X_H)P_{H_2}^{1/2}} \quad [2]$$

because by definition $a_B = 1$ for $P_{H_2} = 0$, or pure metal *B*. The range of integration in Eq. [2] extends to the hydride region in the *B-H* system. In Fig. 1 is shown the plotting of $X_H/(1 - X_H)P_{H_2}^{1/2}$ vs $P_{H_2}^{1/2}$ for the case of the Ti-H system, which will later be used for graphical integration in Eq. [2]. Figure 1 was obtained by replotting McQuillan's data³ on the Ti-H system. In this way the activity of metallic component *B* in the hydride *BH_x* can be determined, and it is equated to the activity of *B* in the *A-B* alloy which is thermodynamically equilibrated with the hydride as well as hydrogen gas. In Fig. 2 thus calculated activities of Ti in "TiH₂" with pure α -Ti used as the standard state are plotted against the hydrogen gas pressure.

The next procedure is to calculate the activity of *B* in the *A-B* alloy with no hydrogen dissolved. This calculation can be made if values of P_{H_2} have been determined over the whole compositional range of hydrogen in the *A-B-H* solution. Along lines of constant

X_A/X_B , which is the most common experimental condition for hydrogen absorption, a Gibbs-Duhem integration yields the following equation for the activity coefficient (γ_B) of B .¹³

$$\begin{aligned} \ln \gamma_B^+ / \gamma_B &= \ln (X_H / P_{H_2}^{1/2}) / (X_H^e / P_{H_2}^{1/2})^+ \\ &+ \left[\int_{X_H^e}^0 \left\{ \left(\frac{\partial \ln (X_H / P_{H_2}^{1/2})}{\partial X_H} \right)_{X_A} / (1 - X_H) \right\} dX_H \right]_{X_A / X_B} \quad [3]^* \end{aligned}$$

*Equation [3] has been yielded from Eq. [12] of Ref. 13, in which $G_H^E = \text{const.} - RT \ln (X_H / P_{H_2}^{1/2})$ for "ideal" H_2 gas, and $m = B$, $k = H$, and $C_k = X_A / X_B$.

where the superscript "+" stands for the binary $A-B$ alloy with no hydrogen dissolved, and X_H^e is the solubility of hydrogen in equilibrium with the hydride.

If values of P_{H_2} are known only along one line of constant X_A/X_B in a very narrow solution range of the $A-B-H$ alloy (e.g., intermetallic compounds), the derivative of the integrand in Eq. [3] cannot rigorously be estimated, and hence the exact value of γ_B^+ cannot be calculated. For this particular case, however, an approximate value of a_B^+ can be estimated upon considering the assumption that the thermodynamic interaction between A and H is much weaker than that between B and H , as follows. The Gibbs-Duhem equation for the ternary $A-B-H$ system under constant temperature and pressure may be written as:

$$X_A d \ln a_A + X_B d \ln a_B + X_H d \ln P_{H_2}^{1/2} = 0. \quad [4]$$

Dividing this equation by $X_A + X_B (= 1 - X_H)$ and then integrating it along a line of constant X_A/X_B , we note that $X_A/(X_A + X_B) = \text{constant} = X_A^+ / X_B^+$ and $X_B/(X_A + X_B) = \text{constant} = X_B^+ / X_B^+$ and we find:

$$X_A^+ \ln a_A^+ / a_A + X_B^+ \ln a_B^+ / a_B = - \int_{P_{H_2}^{1/2}}^0 \frac{X_H dP_{H_2}^{1/2}}{(1 - X_H) P_{H_2}^{1/2}} \quad [5]$$

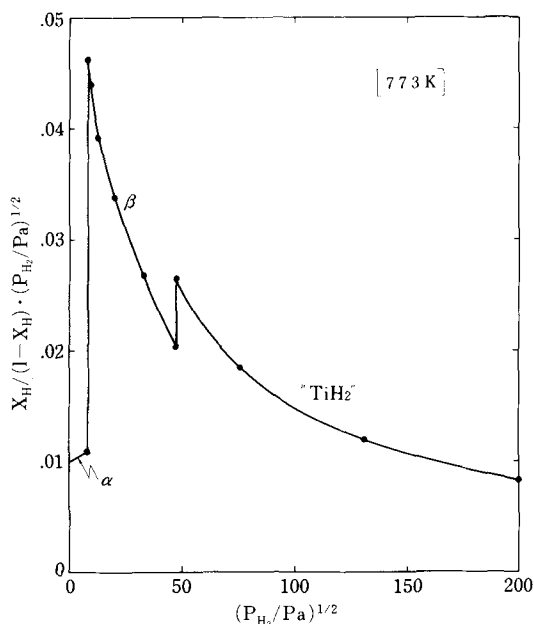


Fig. 1—Replotting of McQuillan's data³ on hydrogen absorption in the Ti-H system at 773 K.

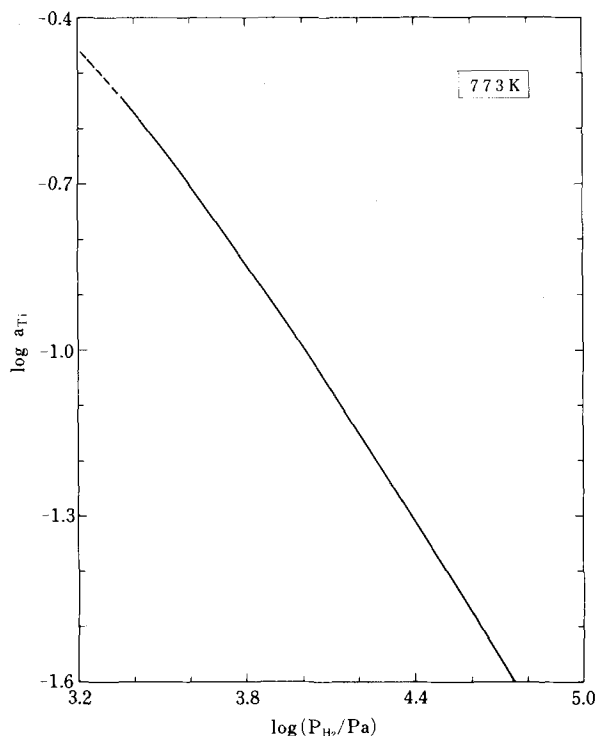


Fig. 2—Dependence of the Ti activity on the hydrogen gas pressure in the Ti-H system at 773 K, calculated from Fig. 1. The standard state for the Ti activity is pure α -Ti.

where the lower integration limit is the value for hydrogen gas in equilibrium with the $A-B$ alloy and the B hydride. By assumption a_A is not so much affected by the dissolution of hydrogen as a_B , and hence γ_A may be assumed to be constant. Accordingly, Eq. [5] becomes:

$$\begin{aligned} \ln a_B^+ / a_B &= - (X_A^+ / X_B^+) \ln (X_A^+ / X_A) \\ &- \frac{1}{X_B^+} \int_{P_{H_2}^{1/2}}^0 \frac{X_H dP_{H_2}^{1/2}}{(1 - X_H) P_{H_2}^{1/2}}. \quad [6] \end{aligned}$$

In this equation a_B is the activity of B in coexisting $A-B$ alloy and B hydride, and it has already been given by Eq. [2]. Thus, the activity of B in hydrogen free alloy $A-B$ can be calculated.

APPLICATION TO THE Ti-Cu SYSTEM

The Ti-Cu binary alloy system has several intermetallic compounds, as shown in Fig. 3. In this work, the three compounds at lower temperatures were investigated by introducing hydrogen in them. At a certain pressure of hydrogen gas, each compound begins to decompose to the next lower compound and the titanium hydride TiH_{2-x} . Under this equilibrium condition, the activity of Ti in the regions of three condensed phase equilibrium is determined by the method described in the preceding section.

EXPERIMENTAL

Starting materials used in this experiment were sponge titanium of 99.8 pct purity and electrolytic copper of 99.96 pct purity. They were weighed, mixed,

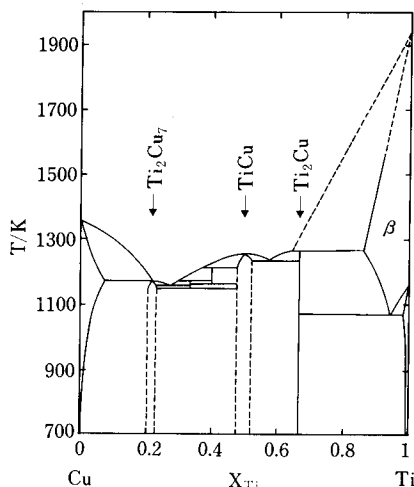


Fig. 3—Phase diagram⁴ of the Ti-Cu system.

and arc-melted so that final compositions could be TiCu_3 , TiCu , and Ti_2Cu . X-ray diffraction patterns showed that the TiCu_3 sample and the Ti_2Cu sample contained trace amounts of TiCu and Cu , respectively, and that the TiCu sample had no detectable amount of other materials. The arc-melted materials were crushed and powdered in an alumina mortar to particles of $300\ \mu\text{m}$ or less diam. The hydrogen gas used in this investigation was taken from the sponge titanium by heating, in which hydrogen had been previously absorbed from 99.9 pct pure hydrogen gas.

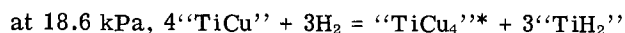
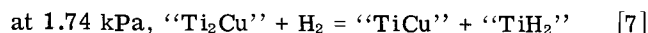
A Sieverts apparatus was used for measuring the pressure and volume of hydrogen gas. The sample chamber made of quartz glass was able to be evacuated to 10^{-2} Pa. Pressure measurements were made with a mercury manometer for >2 kPa and with a dibutylphta-

late manometer for <3 kPa. The sample temperature was controlled within ± 1 K of an aimed temperature. Before starting a run of hydrogen absorption, 0.5 to 1 g of sample powder was preheated for degassing at 973 K in a 10^{-2} Pa pressure for 30 min. The quantity of hydrogen absorbed in a sample was determined by use of the ideal gas law from a pressure change.

In order to identify the species existing in a sample after hydrogen absorption, an X-ray diffraction pattern with $\text{CuK}\alpha$ was taken of the sample which was quenched by pouring water on the chamber surface.

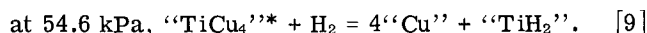
THERMODYNAMIC ACTIVITIES

Figure 4 shows measurements of the pressure of hydrogen gas in equilibrium with intermetallic compounds in the Ti-Cu system at 773 K. These results were obtained by absorption of hydrogen. Desorption studies on TiCu produced the same plateau pressures as for absorption, having slight differences on the positions of longitudinal lines. From X-ray studies, it was found that the three plateaus in Fig. 4 correspond to the following equilibria with " TiH_2 ":



*According to Shunk⁴ (Fig. 3), this compound is designated as Ti_2Cu_7 . In this report, however, the notation " TiCu_4 " is adopted for simplicity.

and



In these equations, the notation, "...", indicates a departure from the stoichiometric compound. Corresponding activities of Ti at 773 K were determined from Fig. 2 and are tabulated in Table I. According to the activity determining principle explained in a preceding section, activities of Ti in hydrogen free " Ti_2Cu ", " TiCu ", " TiCu_4 ", and " Cu " were determined from Table I and Eq. [6]. Rather than Eq. [3], Eq. [6] has been applied because P_{H_2} was measured only along one line of constant $X_{\text{Ti}}/X_{\text{Cu}}$ in the very narrow compositional range of a compound. The integrand in Eq. [6] for the three compounds is shown in Fig. 5, which was obtained from the initial absorption

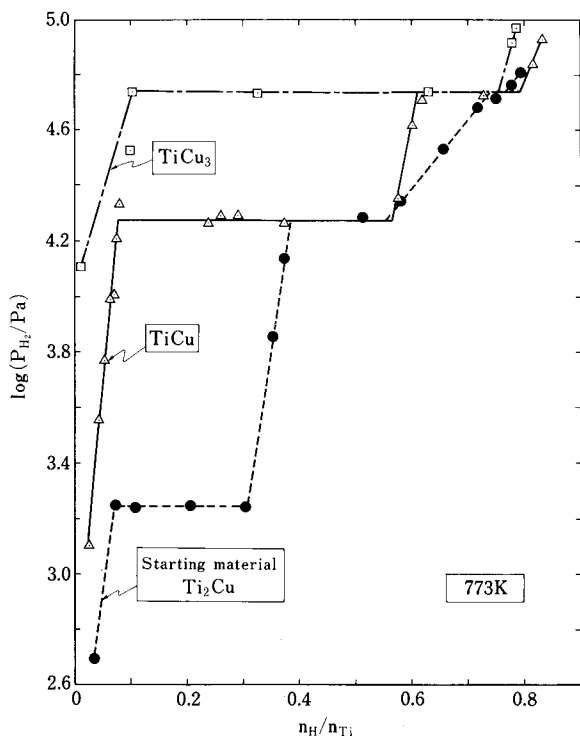


Fig. 4—Measured relationships between the pressure in the hydrogen gas phase and the hydrogen/titanium atom ratio in the alloy phase at 773 K.

Table I. Relation between P_{H_2} and a_{Ti} in " TiH_2 " Equilibrated with Compounds Ti_mCu_n

Equilibrium Between	P_{H_2} /kPa	a_{Ti}^*	Temperature, K
"TiCu"/"TiCu ₄ "/"TiH ₂ "	1.80	0.0366	673
"TiCu ₄ "/"Cu"/"TiH ₂ "	4.80	0.0164	673
"TiCu"/"TiCu ₄ "/"TiH ₂ "	6.87	0.0445	723
"TiCu ₄ "/"Cu"/"TiH ₂ "	16.9	0.0215	723
"Ti ₂ Cu"/"TiCu"/"TiH ₂ "	1.74	0.335	773
"TiCu"/"TiCu ₄ "/"TiH ₂ "	18.6	0.0624	773
"TiCu ₄ "/"Cu"/"TiH ₂ "	54.6	0.0259	773
"TiCu"/"TiCu ₄ "/"TiH ₂ "	54.3	0.0628	823
"TiCu ₄ "/"Cu"/"TiH ₂ "	—	0.0391†	823

*The standard state for a_{Ti} is pure α -Ti.

†Extrapolated from lower temperatures with the partial molar enthalpy of mixing for Ti of -26.6 kJ/mol.

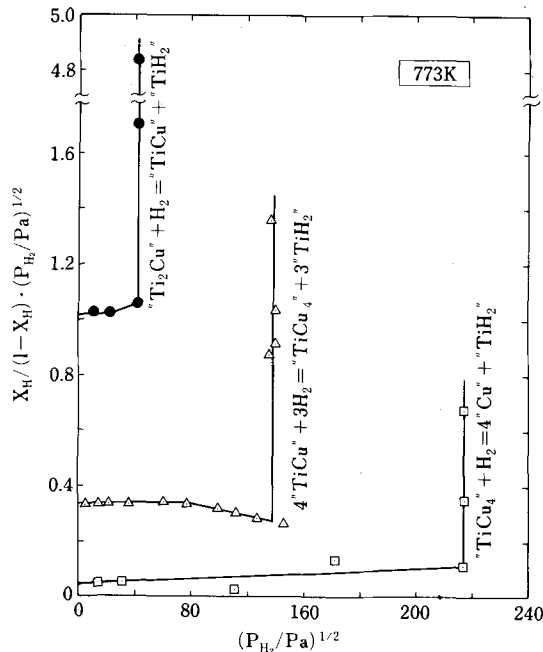


Fig. 5—Replotting of the data for the initial dissolution of hydrogen for $n_H/n_{Ti} < 0.1$ in Fig. 4.

data for $n_H/n_{Ti} < 0.1$ in Fig. 4. Ti activities thus obtained are tabulated in Table II and shown in Fig. 6. The longitudinal broken lines in Fig. 6 connect two endpoints in the one phase region of an intermetallic compound. The horizontal line for the Ti activity at the righthand top in Fig. 6 was determined by virtue of Raoult's law from the solubility of Cu (0.9 mol pct)⁵ in α -Ti. In Fig. 6 are also shown the activities of Cu, whose value of the horizontal line at the lefthand top was determined by virtue of Raoult's law from the solubility of Ti (0.6 mol pct)⁶ in Cu. The longitudinal broken lines for the Cu activity were determined with the use of the following Gibbs-Duhem equation in the one phase region of an intermetallic compound:

$$X_{Ti} d \ln a_{Ti} + X_{Cu} d \ln a_{Cu} = 0. \quad [10]$$

Since the one phase region is very narrow, the com-

Table II. Summary of a_{Ti} and a_{Cu} in Hydrogen free "Ti", "Ti₂Cu", "TiCu", "TiCu₄", and "Cu"

Equilibrium Between	a_{Ti}	a_{Cu}	Temperature, K
"Ti"/"Ti ₂ Cu"	0.991*	0.0167	773
"Ti ₂ Cu"/"TiCu"	0.344†	0.143	773
"TiCu"/"TiCu ₄ "	0.0382	0.782	673
"TiCu"/"TiCu ₄ "	0.0469	0.797	723
"TiCu"/"TiCu ₄ "	0.0644‡	0.765	773
"TiCu"/"TiCu ₄ "	0.0656	0.859	823
"TiCu ₄ "/"Cu"	0.0170	0.997¶	673
"TiCu ₄ "/"Cu"	0.0222	0.996¶	723
"TiCu ₄ "/"Cu"	0.0267	0.994¶	773
"TiCu ₄ "/"Cu"	0.0405	0.992¶	823

*Calculated from the solubility (0.9 mol pct)⁵ of Cu in Ti by assuming Raoult's law for Ti.

†Average of a_{Ti} 's in "Ti₂Cu" and "TiCu" in equilibrium (0.344 ± 0.002).

‡Average of a_{Ti} 's in "TiCu" and "TiCu₄" in equilibrium (0.0644 ± 0.0003).

¶Calculated from the solubility (0.3, 0.4, 0.6, 0.8 mol pct at respective temperatures)⁶ of Ti in Cu by assuming Raoult's law for Cu.

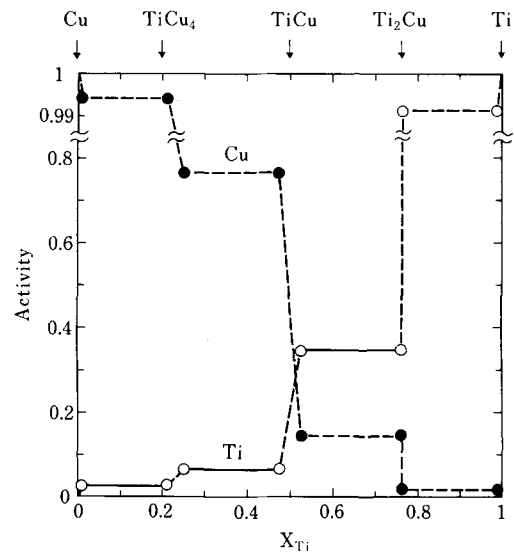


Fig. 6—Activities of Ti and Cu in the Ti-Cu system at 773 K, determined from Fig. 4 with the aid of Figs. 2 and 5.

position therein may be taken as constant, and Eq. [10] can be integrated to:

$$\ln a_{Cu}^l/a_{Cu}^r \cong (X_{Ti}/X_{Cu})^m \ln a_{Ti}^l/a_{Ti}^r \quad [11]$$

where $(X_{Ti}/X_{Cu})^m$ is taken in the middle of the one phase region, and where the superscripts l and r indicate that the activities are taken at the left end and at the right end, respectively, of the one phase region. Thus calculated values of a_{Cu} are listed in Table II.

Standard Free Energies of Formation of "Ti₂Cu", "TiCu", and "TiCu₄"

For a compound $Ti_m Cu_n$, the standard free energy of formation ΔG_f^0 is defined by:

$$\begin{aligned} \Delta G_f^0 &= G_{Ti_m Cu_n}^0 - (m G_{Ti}^0 + n G_{Cu}^0) \\ &= (m G_{Ti} + n G_{Cu}) - (m G_{Ti}^0 + n G_{Cu}^0) \end{aligned}$$

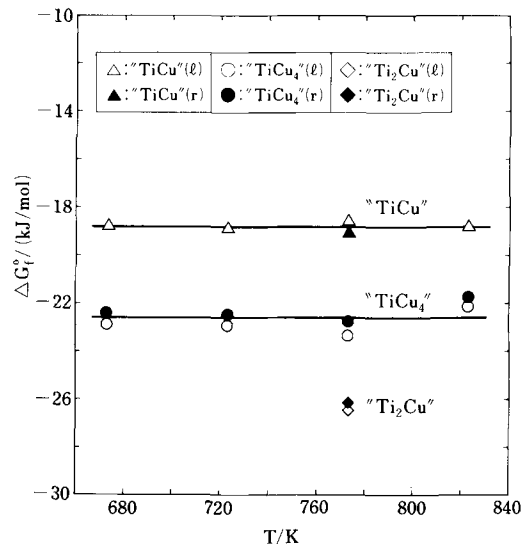


Fig. 7—Standard free energies of formation of "TiCu₄", "TiCu", and "Ti₂Cu", calculated from Fig. 6 and equivalents for other temperatures.

Table III. Standard Free Energies, Enthalpies, and Entropies of Formation for "TiCu₄", "TiCu", and "Ti₂Cu" at 773 K

	ΔG_f^0 , kJ/mol	ΔH_f^0 , kJ/mol	ΔS_f^0 , J/mol·K	Crystal Structure
"TiCu ₄ "	-22.6* ± 0.9†	-22.6	0	ordered Au ₄ Zr ¹⁰
"TiCu"	-18.8* ± 0.3†	-18.8	0	ordered bct (B11) ¹¹
"Ti ₂ Cu"	-26.3* ± 0.2†	—	—	ordered bct (C11) ¹²

*Average of all the values in Fig. 7.
†Maximum difference.

$$= RT (m \ln a_{Ti} + n \ln a_{Cu}) \quad [12]$$

where G_i^0 is the free energy of pure material i . Upon using the activity data listed in Table II, the values of ΔG_f^0 were calculated according to Eq. [12], and they are shown in Fig. 7. This calculation was based on those values of m and n which have been determined from the phase diagram of Fig. 3: TiCu_{3.90} is in equilibrium with "Cu", TiCu_{3.00} with Ti_{0.95}Cu_{1.05}, Ti_{1.05}Cu_{0.95} with Ti_{2.00}Cu, and Ti_{2.00}Cu with "Ti". ΔG_f^0 for the right end of the "Ti_mCu_n" phase region is slightly different from that for the left end. For "TiCu₄" and "TiCu", the temperature dependence of ΔG_f^0 in Fig. 7 was estimated from the pressure composition isotherms at other temperatures,* which are

*McQuillan's data³ were extrapolated to lower temperatures to obtain a relationship like Fig. 2 for determination of a_{Ti} at 673 and 723 K, whose values are listed in Table I.

shown in Fig. 8. The standard enthalpy and entropy of formation, calculated from the temperature variation of ΔG_f^0 , are tabulated in Table III, in which the crystal structures are also shown.

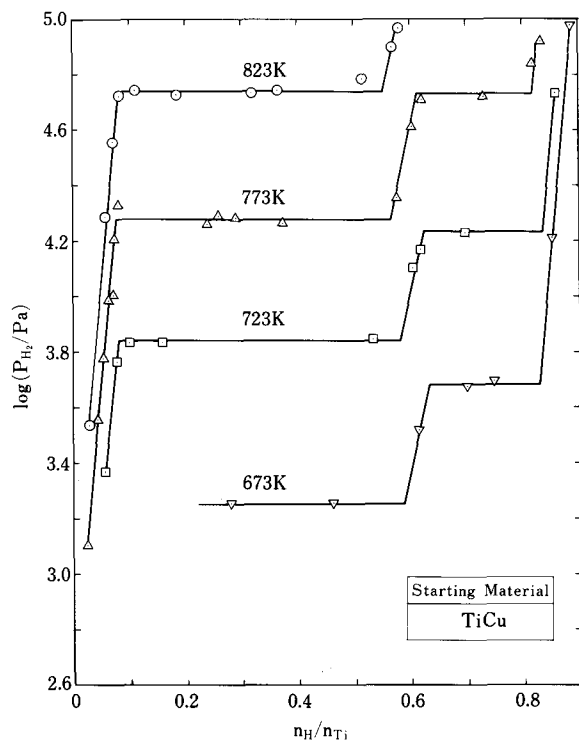


Fig. 8—Measured relationships between the pressure in the hydrogen gas phase and the hydrogen/titanium atom ratio in the alloy phase for initially TiCu compound between 673 and 823 K.

DISCUSSION

The accuracy of the present determination of Ti activities depends strongly on how reliable McQuillan's data³ in Fig. 1 are since these data were used to construct the a_{Ti} - P_{H_2} diagram in Fig. 2. The thorough nature of McQuillan's investigation has made his data widely used,⁷ and in addition good agreement of his data with a later work by Beck⁸ may lead us to a conclusion that McQuillan's data in Fig. 1 is very reliable and precise and so is the calculated a_{Ti} - P_{H_2} relationship in Fig. 2. A cross check of the reliability may be made by comparing the calculated free energy and enthalpy of formation of "TiH₂" with literature values obtained by other methods. According to the JANAF Thermochemical Tables,⁹ ΔH_f^0 for TiH_{1.66}* is

*Extrapolation from TiH_{1.73} has been made.

is -117 kJ/mol, which compares well with -105 kJ/mol estimated at 673 to 823 K in the present work from the temperature variation of ΔG_f^0 . These ΔG_f^0 values for TiH_{1.66} were calculated from the a_{Ti} - P_{H_2} diagram in Fig. 2. In the JANAF Tables, the ΔG_f^0 value for TiH₂ at 773 K is -38.8 kJ/mol, while from Fig. 2 ΔG_f^0 for TiH_{1.66} is -26.8 kJ/mol. This large discrepancy is considered to be attributed partly to the inaccurate estimation of ΔS_f^0 in the JANAF Tables, and partly to the difference in the number of H atoms in the compound formula.

As found from the activity data in Fig. 6, the partial molar free energies show a large change across the one phase region of a compound. On the other hand, as seen in Fig. 7, the standard free energy of formation exhibits a very small change across the one phase region. As seen in Table III, the entropy temperature product for the two compounds is small compared with the free energy. This is the case for most other ordered intermetallic compounds. The entropy change on formation of ordered compounds is due to the vibrational effect, the electronic effect, and the magnetic effect, because the configurational term is zero. The values of ΔS_f^0 in Table III indicate that the sum of these three effects is null in "TiCu" and "TiCu₄".

The present principle for determining activities from the metal-hydrogen equilibration is basically the same as that for the metal-oxygen equilibration. In the present method, a complication, which is not virtually present in the metal-oxygen case, arises owing to the nonstoichiometric nature of the metal hydride. The compositional change of the hydride due to the pressure variation of hydrogen gas gives rise to a significant change in the formation free energy of the hydride, which makes the reaction constant K deviate considerably from the value corresponding to stoichiometry. From Fig. 2, the K value for "TiH₂" varies from 2.86×10^{-2} for $P_{H_2} = 2.25$ kPa to 1.66×10^{-2} for $P_{H_2} = 39.9$ kPa at 773 K. Another complication is that an alloy with an easy hydride former has an appreciable solubility of hydrogen, which makes necessary the correction of measured activities in hydrogen containing alloys. This correction can be made by use of Eqs. [3] or [6]. If no relation of P_{H_2} with X_H in a single phase is experimentally determined, Eqs. [3] and [6] are useless. For this case, however, Sievert's law may be a good approximation, which makes the integration in Eqs. [3] and [6] un-

necessary. According to Sievert's law, $X_H/P_{H_2}^{1/2}$ = constant, and Eq. [6] becomes, upon noting $X_A/X_A^* = 1 - X_H^e$,

$$a_B^+ / a_B = (1 - X_H^e)^{-1}. \quad [13]$$

The above equation can also be derived from the rigorous Eq. [3] by assuming the "strict" Sievert's law, *i.e.* $X_H/P_{H_2}^{1/2}$ is not only constant but also independent of the alloy composition. Under this assumption, the righthand side of Eq. [3] becomes zero and Eq. [13] is obtained. In the Ti-Cu system the values of a_{Ti}^+ / a_{Ti} calculated from Eq. [13] agrees within a ± 5 pct error with those calculated from Eq. [6] and used to derive the a_{Ti} values in Table II from Table I. According to Eq. [6], the correction for the common logarithmic activity of Ti due to the hydrogen dissolution ranged from 0.006 to 0.019 for "TiCu". If the above mentioned complications and difficulties are overcome, the present technique must be very powerful in determining the thermodynamic properties at temperatures as low as 600 K, at which the metal-oxygen equilibration would be doubtful because of the very slow rate of oxidation.

CONCLUSIONS

The metal-hydrogen equilibration has been found useful in order to determine the thermodynamic properties in the Ti-Cu system. The component activities thus determined at 773 K are shown in Fig. 6. The standard free energies of formation for "TiCu₄", "TiCu", and "Ti₂Cu" have also been determined and

are shown in Fig. 7. The standard enthalpies and entropies of formation for "TiCu₄" and "TiCu" have been estimated and are shown in Table III.

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