Thermodynamic Properties of Metal-Hydrogen Systems at Infinite Dilution Limit Measured by EMF Methods

By Shūzi Harada*

The electromotive force (EMF) of H$_2$|H$^+$|M cell (M=transition metals and s-p metals) was measured as a function of temperature. From the measurement, the thermodynamic quantities of hydrogen-metal systems at infinite dilution limit, $\Delta G_m$, $\Delta S_m$ and $\Delta H_m$, were obtained. These values for Ti, V, Nb and Ta (i.e. the exothermic system) were basically in agreement with the values derived from solubility data, respectively. While, in the case of the endothermic system (i.e. Mo, W, Co, Rh, Ir and Pt), the thermodynamic values measured by the EMF method, for instance, $\Delta H < 0$, were different from those of the solubility data. From these systematic measurements, the thermodynamic quantities obtained by the EMF method were discussed on the basis of the bonding nature of metal-hydrogen systems by considering the chemisorption of hydrogen on the metal surface.

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I. Introduction

Thermodynamics of metal-hydrogen systems are necessary to clarify fundamental subjects such as the process of hydrogen absorption and the mechanism of hydride formation\(^{(5)}\). Systematic measurements have been done by using the pressure-composition-temperature (p-c-T) diagram technique, and the heat of formation was evaluated in reference to the position of the host metal in the periodic table\(^{(2)-(4)}\). An empirical relation to reproduce the observed heats of formation for various systems has been proposed by Boom et al.\(^{(5)}\) and Griessen and Driessen\(^{(6)}\). According to Griessen and Driessen, the heat of formation, $\Delta H$, is given by the simple relation, $\Delta H = \alpha \Delta E + \beta$, with $\Delta E = E_F - E_s$, where $E_F$ is the Fermi energy and $E_s$ is the center of the lowest band of the host metal and $\alpha$ and $\beta$ are adjustable parameters. These empirical relations are, however, not fully interpreted in terms of electron theory. There are other techniques to measure thermodynamic quantities. Thermal analysis is a direct method to obtain the heat of formation. By using the differential scanning calorimetry (DSC), the change of the free energy has been obtained as a function of hydrogen concentration\(^{(7)}\). Recently, we have obtained some thermodynamic quantities by means of EMF method\(^{(8)}\), which is classified as an in direct method. These experimental results show that the free energy of mixing decreases with increasing hydrogen concentration, that is, it means that the bonding energy of metal-hydrogen system in hydride phase at high hydrogen concentration region is more stable than that in the solid solution phase. Phase stability of metal-hydrogen systems has been explained on the basis of the lattice distortion theory and electron theory\(^{(7)(9)-(11)}\).

As was mentioned in the previous paper\(^{(8)}\), EMF method is suitable to study the thermodynamic properties of metal-hydrogen systems, especially, at the infinite dilution limit. In the present study, new measurements of EMF's of H$_2$|H$^+$|M cell (M=pure transition metals and s-p metals) have been carried out as a function of temperature and hydrogen concentration. From the value of EMF, the thermodynamic quantities were obtained, and the

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bonding nature of metal-hydrogen systems at the infinite dilution limit is discussed by considering the chemisorption of hydrogen on metal surface.

II. Experimental Procedure

Specimens of transition and s-p metals supplied from the Japan Lamp Industrial Co., LTD., Tokyo, were polished mechanically with emery paper.

EMF measurements were done by using an electrometer (Takeda TR8651) with $10^{14} \Omega$ input impedance. Electrolyte of the EMF cell was 50 mol/m³ H₂SO₄ solution or the solid electrolyte of phosphowolframic acid was used. The mobility of hydrogen ion in a sulfuric acid is high enough to obtain the stable value of EMF. The solid electrolyte was used in order to avoid extra chemical reactions on the surface of the specimens. A pellet of the acid was compressed by a pressure of 29.4 MPa at room temperature in vacuum. The H₂ electrode is made of Pd-H alloy with hydrogen concentration of 0.65 to 1.0 H/M, from which the hydrogen gas evolved spontaneously at room temperature, where the EMF of the electrode is constant under the condition. The calibration of the cell was performed by the reference electrode of Pt.

III. Experimental Results and Analysis

1. Preliminary experiments

Some preliminary experiments have been carried out as follows.

(1) The normality dependence of EMF was obtained by using sulfuric acid.

(2) The value of EMF obtained by using 50 mol/m³ H₂SO₄ solution as electrolyte was compared with that obtained by use of the solid electrolyte of phosphowolframic acid.

(3) Orientation dependence of EMF was examined by using a single crystal specimen.

As shown in the previous paper, the sulfuric acid is suitable as the electrolyte of H₂|H⁺|Pd cell. The acid solution, however, dissolves most of s-p metals and transition metals except noble metals. Therefore, it needs careful attention to use sulfuric acid. In the case of Ti, the normality dependence of EMF of H₂|H⁺|Ti cell behaved as shown in Fig. 1. The abscissa of the figure means the time after cutting the specimen in electrolyte to obtain a clean surface of Ti. Using the electrolyte with the normality less concentrated than 2000 mol/m³, the value of EMF was gradually increasing with time and became constant as shown in Fig. 1(a). The constancy of the process is mainly due to the formation of passivity, because the value of EMF of a passivating Ti which was made by oxidation at 1173 K was equal to 0.53 V and the value did not depend on the normality (50–18000 mol/m³). The effect of passivation on the value of EMF will be mentioned in a following section. When the

\[ 500 \text{ mol/m}^3 = 1 \text{ N.} \]
normality exceeded 2500 mol/m³, the value of EMF was negative, which was due to the chemical reaction between Ti electrode and acid solution. Especially, at the value of -0.47 V in Fig. 1(c), the evolution of hydrogen due to chemical reaction was observed. A small shoulder at 150 s in the figure (c) was equal to the flat stage of -0.35 V, shown in Fig. 1(b). The value of EMF obtained by using the solid electrolyte of phosphowolframic acid which was used in order to avoid extra chemical reactions on the surface of the specimen was equal to that obtained by use of the 50 mol/m³ sulfuric acid within experimental error. Accordingly, the equilibrium value of EMF, 0.53 V, can be adopted for the Ti which exhibits passivity in the 50 mol/m³ sulfuric solution. In the present study, the solid electrolyte was used for specimens which react with dilute H₂SO₄ solution or are difficult to be formed into electrode; they are V, Cr, Mn, Fe, Zn, Ga, Sn, Pb, Sb, Bi, Se and Te.

The orientation dependence of EMF was examined by using a single crystal of Ti, but it was not detected within experimental error.

2. Temperature and hydrogen concentration dependence of EMF

Figures 2(a) and (b) show typical curves of EMF of the H₂|H⁺|Ti-H(+) cell as the function of temperature and hydrogen concentration, where the electrolyte is a 50 mol/m³ sulfuric solution. Hydrogenation of Ti was done in a reaction cell by Sievert's technique. The amount of absorbed hydrogen was measured by a gas volumetric method in a vacuum cell. From these measurements, the thermodynamic quantities of metal hydrogen systems are obtained by using the following equations:

\[
\Delta G = -ZF \epsilon, \quad (1)
\]

\[
\Delta S = -\frac{\partial \Delta G}{\partial T} = ZF(\partial \epsilon/\partial T), \quad (2)
\]

and

\[
\Delta H = \Delta G + T \Delta S, \quad (3)
\]

where \(\Delta G\), \(\Delta S\) and \(\Delta H\) mean the partial molar mixing free energy, entropy and enthalpy, respectively. \(F\) in the equations is Faraday's constant which is equal to unity in eV units, \(Z\) is the valence of a hydrogen ion, that is \(Z=1\), and \(\epsilon\) the experimental value of EMF of the cell. In Fig. 3(a), (b) and (c), the partial quantities at 293 K of Ti-H systems are shown as the function of hydrogen concentration. The concentration range of the plateau indicates the coexistence of the two phases of hydrogen solid solution and hydride. With the help of the Gibbs-Duhem relation, we can obtain the mixing free energy, entropy and enthalpy.

\[
\Delta Q_{(\epsilon)} = (1-c) \int_0^c \Delta \tilde{Q} / (1-c') \, dc', \quad (4)
\]

where \(c\) is the hydrogen concentration in the Ti-H alloy and \(Q\) means the thermodynamic quantity. The results for \(\Delta G\), \(\Delta S\) and \(\Delta H\) are shown in Fig. 4(a), (b) and (c), respectively. According to a p-c-T measurement by Antonova\(^1\), the values of \(\Delta G\), \(\Delta S\) and \(\Delta H\) for Ti-H\(_{1.61-1.97}\) alloys at 298 K are -82.9 to -85.9 kJ/mol, -105.2 to -125.6 J/mol·K and -114.4 to -123.4 kJ/mol, respectively. The values obtained by the present results
shown in Figs. 4(a)–(c) are about halves of the above data.

Typical EMF curves of the \( H_2|H^+|M \) cell (\( M = \) transition metals and s-p metals which are pure metals) are summarized in Figs. 5(a), (b), (c) and (d) as the function of temperature, where the electrolyte is the 50 mol/m\(^3\) sulfuric acid. In the measurements, the value of EMF of the cell is equilibrium voltage after cutting the specimen in the electrolyte as mentioned before. Many metals, except for noble metals, exhibit passivity in the electrolyte\(^{13}\). From these measurements, partial quantities of \( \Delta G \), \( \Delta S \) and \( \Delta H \) are acquired as shown in Fig. 6(a), (b) and (c). Closed marks in Fig. 6(a) mean the value obtained by using the solid electrolyte.

**IV. Discussion**

The experimental value of EMF, \( \varepsilon \), is related to the chemical potential of hydrogen atom in a metal, \( \mu^\text{Metal}_H \), and that in the gas phase, \( \mu^\text{H}_H \), by the following equation\(^{8}\):

\[
\mu^\text{Metal}_H - \mu^\text{H}_H = -ZeF
\]

and the right hand side of the equation is equal to the relative partial molar free energy, \( \Delta G \), defined by eq. (1).

The chemical potential, \( \mu^\text{Metal}_H \) is given by\(^{14}\)

\[
\mu^\text{Metal}_H = kT \ln \left( \frac{c/\beta}{1-c/\beta} \right) + z_{BA} E_{HM} + \Delta G_i + (c/\beta) z_{BB} E_{HH},
\]

where \( z_{BA} E_{HM} + (c/\beta) z_{BB} E_{HH} + \Delta G_i \) can be rewritten as \( E_H - TS_H \). The first term on the right-hand side comes from the mixing entropy, the second and the last term are hydrogen-metal and hydrogen-hydrogen interaction energies in a metal and the third term, \( \Delta G_i \), is the internal free energy of hydrogen induced by the internal vibration. The ratio of the hydrogen to metal atoms is indicated by \( c \), and \( \beta \) means the ratio of the number of interstices to that of lattice points, \( Z_H \) is the co-ordination number of the nearest neighbor interstices around each interstice and \( z_{BA} \) means the number of interstices around a host metal atom.

The chemical potential, \( \mu^\text{H}_H \), is expressed by\(^6\)

\[
\mu^\text{H}_H = -kT \ln \left( q_H/N \right)^{1/2} + 1/2E_D,
\]

where the first term on the right-hand side comes from the partition function of rotational, translational and vibrational freedoms.
of $H_2$ molecules. The partition function of a hydrogen molecule is written by

$$q_H = (2\pi m k T)^{1/2} (V / h^2) (T / 2\theta_e)$$

$$\times (1 - \exp(-\theta_e / T))^{-1},$$

(8)

the characteristic temperature $2\theta_e$ and $\theta_e$ are 171 K and 6140 K for $H_2$, respectively (14), where $m$, $V$ and $h$ are the mass of hydrogen, volume of system and Planck constant, respectively. The standard value $\ln (q_H / N)^{1/2}$ is $-3.60$. The dissociation energy is denoted by $E_D$ ($1/2E_D = 2.27$ eV).

Accordingly, the partial molar free energy, $\tilde{G}$, is obtained by the following equation:

$$\Delta \tilde{G} = -\varepsilon = \mu_H^{\text{Metal}} - \mu_H^{H_2} = E_H - 1/2 E_D + kT$$

(9)

By using eq. (3), the partial molar enthalpy and entropy are written by

$$\Delta \tilde{H} = -\varepsilon + T(\partial \varepsilon / \partial T) = E_H - 1/2 E_D,$$

(10)

$$\Delta \tilde{S} = (\partial \varepsilon / \partial T)$$

$$= -k \left[ \ln \left( \frac{c / \beta}{1 - c / \beta} \right) + \ln \left( q_H / N \right)^{1/2} - S_H \right],$$

(11)

respectively. These are the fundamental equations in the present discussion.

It is difficult to measure the dilute hydrogen concentration in a pure metal by gas volumetric method. According to EMF method, we can evaluate the value by using eq. (11). For instance, hydrogen concentration, $c / \beta$, in the present specimen of Ti, Zr, Mo and Cu is $7.6 \times 10^{-12}, 1.0 \times 10^{-8}, 1.1 \times 10^{-4}$ and 0.02, respectively, where $k$ is $8.62 \times 10^{-5}$ eV/K and $\partial \varepsilon / \partial T = -0.0027$ V/K, $-0.0021$, $-0.0011$ and $-0.0011$, $S_H = 2.1$, 2.4, 0.1 and 5.3 are used, respectively. Such an amount of hydrogen was, however, not detected by a gas volumetric method, for instance Mo and Cu.

Let us compare the bonding energies obtained from the present experiment with previous data from p-c-T measurements. Thermodynamically, bonding energy of metal-hydrogen system is equal to the partial enthalpy as shown in eq. (10). According to the solubility data, the value of heat of solution is either positive or negative. By the Flanagan's review, the values of the partial molar enthalpy at infinite dilution, $\Delta \tilde{H}$, for Ti, V, Ta, Nb and Zr are in the region of $-0.3$ to $-0.54$ eV, that for Pd is $-0.09$ eV, and for Mo, Rh, Co, Ag and Cu are in the region of $+0.28$ to $+0.78$ eV (14). The present values of $\Delta \tilde{H} = E_H - 1/2 E_D$ from EMF measurements are, however, negative for all metals. The discrepancy between the solubility data and the present EMF data

$$\tilde{1} \text{ eV} = 1.6022 \times 10^{-19} \text{ J}.$$
Fig. 5 Typical EMF curves of \( \text{H}_2|\text{H}^+|\text{M} \) cell (M=transition metals). (a) Pt, Pd, Ag, Cu and Ni, (b) Au, Mo, Zr and Al, (c) Rh, W and Co and (d) Ir, Nb and Ta.
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seems to be enhanced for pure noble metal. In order to explain this discrepancy, we postulate that thermodynamic properties obtained by the EMF method are not due to the bulk nature of metal but depend on the surface one. There are a few experimental grounds to support the above assumption as follows: When terminals of the cell were connected, a flow of current over several days was observed. By shortening, however, hydrogen atoms are not stored up in metal, for instance in Pd, Ni and Ti, but deposit as hydrogen molecules. That is, an electrode reaction occurs not in metal but on the interface between metal and electrolyte. Another reason is that noble metals were quite sensitive to hydrogen gas. When hydrogen gas introduced into the noble metal electrode, the value of EMF of the cell became zero volt immediately. In other words, the noble metal and hydrogen gas system makes a standard hydrogen electrode. The above assumption leads to the following expression for thermodynamic eqs. (9)-(11). Since the final state of hydrogen is molecule on metal electrode, the chemical potential will be expressed as the value of hydrogen molecule. Therefore,

\[
\Delta G = \mu_{H_2}^{\text{Metal}} - \mu_{H_2}^{\text{H}_2} = E'_{H_2} + kT \ln \left( \frac{c'/\beta'}{1-c'/\beta'} \right) - S'_{H_2}, \quad (9')
\]

\[
\Delta H = E'_{H_2}, \quad (10')
\]

\[
\Delta S = -k \ln \left( \frac{c'/\beta'}{1-c'/\beta'} \right) - S'_{H_2}, \quad (11')
\]

where \( \mu_{H_2}^{\text{H}_2} = 0 \) is used, and the primes are used to indicate the thermodynamic state on surface, which is caused by the chemisorption of
hydrogen molecule on metal surface. The negative value of $\Delta \bar{H}$ shown in Fig. 6(c) is accordingly explained by the chemisorption energy, because it is negative value for all metals\(^{(15)}\). This analysis should be applied to hydrogenated specimen, for instance Ti-H alloy. As mentioned before, the thermodynamic values obtained by the EMF method were about halves of the solubility data. The disagreement may be explained by the above reason. Thermodynamic data of surface are necessary to clarify the process of hydrogen absorption, and, therefore, EMF technique may be a powerfull method because the value of EMF is sensitive to the surface condition.

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