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Journal of Alloys and Compounds 330–332 (2002) 48–51

Journal of ALLOYS AND COMPOUNDS

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Magnetic field effect on the heat of reaction in metal-hydrogen systems[☆]

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Abstract

The effects of magnetic fields were generally formulated on the thermodynamic properties of chemical reactions. The magnetic field-induced change in the heat of reaction was calculated for the metal–hydrogen system, especially for $LaCo_5$-H_2, on the basis of the general formulation. Independently of this, the heat of reaction under the influence of magnetic fields was estimated from the temperature dependence of the equilibrium hydrogen pressure. The agreement between both the results indicated that magnetic fields influence the heat of reaction in metal–hydrogen systems.

Keywords: Heat of reaction; $LaCo_5$–H_2; Magnetic field effect; Thermodynamic property

1. Introduction

Magnetic fields are recognized as influencing chemical reactions on various aspects [1]. In particular, we theoretically and experimentally showed magnetic field-induced effects (MFE's) on chemical equilibria [2]. In fact, applied strong magnetic fields changed the equilibrium pressure and the electrode potential which were the measure of the chemical equilibrium in metal–hydrogen reactions: The equilibrium hydrogen pressure for the system $LaCo_5$-H_2 was increased 50% by a magnetic field of 26 T, associated with desorption of hydrogen [3]. Moreover, the equilibrium potential for the $LaCo_5H_x$ electrode in an alkaline solution was shifted -1.64 mV by an applied magnetic field of 15 T [4]. However, the heat of reaction, one of the important thermodynamic quantities, has not been studied from the viewpoint of MFE so far.

First, in this paper, we consider how the thermodynamic properties of chemical reaction are influenced by magnetic fields through magneto-static energy. Here the MFE's are systematically formulated for some thermodynamic quantities, such as the equilibrium constant, the heat of reaction (the change in enthalpy), the change in free energy and the change in entropy. Such phenomena are generally termed as magneto-thermodynamic effects. Next, we apply the general formulation to metal–hydrogen systems, especially to the system $LaCo_5$-H_2 and calculate the change in the heat of reaction caused by magnetic fields. Independently of this calculation, the heat of reaction under the influence of magnetic fields is determined from the temperature dependence of the equilibrium hydrogen pressure in magnetic fields. Finally, we discuss the existence of the MFE on the heat of reaction.

2. Magneto-thermodynamic effects

Let us consider a chemical reaction as

$$0 = \sum_{i=1}^{k} \nu_i A_i \tag{1}$$

where A_i and ν_i denote the molecular formula and the stoichiometric coefficient for the ith component, respectively. The sign of ν_i is negative for the reactants and positive for the products. In the reaction the changes in the mole numbers are presented by one parameter, the extent of reaction ξ, as $dN_i = \nu_i \, d\xi$. Below we measure every thermodynamic quantity per unit reaction ($d\xi = 1$mol). The equilibrium condition for chemical reaction is written by

$$\sum_{i=1}^{k} \nu_i \mu_i = 0 \tag{2}$$

where μ_i is the chemical potential of the ith component under the influence of a magnetic field strength **H**. We

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[☆] This paper is presented at the International Symposium on Metal–Hydrogen Systems, Noosa, Australia, 1–6 October, 2000.

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0925-8388/02/$ – see front matter
PII: S0925-8388(01)01548-1

assume a reaction between ideal gases. The chemical potential of an ideal gas consists of the non-magnetic term $\mu_i^{(0)}$ and the magnetic one $\mu_i^{(m)}$, which originates from the magneto-static energy.

$$\mu_i = \mu_i^{(0)} + \mu_i^{(m)} = \mu_i^* + RT \ln \frac{P_i}{P^*} - \int_0^H \mu_0 \, \mathbf{m}_i \, \mathrm{d}\mathbf{H} \qquad (3)$$

μ_i^* is the standard chemical potential at a temperature T and the standard pressure P^* in zero magnetic field [2]. P_i and $\mathbf{m}_i$ are the partial pressure and the molar magnetization for the ith component. μ_0 is the permeability of a vacuum. It is noted that the molar magnetization of the ith component is a function of temperature T but the integration is performed at a constant T.

Substituting Eq. (3) into Eq. (2) gives

$$\sum_{i=1}^{k} \nu_i \left(\mu_i^* + \mu_i^{(m)}\right) = -RT \sum_{i=1}^{k} \nu_i \ln \frac{P_i}{P^*} = -RT \ln K_P \qquad (4)$$

where K_P is the (pressure) equilibrium constant. K_P is a function of temperature and magnetic field. Comparing the equilibrium constant in zero field and that in a magnetic field, we obtain the MFE on the equilibrium constant.

$$\ln K_P^{[H]} - \ln K_P^{[0]} = -\frac{g^{(m)}}{RT} \qquad (5)$$

The superscripts [H] and [0] denote the quantities in the magnetic field and zero field, respectively. $g^{(m)}$ is the change in magnetic free energy per unit reaction.

$$g^{(m)} = \sum_{i=1}^{k} \nu_i \mu_i^{(m)} = -\sum_{i=1}^{k} \nu_i \int_0^H \mu_0 \mathbf{m}_i \, \mathrm{d}\mathbf{H} \qquad (6)$$

The reaction is accompanied with the heat of reaction (the change in enthalpy) ΔH^0, the change in free energy ΔG^0 and the change in entropy ΔS^0 per unit reaction. Below we omit the superscript 0 in these symbols for simplification, i.e. ΔH in place of ΔH^0. These thermodynamic quantities are related to the equilibrium constant by:

$$\Delta H = RT^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln K_P \qquad (7)$$

$$\Delta G = -RT \ln K_P \qquad (8)$$

$$\Delta S = \frac{1}{T} (\Delta H - \Delta G) \qquad (9)$$

where the first equation is the van't Hoff relation. The MFE's on the thermodynamic quantities are derived by using Eq. (5).

$$\Delta H^{[H]} - \Delta H^{[0]} = g^{(m)} - T \frac{\mathrm{d}g^{(m)}}{\mathrm{d}T} \qquad (10)$$

$$\Delta G^{[H]} - \Delta G^{[0]} = g^{(m)} \qquad (11)$$

$$\Delta S^{[H]} - \Delta S^{[0]} = -T \frac{\mathrm{d}g^{(m)}}{\mathrm{d}T} \qquad (12)$$

3. Metal–hydrogen systems

In a so-called plateau region of a metal–hydrogen system, MH_a is reacted with hydrogen to produce MH_b.

$$\frac{2}{b-a} MH_a + H_2 \rightleftharpoons \frac{2}{b-a} MH_b \qquad (13)$$

We assume that both are ferromagnetic and that the magnetization is easily saturated up to the saturation magnetization $m_a^{(s)}$ or $m_b^{(s)}$ even in low fields. The change in magnetic free energy is given by:

$$g^{(m)} = 2 \, \mu_0 H \frac{m_a^{(s)} - m_b^{(s)}}{b-a} = 2B \, \Delta M_s \qquad (14)$$

where ΔM_s is the change in saturation magnetization per desorbed mole of hydrogen atoms. B is the magnetic field expressed in T unit, that is, $B = \mu_0 H$. Consequently, the MFE's in the metal–hydrogen system are derived according to Eqs. (10)–(12), as:

$$\Delta H^{[H]} - \Delta H^{[0]} = 2B \, \Delta M_s - 2BT \frac{\mathrm{d}}{\mathrm{d}T} \Delta M_s \qquad (15)$$

$$\Delta G^{[H]} - \Delta G^{[0]} = 2B \, \Delta M_s \qquad (16)$$

$$\Delta S^{[H]} - \Delta S^{[0]} = -2BT \frac{\mathrm{d}}{\mathrm{d}T} \Delta M_s \qquad (17)$$

It is understood that the MFE on the heat of reaction is due to ΔM_s itself (the first term in Eq. (15)) and its differentiation with respect to temperature (the second term).

There are two kinds of reactions in the system $LaCo_5$-H_2, corresponding to two plateaus of the $\alpha - \beta$ and the $\beta - \gamma$ regions.

$$0.645LaCo_5H_{0.3} + H_2 \rightleftharpoons 0.645LaCo_5H_{3.4} \qquad (18)$$

$$2.22LaCo_5H_{3.4} + H_2 \rightleftharpoons 2.22LaCo_5H_{4.3} \qquad (19)$$

The heat of reaction ΔH is -42.5 kJ (mol $H_2)^{-1}$ in the $\alpha - \beta$ region and -31.3 kJ (mol $H_2)^{-1}$ in the $\beta - \gamma$ region [5]. The three phases, the α $LaCo_5H_{0.3}$, the β $LaCo_5H_{3.4}$ and the γ $LaCo_5H_{4.3}$ are ferromagnetic and the saturation magnetization decreases in this order [6]. Moreover, a previous experiment yielded the temperature dependence of ΔM_s as shown in Fig. 1 [7].

Hence, we calculate the MFE on the heat of reaction according to Eq. (15) assuming a unit magnetic field ($B = 1$ T) is applied. Fig. 2 illustrates the calculated result. Above 270 K the magnetic field causes the absolute value of ΔH to increase in the $\alpha - \beta$ region in contrast to decrease in the $\beta - \gamma$ region. This contrasting behavior

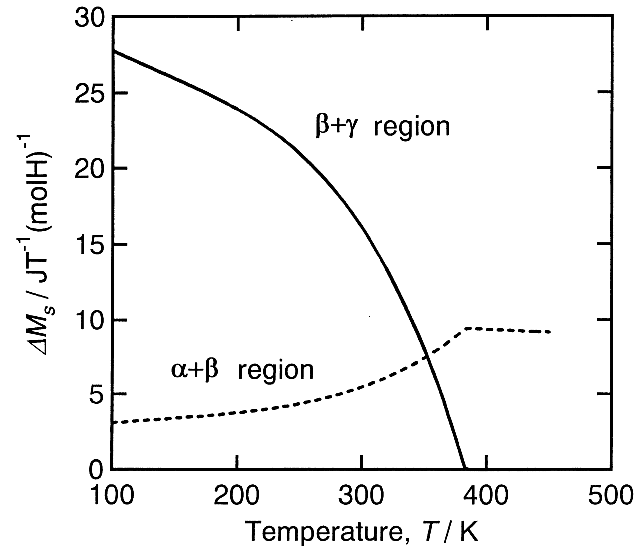

Fig. 1. Temperature dependence of ΔM_s for the $\alpha-\beta$ and the $\beta-\gamma$ regions for the system $LaCo_5$-H_2.

originates in the opposite signs of the temperature dependence of ΔM_s between the two regions and the second term dominates in Eq. (15). It is reasonable to evaluate the MFE as the fractional change,

$$\Gamma_H \equiv \frac{|\Delta H^{[H]}| - |\Delta H^{[0]}|}{|\Delta H^{[0]}|} \tag{20}$$

In the $\beta-\gamma$ region Γ_H is calculated to vary from -0.324% to -0.477% when the magnetic field of 1 T is applied in the temperature range between 293 and 343 K. This MFE is enhanced in proportion to the magnetic field because of Eq. (15). Accordingly, the value of Γ_H in 12 T ranges from -0.89% to -5.72% in the same temperature range.

4. Discussion

In metal–hydrogen systems, the equilibrium hydrogen pressure P_{H_2} is related to ΔH and ΔS.

$$\ln \frac{P_{H_2}}{P*} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{21}$$

This relationship stands for the respective cases in zero field and a magnetic field. It is well known that if the experimental relationship between ln P_{H_2} and $1/T$ is linear, ΔH can be obtained. Fig. 3 shows the ln P_{H_2} vs. $1/T$ plots in zero field and 12 T for the $\beta-\gamma$ region in $LaCo_5$-H_2, which have been derived from the equilibrium hydrogen pressures in magnetic fields [7]. Both the curves for 0 T and 12 T are linear and ΔH is determined to be -31.3 kJ (mol H_2)$^{-1}$ in 0 T and -30.0 kJ (mol H_2)$^{-1}$ in 12 T. Accordingly, the value of Γ_H is estimated to be -4.15%. It must be noted that this value is an average in the temperature range between 293 and 343 K. Actually $\Delta H^{[H]}$ is temperature-dependent as illustrated in Fig. 2. We recognize that this estimated value $\Gamma_H = -4.15\%$ agrees satisfactorily with the calculated ones $\Gamma_H = -3.89\% \sim -5.72\%$ from both the viewpoints of sign and magnitude. This agreement indicates the validity of the present formulation for the MFE on the heat of reaction.

In conclusion, the heat of reaction is influenced by magnetic fields as predicted by the general formulation for the magneto-thermodynamic effects. It is hoped to observe

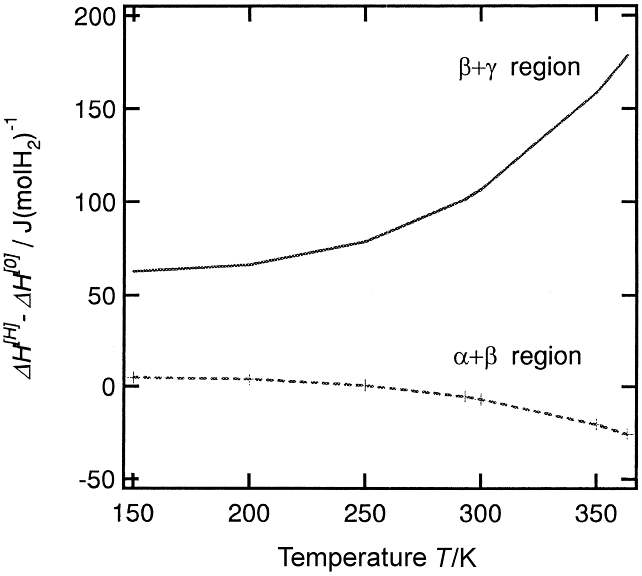

Fig. 2. Magnetic field-induced effects on the heat of reaction in the $\alpha-\beta$ and the $\beta-\gamma$ regions for the system $LaCo_5$-H_2 when a unit magnetic field ($B=1$ T) is applied.

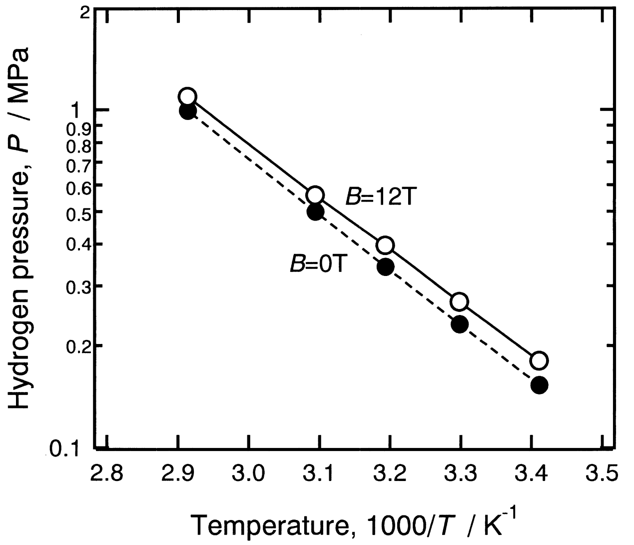

Fig. 3. Temperature dependence of the equilibrium hydrogen pressure in zero field and a magnetic field of 12 T in the $\beta-\gamma$ region for the system $LaCo_5$-H_2.

the heat of reaction under the influence of magnetic fields directly.

Acknowledgements

This study was supported by a Grant-in-Aid for Science Research (No. 1045035) from the Ministry of Education, Science, Culture and Sports of Japan. The author would like to thank F. Ishikawa for his useful discussion.

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