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Change in the heat of reaction by magnetic fields in $LaCo_5$–H_2

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Abstract

We experimentally investigated the effects of magnetic fields on the heat of reaction by examining the metal–hydrogen system $LaCo_5$–H_2. The heat of reaction was measured in zero field and a magnetic field by the logarithmic pressure vs. inverse temperature method and the calorimetric one. Both the methods gave generally the same results that the magnetic field caused the absolute value of the heat of reaction to increase a little in the $\alpha+\beta$ region and decrease considerably in the $\beta+\gamma$ region. These agree well with the calculation based on the general formulation of magneto-thermodynamic effects in chemical reactions. This is the first observation of the magnetic field effect on the heat of reaction.

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

1. Introduction

Recently there has been a growing interest in magnetic fields effects (MFEs) on chemical systems [1–3]. However, the heat of reaction, one of the important chemical quantities, has not been studied from this point of view so far. In our related paper [4], we formulated the magnetic field-induced change in the heat of reaction (the change in enthalpy) ΔH^0 for general chemical reactions. Below we omit the superscript 0 from ΔH^0 for simplification. Then, we applied this formulation to metal–hydrogen systems and showed the possibility of an experimental observation of the MFE on the heat of reaction. The purpose of this study is to detect the change in the heat of reaction caused by magnetic fields.

The system $LaCo_5$–H_2 is excellent for observing various MFEs because the ferromagnetic moment depends strongly on the hydrogen composition of the hydride and the magnetic free energy possibly becomes comparable with thermal energy at room temperature in high magnetic fields. We have two kinds of reactions in this system which correspond to two plateau regions [5].

$$0.645LaCo_5H_{0.3} + H_2 \rightleftharpoons 0.645LaCo_5H_{3.4} \quad (1)$$

$$2.22LaCo_5H_{3.4} + H_2 \rightleftharpoons 2.22LaCo_5H_{4.3} \quad (2)$$

When each reaction proceeds towards the right-hand side, heat is liberated with $\Delta H = -42.5$kJ (mol H_2)$^{-1}$ in the $\alpha+\beta$ region (Eq. (1)) and $\Delta H = -31.3$ kJ (mol H_2)$^{-1}$ in the $\beta+\gamma$ region (Eq. (2)). The three hydrides, the α phase $LaCo_5H_{0.3}$, the β phase $LaCo_5H_{3.4}$ and the γ phase $LaCo_5H_{4.3}$ are ferromagnetic and the saturation magnetization is decreased in this order [6]. We use the quantity ΔM_s as the change in saturation magnetization per desorbed mole hydrogen atom.

For a ferromagnetic metal–hydrogen system, the magnetic field-induced change in the heat of reaction is expressed by the following equation [4]:

$$\Delta H^{[H]} - \Delta H^{[0]} = 2B\Delta M_s - 2BT \frac{d}{dT} \Delta M_s \quad (3)$$

where the superscripts [0] and [H] denote the quantities in the absence of a magnetic field and that under the influence of a magnetic field, respectively. B is the magnetic field represented in T unit, that is, $B = \mu_0 H$. In the right-hand side of Eq. (3), the first and the second terms are due to the change in free energy ΔG^0 and the change in entropy ΔS^0, respectively. Below we evaluate the magnetic field-induced change by the fractional change defined by:

$$\Gamma_H = \frac{|\Delta H^{[H]}| - |\Delta H^{[0]}|}{|\Delta H^{[0]}|} \quad (4)$$

Table 1 lists the calculated values of Γ_H when a magnetic field of 5 T is applied to the system $LaCo_5$–H_2. We remark two features in Table 1 as follows:

1. The sign of Γ_H is opposite to each other between the two regions. That is, as the magnetic field is applied,

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Table 1
Magnetic field effects on the heat of reaction when a magnetic field of 5 T is applied to $LaCo_5$–H_2

Region	Temp. (K)	$\Delta H^{[0]}$ [kJ (mol H_2)$^{-1}$]	ΔM_s [JT^{-1} (mol H)$^{-1}$]	$(d/dT)\Delta M_s$ [JT^{-1} (mol H)$^{-1}$ K^{-1}]	$\Delta H^{[H]} - \Delta H^{[0]}$ [J (mol H_2)$^{-1}$]	Γ_H^{cal} (%)
$\alpha+\beta$	293	−42.5	5.29	2.69×10^{-2}	−26.0	0.06
	323	−42.5	6.25	3.86×10^{-2}	−62.3	0.14
$\beta+\gamma$	303	−31.3	15.7	-1.29×10^{-1}	548	−1.75
	333	−31.3	11.1	-1.78×10^{-1}	704	−2.25

the absolute value of the heat of reaction is increased in the $\alpha+\beta$ region. In contrast, it is decreased in the $\beta+\gamma$ region.

2. The MFE in the $\beta+\gamma$ region is one order of magnitude larger than that in the $\alpha+\beta$ region.

Both the features originate mainly from the sign and magnitude of $(d/dT)\Delta M_s$ in Eq. (3). The above two features are examined in later experiments.

2. Experiment 1

2.1. Method

In this experiment, we measured the equilibrium hydrogen pressures as a function of temperature in the absence and under the influence of the magnetic field in order to employ the $\ln P$ vs. $1/T$ method. Fig. 1 illustrates the experimental system. The $LaCo_5$ compound was prepared by the arc-melting method and annealed at 1223 K for 48 h for homogenization. Powder X-ray diffraction showed single phase of the $CaCu_5$-structure. The compound of 25 g was introduced into a Cu-made reactor which was connected by a stainless steel-made capillary to pressure–composition isotherm (P–C–T) manifolds. The magnet was cryo-cooled superconducting type and produced the maximum field of 5 T in the bore of 60 mm at room temperature. The temperature was controlled with a water jacket in the temperature range between 293 and 323 K for the $\alpha+\beta$ region and between 303 and 333 K for the $\beta+\gamma$ region.

2.2. Results

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

$$\ln\frac{P_{H_2}}{P*} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (5)$$

This relationship holds in zero field as well as in a magnetic field. Fig. 2 shows the ln P_{H_2} vs. $1/T$ plots in zero field and 5 T for $LaCo_5$–H_2. All the curves plotted are linear; as a consequence, the effective value of ΔH can be determined as listed in Table 2. It must be noted that

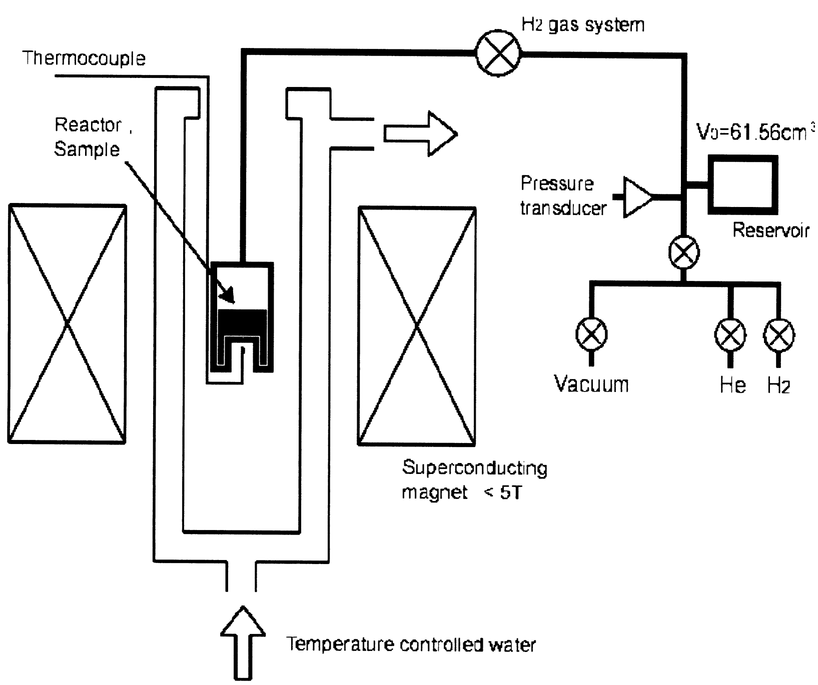

Fig. 1. Experimental system which is employed to observe the heat of reaction in a magnetic field for the metal–hydrogen system.

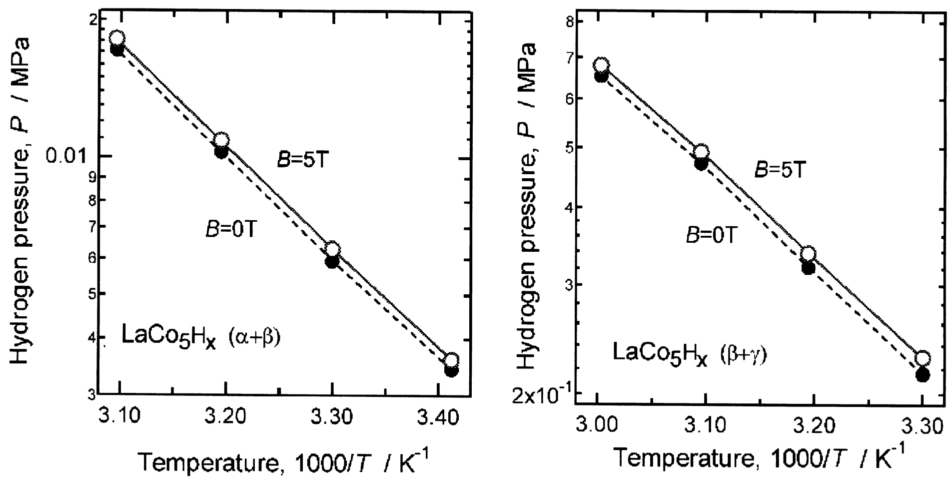

Fig. 2. ln P_{H_2} vs. $1/T$ plots in zero field and 5 T in the $\alpha+\beta$ and the $\beta+\gamma$ regions for $LaCo_5$–H_2.

these values are averages in the temperature range of the experiment. However, we recognize that the observed values of Γ_H are consistent in the calculated ones in both sign and magnitude.

3. Experiment 2

3.1. Method

The method adopted in this experiment was calorimetric. The experimental system used was generally the same as the one used in Experiment 1. The temperature change of the reactor was measured when a certain amount of hydrogen was absorbed. The temperature of the reactor T_m was monitored by Cu–Constantan thermocouples which were inserted into the reactor. The temperature of the reactor was set at 323±0.1 K before reaction. The change in hydrogen composition Δx was determined from the hydrogen pressure P by using the P–C–T manifolds. A set of the values P, T_m and Δx was logged every 0.1 s during a reaction. Such procedures were repeated four times in zero field and the magnetic field of 5 T.

3.2. Results

Fig. 3 exemplifies the time variations in the values P, T_m and Δx during the absorption process of hydrogen. The rise in temperature indicates that ΔH is negative. Basically the ratio of the change in temperature to the change in hydrogen composition, $\Delta T/\Delta x$, is proportional to the heat of reaction. Although heat escaped gradually from the reactor during the reaction, the reaction was almost completed by the time when the temperature attained the peak value. Thus, in this study, we adopted the ratio $\Delta T/\Delta x$ at the peak as the quantity which was proportional to ΔH.

Table 3 lists the averages between four data of $\Delta T/\Delta x$.

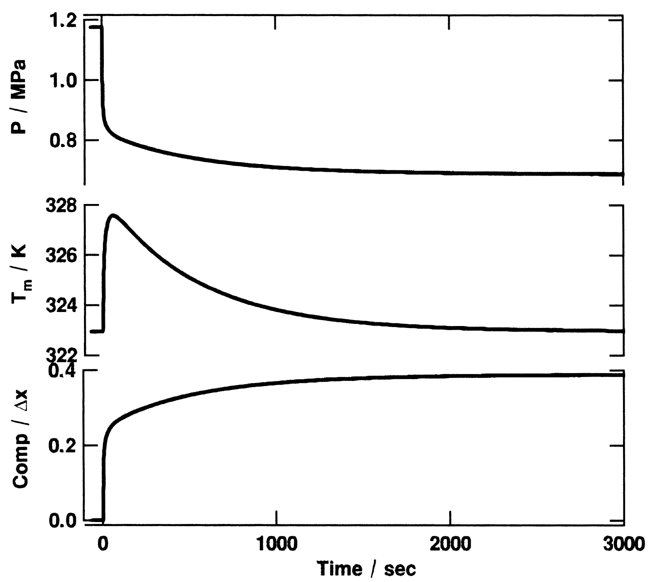

Fig. 3. Time variations in hydrogen pressure P, the temperature of the reactor T_m and the change in hydrogen composition Δx in the absorption process of hydrogen at $T=323$ K under $B=5$T in the $\beta+\gamma$ region for the system $LaCo_5$–H_2.

Table 2
Heat of reaction in zero field and 5 T in $LaCo_5$–H_2 by the ln P vs. $1/T$ method

Region	Temp. (K)	$\Delta H^{[0]}$ (kJ (mol H_2)$^{-1}$)	$\Delta H^{[H]}$ (kJ (mol H_2)$^{-1}$)	Γ_H^{obs} (%)	Γ_H^{cal} (%)
$\alpha+\beta$	293–323	−42.3∓0.5	−42.3∓0.3	0.0±1.8	0.06 to 0.14
$\beta+\gamma$	303–333	−31.1∓0.4	−30.5∓0.3	−1.9∓1.8	−1.75 to −2.25

Table 3
Magnetic field effects on the heat of reaction at 323 K in $LaCo_5$–H_2 by the calorimetric method

Region	Magnetic field (T)	$\Delta T/\Delta x$ (K/x)	Γ_H^{obs} (%)	Γ_H^{cal} (%)
$\alpha+\beta$	0	27.5±0.9	−0.4∓6.9	0.14
	5	27.4±1.0		
$\beta+\gamma$	0	19.2±0.3	−5.0∓2.1	−2.06
	5	18.2±0.1		

Then, we evaluate the magnetic field effect on the heat of reaction as the fractional change Γ_H from $\Delta T/\Delta x$ as:

$$\Gamma_H = \frac{(\Delta T/\Delta x)^{[H]} - (\Delta T/\Delta x)^{[0]}}{(\Delta T/\Delta x)^{[0]}} \qquad (6)$$

where the superscripts [H] and [0] again denote the values obtained in a magnetic field and zero field, respectively. We recognize that Γ_H in the $\beta+\gamma$ region is clearly negative and its value is comparable with the calculated one $\Gamma_H = -2.06\%$. On the other hand, Γ_H in the $\alpha+\beta$ region is positive, showing noticeable error. However, this fact is consistent with the calculation which predicted small magnetic field effects in this region.

4. Conclusions

We have observed the magnetic field-induced changes in the heat of reaction for the system $LaCo_5$–H_2 by two methods. As a result, it has been verified that the heat of reaction is changed by the magnetic field in accordance with the calculation which is based on the general theory for the magneto-thermodynamic effects in chemical reactions [4]. This is the first observation of the magnetic field effect on the heat of reaction.

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