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Activation energies for the desorption of H_2, H^- and electron from saline hydrides heated in vacuum

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Abstract

To study the thermodynamic and thermionic properties of saline hydride (MH_n, $n = 1$ or 2; M = Li, Na, Mg, Ca or Sr), powders (ca. 1 mg) were deposited on a molybdenum heater, and the currents of H^- and electrons (e^-) desorbed directly from the hydrides were measured in vacuum as a function of temperature (T) up to 1100 K at a constant rate. A dual mass spectrometer system, in which the H_2 desorbed from MH_n was converted into $H_2{}^+$ by electron impact, was used. The temperature-programmed desorption spectra for H^-, e^- and H_2 were analyzed using a leading edge method. The following results were obtained: (1) each desorption became appreciable at an appearance temperature, which increased in the order of H_2 (ca. 700 K) and both e^- and H^- (above ca. 800 K); (2) the activation energies (E^0, E^e and E^- in kJ mol^{-1}) for the desorption of H_2, e^- and H^- were as follows — LiH (95, 596, 660), NaH (60, 221, 173), MgH_2 (91, 335, 318), CaH_2 (87, 428, 612) and SrH_2 (63, 354, 308); (3) as T increased from ca. 900 to 940 K in the case of LiH, E^e corresponding to the work function increased from ca. 580 to 600 kJ mol^{-1}; (4) such an increase was caused by a decrease in the surface density of these active sites (e.g., Li) which were created by thermal decomposition (e.g., $LiH \rightarrow Li + \frac{1}{2}H_2$) and also which promoted the desorption of e^- and H^-.

Keywords: Alkali metal hydride; Alkaline earth hydrides; Desorption energies; Thermal negative hydride ion; Thermal electron; Hydrogen gas liberation

1. Introduction

The saline hydrides (MH_n) such as NaH and CaH_2 are thermally so unstable that they readily decompose thermally ($MH_n \rightarrow M + \frac{1}{2}nH_2$) at temperatures lower than 1000 K [1]. In addition, they have the unique property of desorbing both thermal electrons (e^-) and negative hydride ions (H^-) when they are heated in vacuum up to 800 K [2–10], as shown typically in Figs. 1 and 2. In this, a powder sample (ca. 1 mg) deposited on a molybdenum ribbon was heated stepwise at ca. 30 K every ca. 0.5 h. The currents (J^- and I^-) of e^-'s and H^-'s were measured with a mass spectrometer. In general, H^- cannot normally be produced by an atomic or molecular beam thermal ionization method because the electron affinity (ca. 80 kJ mol^{-1}) of H is much smaller than the work function (usually $\phi \geq 150$ kJ mol^{-1}) of any solid surface from which the negative ions to be produced from the incident sample atoms or molecules are to be desorbed [11].

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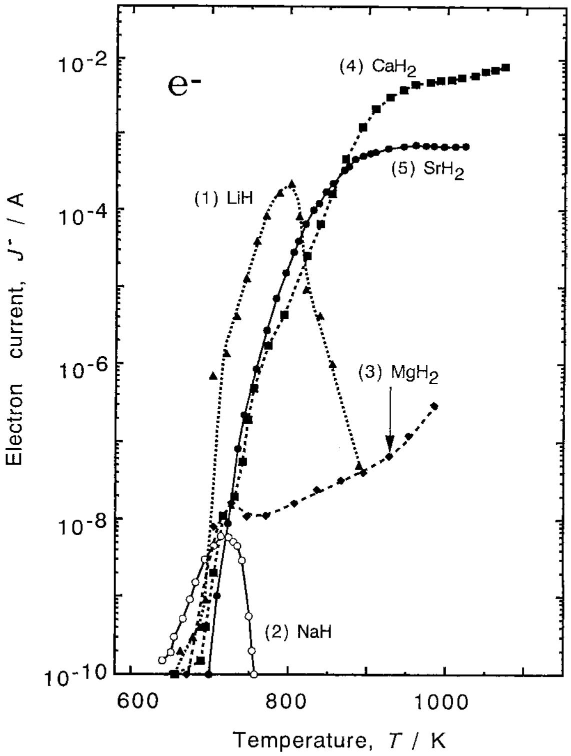

Fig. 1. Temperature dependence of the current (J^-) of thermal electron desorbed from five saline hydrides (1)–(5) heated stepwise by ca. 30 K at ca. 0.5 h intervals. It should be noted that the appearance temperature of each desorption due to the stepwise heating is generally much lower than that due to the constant rate heating (see Section 3.1.).

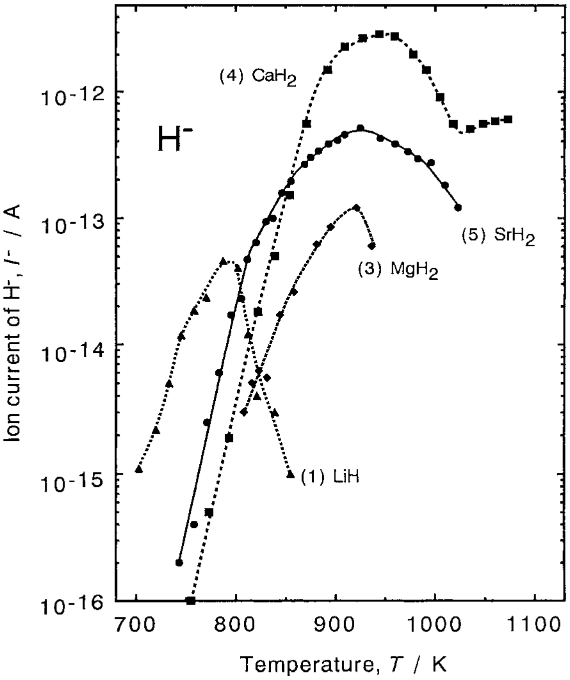

Fig. 2. Sample temperature (T) vs. the mass-analyzed ion current (I^-) of H^- desorbed from each hydride by the stepwise heating. These data were obtained simultaneously together with those in Fig. 1. In the case of NaH, H^- cannot be detected by the stepwise heating because NaH is thermally so unstable that NaH deposited on R is thoroughly depleted before reaching to a temperature (probably less than ca. 700 K) high enough to desorb H^-.

This unique property is very interesting from the point of view of thermochemistry and, it is important and valuable to determine the activation energies for the desorption of both H^- and e^- together with H_2 from the thermal decomposition of MH_n. This paper summarizes the experimental data and analytical results obtained from five hydrides by using a technique developed in our laboratory.

2. Experimental method

The experimental apparatus used in this work is schematically shown in Fig. 3. A powder sample (ca. 30–350 mesh) of metal hydride (ca. 1 mg) was deposited in a small box (ca. 0.1 cm wide, 0.2 cm long and 0.05 cm high) at the center of a molybdenum ribbon (R), and heated in vacuum to ca. 1100 K at a constant rate ($\beta = 1 - 10\,\mathrm{K\,s^{-1}}$) using a temperature programme. The sample temperature (T) was monitored with a chromel–alumel thermocouple (A) spot-welded onto the bottom of the box.

The acceleration voltage (V_a) for focusing H^- directly desorbed from the sample (S) was calculated to be ca. 550 V in the 180° deflection type mass spectrometer, where the ion path radius was 2.5 cm and the analyzing magnetic field (H) was 1350 G. The current (I^-) of H^- ions collected on the Faraday cup (C) was measured with a femtoampere meter. The total negative current (J^-) almost entirely (more than 99%) owing to e^- desorbed directly from S was collected with the first slit plate (P_1). The rate of H_2 desorbed by the thermal decomposition of S was measured as the current (I^+) of H_2^+ using a quadruple-

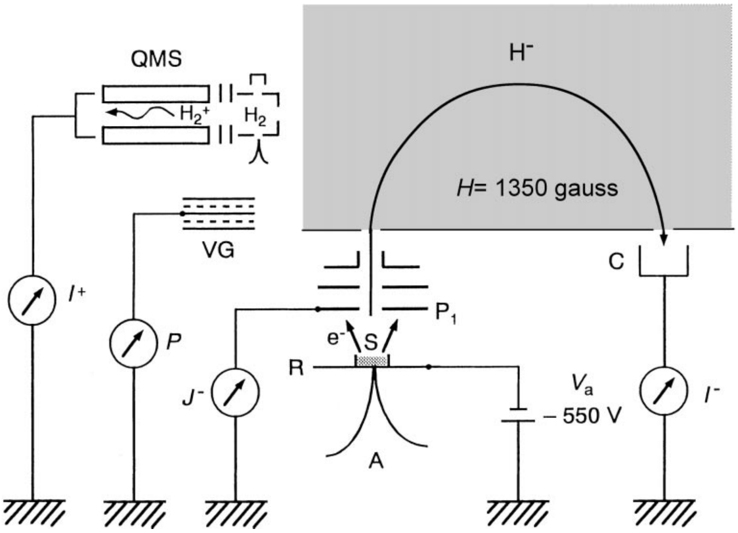

Fig. 3. Schematic diagram of our dual mass spectrometer system employed in this work.

type mass spectrometer (QMS), where the energy and current of those bombarding electrons to convert H_2 into H_2^+ were ca. $3 \times 10^3\,kJ\,mol^{-1}$ and 40 μA, respectively. The residual gas pressure (P) attained by an oil diffusion pump with a liquid nitrogen trap was usually ca. 1×10^{-4} Pa, which was measured with a vacuum gauge (VG) of the Bayard–Alpert type. By mass spectrometry, the residual gases were found to consist mainly of H_2O, CO, O_2, CO_2 and hydrocarbons.

By the above method and technique, the desorption rates (I^-, J^- and I^+) of H^-, e^- and H_2 originating from the heated MH_n were measured simultaneously as a function of T in order to determine the activation energies (E^-, E^e and E^0) for their desorption from each sample.

3. Results and discussion

3.1. Pattern of desorption spectra

Temperature-programmed desorption spectra observed with MgH_2 and CaH_2 are shown in Figs. 4 and 5, respectively. Each figure indicates that (1) initially H_2 is thermally desorbed around 700 K, (2) there is a peak around 800 K, and finally (3) the

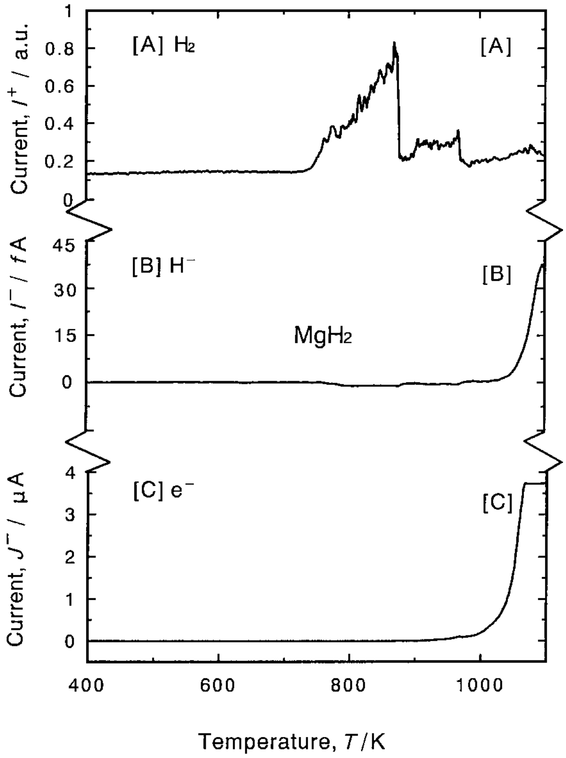

Fig. 4. Temperature-programmed desorption spectra obtained with (A) H_2 (detected as H_2^+), (B) H^- and (C) e^- desorbed from MgH_2 by heating at the rate of ca. $4\,K\,s^{-1}$.

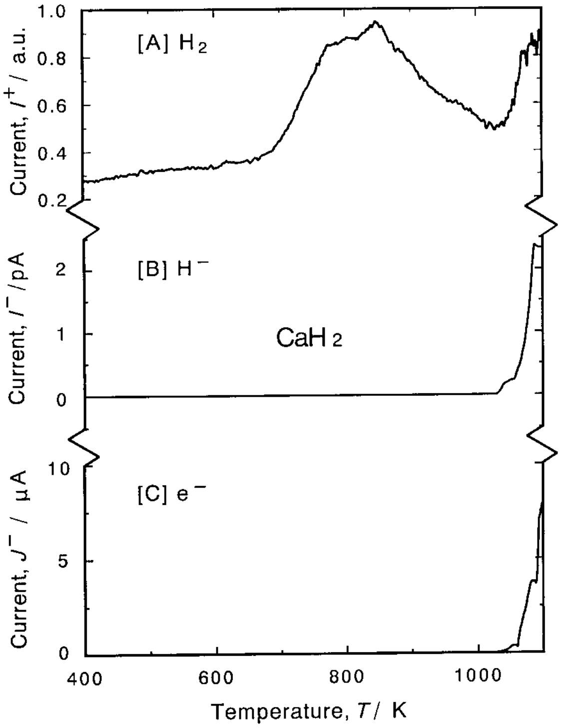

Fig. 5. Temperature-programmed desorption spectra observed with CaH_2 at the rate of ca. 4 K s^{-1}.

electronic and ionic desorptions occur at a higher temperature above 900 K. This pattern is reasonably explained by our desorption model that both e^- and H^- are desorbed from those active sites (low work function spots, mainly consisting of M) created by the thermal decomposition reaction of $MH_n \rightarrow M + \frac{1}{2}nH_2$ [10].

A similar pattern was observed with SrH_2 (see Fig. 6) and also with LiH and NaH, thereby indicating again that neither e^- nor H^- can be desorbed before the active sites (M) are created by strong desorption of H_2.

3.2. Determination of activation energies

To determine the activation energy of each desorbate from such spectra as shown above, we can usually adopt a heating rate variation method [12], where the quantitative relation between the heating rate (β) and the desorption peak appearance temperature (T_p) must be determined correctly under the condition of constant sample amount (A_0). In this work, however, it is generally very difficult to determine T_p correctly, as may readily be seen from Figs. 4–6. In addition, it is very difficult to keep A_0 constant in each run as the samples are powders and also very reactive to moisture $(MH_n + nH_2O \rightarrow M(OH)_n + nH_2)$. It should be noted that neither H^- nor e^- can be desorbed from such moist samples.

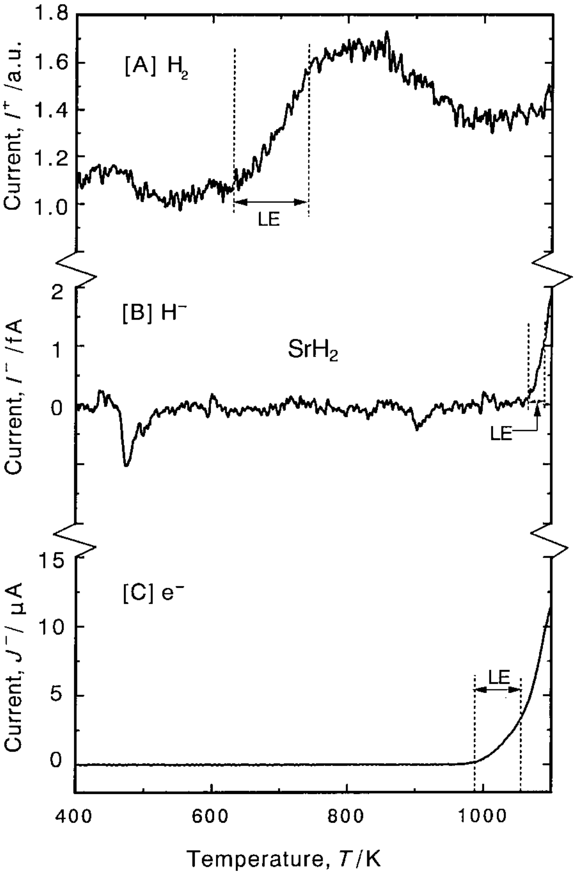

Fig. 6. Typical example of the spectra observed with SrH_2 ($\beta \approx 4\,K\,s^{-1}$). LE indicates the temperature range of each leading edge.

Consequently, we adopted a leading edge analysis method [13], which made it possible to determine the activation energy (E^0 or E^-) for the desorption of H_2 or H^- on the basis of Eq. (1).

$$\frac{d(\ln I^{+-})}{d(1/T)} = -\frac{E^{0-}}{R}. \tag{1}$$

Here, T corresponds to the region of a leading edge (LE, see Fig. 6) where the sample amount desorbing H_2 or H^- is estimated to be more than 95%. With respect to the desorption energy (E^e) of e^-, we have employed Eq. (2).

$$\frac{d(\ln J^-/T^2)}{d(1/T)} = -\frac{E^e}{R}, \tag{2}$$

which is based on Richardson's equation [11], and hence E^e is equivalent to the work function (ϕ) of those active sites (M) from which e^- and H^- are desorbed.

From the slope of each straight line as shown in Fig. 7, the activation energy of each desorbate is readily determined according to Eq. (1) or (2). The values of E are summarized in Table 1. Previous work with the positive ionic and neutral desorptions from alkali halide films has already shown that the leading edge analysis method is as reliable as the heating rate variation method [14].

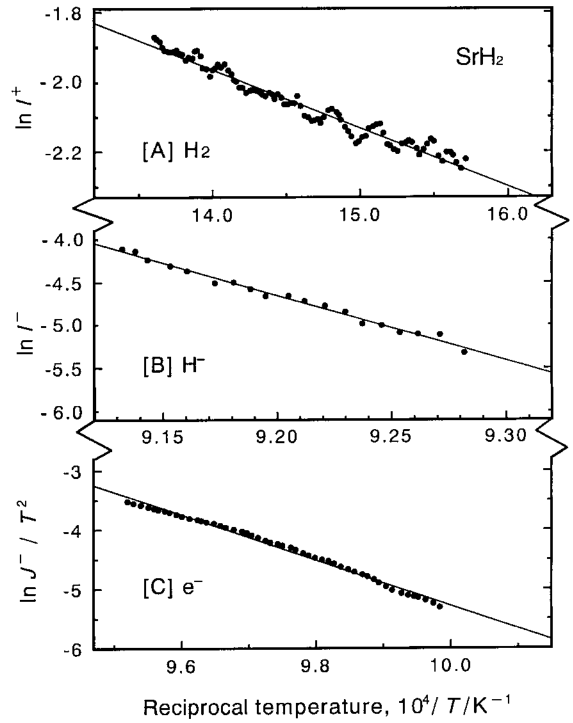

Fig. 7. Reciprocal temperature in a leading edge region (LE, see Fig. 6) vs. natural logarithm of the desorption rate of (A) H_2, (B) H^- or (C) e^- originating from SrH_2.

Table 1
Activation energies (E^0, E^e and E^-) for the desorption of H_2, e^-'s and H^- ions from metal hydrides

Sample	E^0 (kJ mol^{-1})	$E^e(\phi)$ (kJ mol^{-1})	E^- (kJ mol^{-1})
LiH	95 ± 15	596 ± 8	660 ± 42
NaH	60 ± 11	221 ± 23	173 ± 25
MgH_2	91 ± 13	335 ± 15	318 ± 32
CaH_2	87 ± 10	428 ± 17	612 ± 28
SrH_2	63 ± 8	354 ± 25	308 ± 37

3.3. Thermal decomposition and work function

As already stated above, those active sites (M) promoting the desorption of e^- and H^- are produced by the thermal decomposition ($MH_n \rightarrow M + \frac{1}{2}nH_2$). Accordingly, the work function ($\phi \equiv E^e$) is dependent on the percentage (L_H) of decomposition and the surface density of active sites. In order to check this prediction, the temperature dependence of ϕ was studied. From the slope of line (2) exemplified with LiH in Fig. 8, ϕ was determined to be 583 ± 3

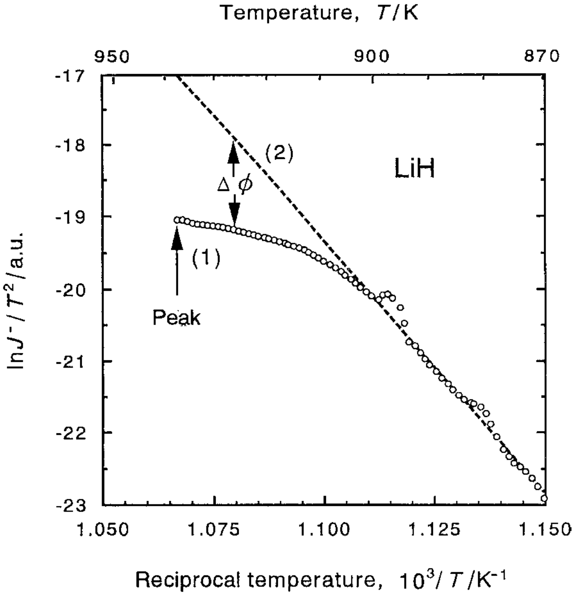

Fig. 8. Richardson plot obtained with LiH. The "Peak" indicates the temperature at which J^- becomes maximum (see curve (1) in Fig. 9).

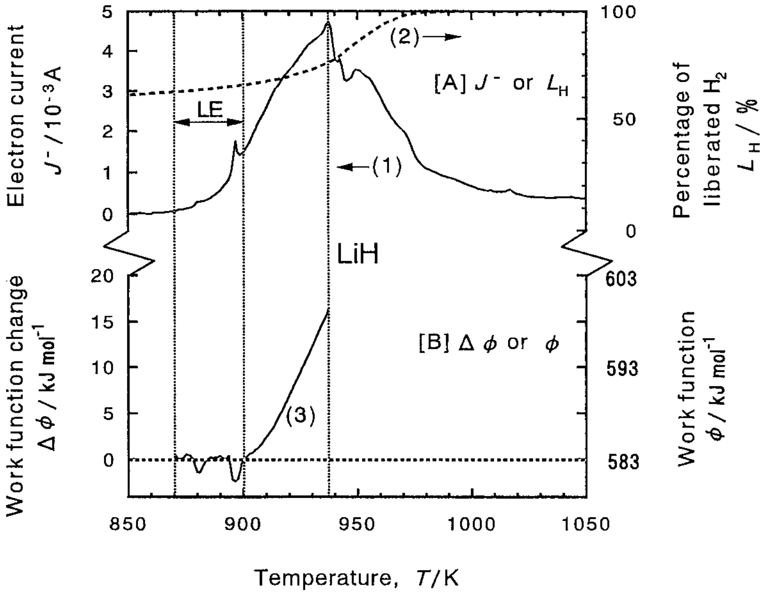

Fig. 9. Temperature dependence of (1) the electron current, (2) the percentage of liberated hydrogen, and (3) the work function or its change observed with LiH.

kJ mol^{-1}. The work function change ($\Delta\phi$) indicated in Fig. 8 was evaluated from Eq. (3), as

$$\Delta\phi = RT \ln\left(\frac{J_2^-}{J_1^-}\right), \quad (3)$$

where J_1^- and J_2^- are the electron currents corresponding to curve (1) and line (2), respectively, at a given temperature. The results from LiH are summarized in Fig. 9. In the LE region (870–900 K), ϕ is constant at 583 ± 3 kJ mol^{-1}, and L_H is nearly constant at 64 ± 1% (see curve (2) in Fig. 9), which is readily evaluated from the integrated current of I^+ (proportional to the desorption rate of H_2). With an increase in T from 900 to 937 K, L_H increases from 66 to 77% and, accordingly, ϕ also increases by up to $\Delta\phi \approx 16$ kJ mol^{-1} at 937 K (see curve (3) in Fig. 9) at which J^- exhibits a maximum (see curve (1) in Fig. 9). The increase in ϕ indicates that the surface density of the active sites (Li) is decreased by a rapid desorption of Li together with H_2. A similar phenomenon was observed with the other hydrides, too.

Richardson plots obtained with LiH by several runs at $\beta \approx 4$ K s^{-1} are exemplified in Fig. 10. Lines (1)–(3) gave values of $\phi = 603 \pm 2, 601 \pm 2$ and 584 ± 3 kJ mol^{-1}, respectively. The three lines do not overlap with each other mainly because of unequality in A_0 (see Section 3.2.), but their slopes are nearly the same, thus giving the mean value of 596 ± 8 kJ mol^{-1}. The analytical results achieved in this way are summarized in Table 1.

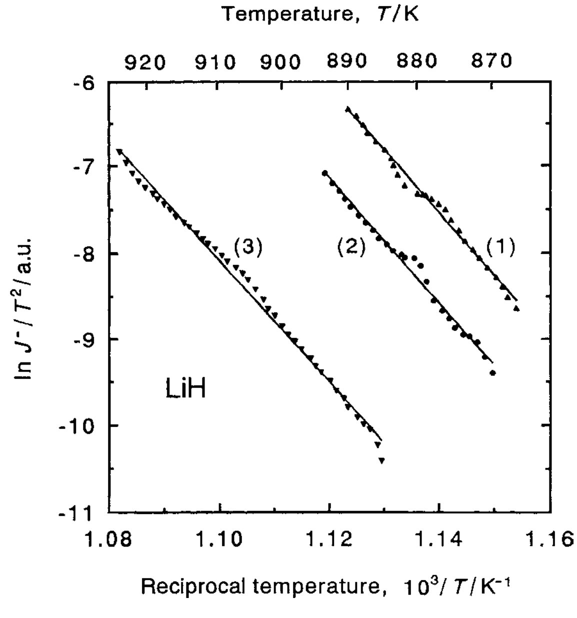

Fig. 10. Richardson plots obtained with LiH in several runs at $\beta \approx 4$ K s^{-1}.

To the best of our knowledge, such results have not yet been reported by any other group.

4. Conclusion

The experimental data and analytical results achieved in this work lead to the conclusion that the present method is useful for determining the desorption energies of H_2, H^- and e^- from saline hydrides heated in vacuum and also for clarifying the relation between the work function (ϕ) of the active sites and the percentage (L_H) of liberated H_2 owing to the activation reaction of $MH_n \rightarrow M + \frac{1}{2}nH_2$.

Much further work, however, is needed to clarify the elementary surface processes of both ionic and electronic desorptions. Especially to determine the surface density of the active sites (M), the desorption rate of M also should be measured together with the rates of H_2, H^- and e^-. In addition, the temperature range should be extended up to ca. 1500 K to obtain more detailed spectra.

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