

Desorption energy of H^- from heated saline hydrides and their work function effective for thermal electron emission

Hiroyuki Kawano*, Naoshi Serizawa, Makiko Takeda, Takanori Maeda, Akihide Tanaka, Yongfa Zhu¹

Department of Chemistry, Faculty of Science, Ehime University, Bunkyo, Matsuyama 790-77, Japan

Abstract

For the thermochemical study of negative hydride-ion desorption from powdery saline hydride (MH_n , $n = 1$ or 2) deposited on a molybdenum ribbon heater, both negative-ionic and electronic desorption currents from MH_n were measured simultaneously as a function of sample temperature (ca. 700–800 K) by using a mass spectrometer, thereby yielding the new data that the desorption energy (E^-) of H^- and the work function (ϕ) of the desorbing surface of MH_n are, respectively, 536 and 318 kJ mol^{-1} for LiH, 728 and 492 kJ mol^{-1} for CaH_2 , and 937 and 702 kJ mol^{-1} for SrH_2 . Our energy cycle, consisting of the four indirect processes equivalent in reaction energy to the direct desorption of H^- from MH_n , indicates that the theoretical values of $E^- - \phi$ are 227, 224 and 227 kJ mol^{-1} for LiH, CaH_2 and SrH_2 , respectively. They are in good agreement with our respective experimental values of 218, 236 and 235 kJ mol^{-1} within the experimental error of ca. $\pm 5\%$. This agreement indicates that the desorption of H^- from MH_n is explained reasonably well by our simple model based on chemical thermodynamics.

Keywords: Energy cycle; Negative hydride ion; Saline hydride; Thermal desorption energy; Work function

1. Introduction

From the viewpoint of physical chemistry, saline hydrides (MH_n , $n = 1$ or 2), such as LiH and SrH_2 , are very interesting because they are thermally so unstable that hydrogen gas is readily liberated at relatively low temperatures [1]. Even at 700 K, for example, the saturation pressure of H_2 in the equilibrium of $\text{CaH}_2(\text{solid}) \rightleftharpoons \text{Ca}(\text{solid}) + \text{H}_2(\text{gas})$ in a closed system is as high as ca. 10^{-1} Pa [2]. This instability suggests that the heated sample surface may have a relatively low work function (ϕ) due to the ‘active sites’ of M (solid) produced after the preferential liberation of H_2 from MH_n and, hence, that H^- may be desorbed

together with H_2 when the surface is kept at a temperature high enough to emit thermal electrons (e^-). In the field of surface science, it is very important to determine both ϕ and the desorption energy (E^-) of H^- from heated solid samples and also to clarify the main factors governing the desorption. In addition, it is very advantageous to develop a new convenient method to generate gaseous negative ions (e.g., H^-) from solid samples (e.g., CaH_2). It should be noted that hydrogen has a very small electron affinity ($< 100 \text{ kJ mol}^{-1}$) in contrast to halogens ($> 300 \text{ kJ mol}^{-1}$) and, hence, H^- can hardly be produced by a negative surface ionization method, where sample gas (or vapor) is directed onto a glowing metal surface [3].

From the aforementioned points of view, we have examined the desorption under various conditions and found that H^- is readily desorbed by merely heating of CaH_2 up to ca. 800 K [4]. In order to obtain further

*Corresponding author. Fax: 81-89-927-9590; e-mail: kawano@dpc.ehime-u.ac.jp

¹On leave from the Department of Chemistry, Tsinghua University, Beijing, 100084, P.R. China

information on desorption, we have made an additional study with LiH and SrH₂. This paper summarizes the important results achieved by thermochemical analysis of our experimental data, thereby yielding the conclusive evidence that our simple model invented to explain the desorption of H⁻ from CaH₂ [5] is generally applicable to MH_{*n*} and also that our new data on E^- and ϕ are reliable, in spite of a rather poor reproducibility in desorption currents of both H⁻ and e⁻.

2. Experimental

The experimental apparatus and method employed in this work are virtually the same as in the previous works [4–6]. As shown in Fig. 1, a powdery sample (S) of saline hydride (ca. 10 mg) deposited on the central part (ca. 0.1 cm²) of a molybdenum ribbon (R) with an Alumel-Chromel thermocouple (A) was heated to a high temperature ($T \approx (700\text{--}900)$ K) in a high vacuum (ca. 10⁻⁵ Pa). The total negativity current (I^- , almost entirely consisting of electron current) extracted by the voltage of V_0 (usually 90 V) was collected with the first slit plate (P₁). The acceleration voltage (V_a) necessary for focusing H⁻ in our mass spectrometer (180° deflection with an ion path radius of 2.5 cm in an analyzing magnetic

field of 1350 gauss) is theoretically evaluated to be ca. 550 V. The current (i^-) of H⁻ collected with a Faraday cup (C) was measured simultaneously with I^- .

A typical mass spectrum observed with SrH₂ is shown in Fig. 2, where T is 710 K and I^- is $\sim 4 \mu\text{A}$. Peak (1) appearing at $V_a \approx 540$ V corresponds to H⁻ desorbed directly from SrH₂ on R. On the other hand, peak (2) at ca. 620 V changes in mass position according to V_0 , and hence, it originates from H⁻ desorbed by electron impact at the sample (SrH₂) gradually accumulated onto P₁ during repeated runs (see insert in the figure). A similar mass spectrum was observed also with LiD, showing two peaks ($V_a \approx 270$ and 350 V) of D⁻ produced by the different mechanisms of thermal ion desorption [4–6] and electron-simulated ion desorption [7–9].

3. Results and discussion

Prior to repeated runs, a preliminary heating of MH_{*n*} up to ca. 850 K was carried out for several hours in order to remove adsorbed gases and also to enhance the stability in desorption currents (i^- and I^-) of H⁻ and e⁻ from the powdery sample under study. Temperature dependence of i^- and I^- from SrH₂ is exemplified as lines (1) and (2) in Fig. 3, respectively, where T was changed nearly every 0.5 h after the

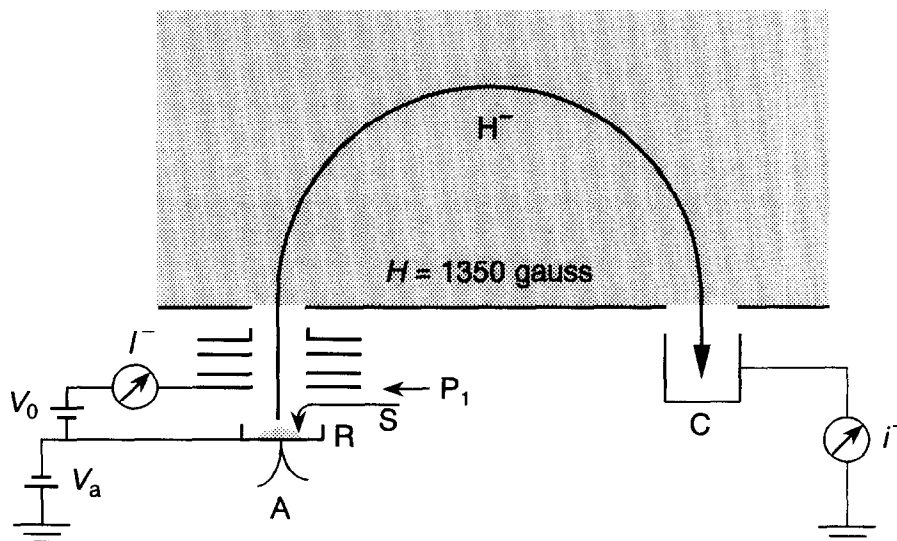


Fig. 1. Schematic diagram of the instrument employed for this work.

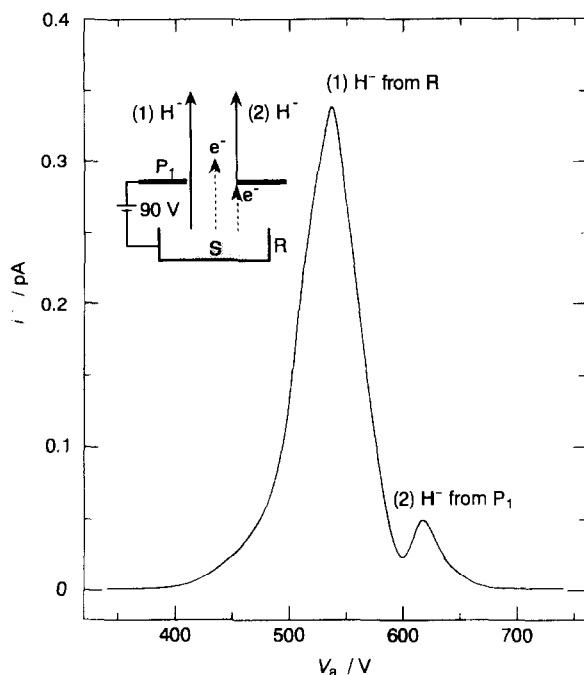


Fig. 2. Typical mass spectrum observed with SrH₂ heated to 710 K.

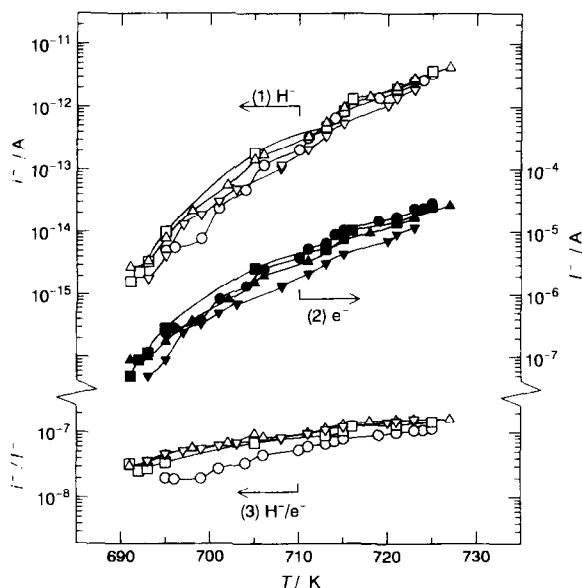


Fig. 3. Temperature dependence of: (1) – the collector current (i^-) of H⁻; (2) – the total current (I^-) mainly consisting of e^- ; and (3) – the current ratio (i^-/I^-) measured with SrH₂ heated at 5×10^{-5} Pa.

preliminary heating mentioned above. From run to run, however, each desorption current at any temperature varies largely, by up to $\pm 70\%$; very poor in reproducibility compared with that from a thin film (less than 10^3 molecular layers) of alkali halide (MX) deposited on a metal heater [10,11], where the current of M^+ or X^- is usually reproducible to less than $\pm 10\%$ on repeated runs. Such a large variation is generally observed with CaH₂ and LiH, too. This is probably because the effective surface area for each desorption from the powder of MH_{*n*} cannot be kept constant during repeated runs and also because the surface composition ($M : H = 1 : n$ at first) of MH_{*n*} is gradually changed during runs owing to the difference in thermally dissociative evaporation rate between M and H. The latter may be supported by the fact that I^- from LiH kept at 770 K in the course of the preliminary heating mentioned above, for example, spontaneously increased up to ca. nine times almost within 6 h, corresponding to a decrease in ϕ of 14 kJ mol^{-1} due to the formation of active sites (mainly composed of M) with lower values of ϕ . Lines (3) of Fig. 3 indicate that the ratio (i^-/I^-) increased ca. five times with an increase in T from ca. 690 to 730 K, thereby suggesting that E^- is larger than ϕ .

From the slopes of lines (1) and (2), as exemplified in Fig. 4, E^- and ϕ for SrH₂ are determined to be 937 ± 38 and $702 \pm 32 \text{ kJ mol}^{-1}$, respectively, while $E^- - \phi$ is determined to be $235 \pm 24 \text{ kJ mol}^{-1}$ from line (3), as a typical example. In a similar way, the values of E^- , ϕ and $E^- - \phi$ are measured with CaH₂ and LiH from the respective slopes of lines (1–3), exemplified in Figs. 5 and 6. The experimental data thus achieved are summarized in Table 1. To the best of our knowledge, such data have not yet been obtained by any other group of workers. With respect to NaH, neither E^- nor ϕ could be determined successfully, because it is thermally more unstable than the above-mentioned hydrides [6].

On the basis of the foregoing results and discussion, consideration of the surface processes of $MH_n/n \rightarrow M/n + H$ and $H + e^- \rightarrow H^-$ on the active sites having the value of ϕ leads to the energy cycle illustrated in Fig. 7, thereby yielding

$$E^- \equiv \sum E_i = -\Delta H/n + D/2 + \phi - A \quad (1)$$

Here, ΔH , D and A are the heat of formation of MH_{*n*},

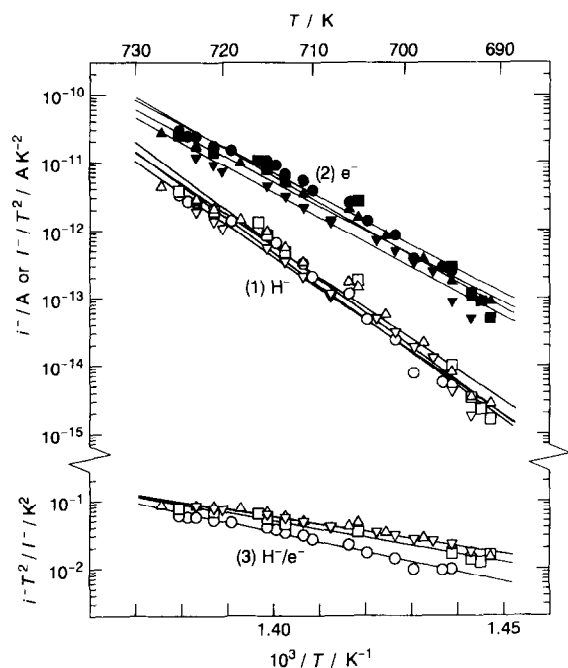


Fig. 4. Reciprocal of the sample temperature (T) vs. (1) – collector current (i^-) of H^- , (2) – the electron current (I^-) divided by T^2 , and (3) – the ratio (i^-T^2/I^-) observed with SrH_2 .

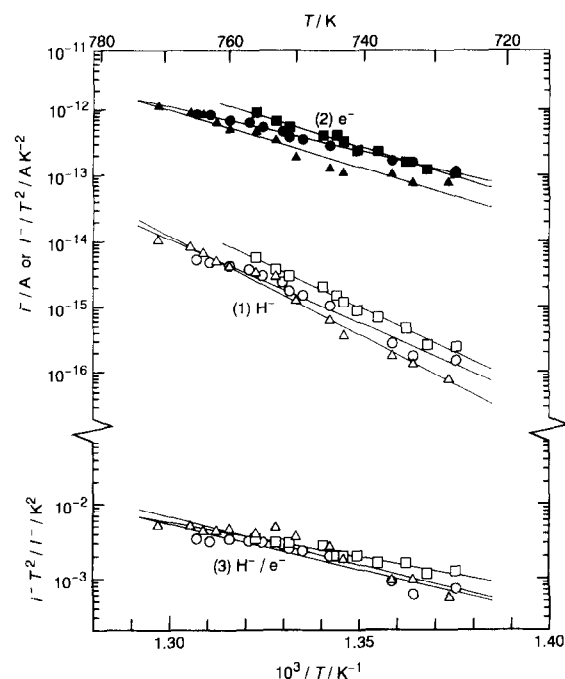


Fig. 6. Reciprocal temperature ($1/T$) vs. (1) – i^- , (2) – I^-/T^2 , and (3) – i^-T^2/I^- measured with LiH .

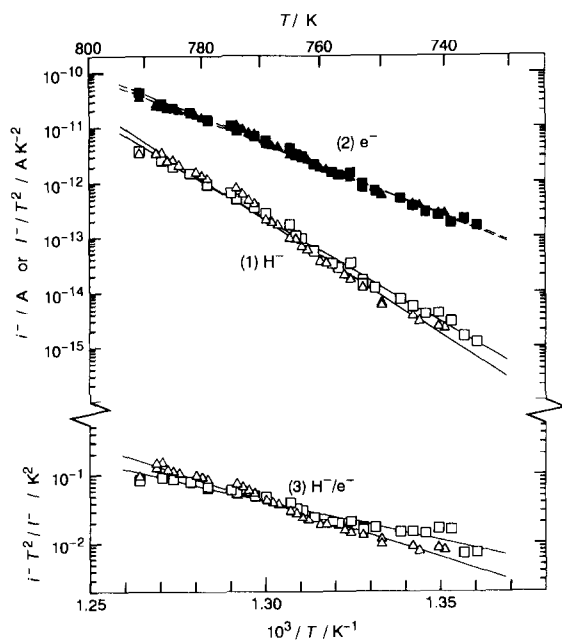


Fig. 5. Reciprocal temperature dependence of (1) – the current (i^-) of H^- , (2) – the electron current (I^-) divided by T^2 , and (3) – the ratio (i^-T^2/I^-) found with CaH_2 .

Table 1

Summary of our experimental data and analytical results achieved by our model using published thermochemical data. Here, E^- is the desorption energy of H^- from heated saline hydride (MH_n), ϕ the work function effective for thermal electron emission from the heated hydride, ΔH the heat of formation of MH_n , D the dissociation energy of H_2 , and A the electron affinity of H

Sample	Experimental value/(kJ mol ⁻¹)			
	E^-	ϕ	$E^- - \phi$	
LiH	536 ± 24	318 ± 17	218 ± 28	
CaH_2	728 ± 15	492 ± 8	236 ± 17	
SrH_2	937 ± 38	702 ± 32	235 ± 24	
Sample	Theoretical value/(kJ mol ⁻¹)			
	$\Delta H/n$	$D/2$	A	$E^- - \phi$
LiH	-94	221	88	227
CaH_2	-91	221	88	224
SrH_2	-94	221	88	227

(solid), dissociation energy of H_2 (gas), and the electron affinity of hydrogen (gas), respectively. Their values cited from thermochemical tables [12,13] are listed in Table 1, where each value corresponds to the temperature range ($T \approx (700-800)$ K) covered in this work. Both E^- and ϕ , measured with each MH_n , are

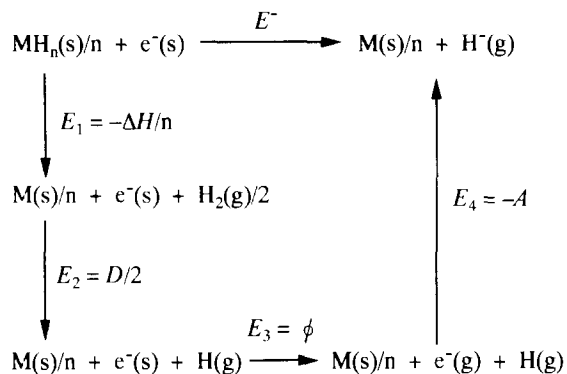


Fig. 7. Energy cycle for evaluating the desorption energy (E^-) of H^- from heated saline hydride (MH_n).

quite different among the three samples. The difference ($E^- - \phi$) determined experimentally with each MH_n , however, is in good agreement with that derived theoretically from our cycle. This fact indicates that (1) our experimental method is free from systematic errors, (2) our theoretical model on the desorption is reasonable from the viewpoint of surface chemistry, and (3) our new data on E^- and ϕ are reliable, although good reproducibility has not yet been attained.

It is well known that ϕ is subject to change due to residual gas adsorption [14,15]. Nevertheless, our model holds, irrespective of such a change because E^- also changes according as $E^- - \phi = \text{constant}$ in the temperature range employed for repeated runs.

4. Conclusions

The experimental data and analytical results described in this work lead to the following conclusions:

1. In the order of LiH , CaH_2 and SrH_2 , E^- and ϕ increase from ca. 540 to 940 kJ mol^{-1} and from ca. 320 to 700 kJ mol^{-1} , respectively.
2. The difference ($E^- - \phi$), on the other hand, is virtually independent of sample species, nearly constant at ca. 230 kJ mol^{-1} , which is in good agreement with that (ca. 226 kJ mol^{-1}) derived theoretically from our simple model based on chemical thermodynamics.
3. The desorption of H^- from MH_n is governed mainly by the four factors of ΔH , D , A and ϕ in addition to T , and the desorption current of H^- is

generally expressed by

$$i^- = C \exp[(\Delta H/n - D/2 - \phi + A)/RT] \quad (2)$$

where C is a constant independent of T .

Further work, however, is necessary to clarify the relation between ϕ and the chemical composition of the sample surface (active sites) during runs and also to theoretically derive the pre-exponential factor corresponding to C in Eq. (2).

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 08555077) from the Ministry of Education, Science and Culture.

References

- [1] W.M. Mueller, J.P. Blackledge and G.G. Libowitz, *Metal Hydrides*, Academic Press, New York, 1968.
- [2] H. Kawano, Y. Ashida, H. Nagayasu and N. Serizawa, *Proceedings of the Third Workshop on Negative Ion Formation and Beam Handling*, KEK, Tsukuba, Aug. 1993, p.113 [Chem. Abstr., 121 (1994) 219264q].
- [3] H. Kawano and F.M. Page, *Int. J. Mass Spectrom. Ion Phys.*, 50 (1983) 1.
- [4] H. Kawano, Y. Ashida, H. Nagayasu, N. Serizawa and H. Ohta, *Proceedings of the Symposium on Negative Ion Sources and their Applications*, NIFS, Toki, Dec. 1994, p.89.
- [5] H. Kawano, N. Serizawa and M. Takeda, *Appl. Phys. Lett.*, 6 (1995) 3904.
- [6] H. Kawano, H. Nagayasu, N. Serizawa, H. Ohta, M. Takeda, M. Wada and M. Sasao, *Rev. Sci. Instrum.*, 67 (1996) 1190.
- [7] H. Kawano, *Int. J. Mass Spectrom. Ion Processes*, 104 (1991) 23.
- [8] H. Kawano, Y. Ashida, H. Nagayasu, M. Wada, M. Sasao and K. Miyake, *Rev. Sci. Instrum.*, 65 (1994) 1227.
- [9] M. Wada, H. Kawano and M. Sasao, *Rev. Sci. Instrum.*, 67 (1996) 1233.
- [10] H. Kawano, *J. Chem. Phys.*, 78 (1983) 7012.
- [11] H. Kawano, T. Kenpō and Y. Hidaka, *Int. J. Mass Spectrom. Ion Processes*, 67 (1985) 331.
- [12] I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim, 1989.
- [13] D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, NBS, 2nd edn., Washington, 1971.
- [14] H. Kawano, K. Ohgami, K. Funato and J. Nakamura, *Vacuum*, 46 (1995) 1139.
- [15] H. Kawano, K. Ohgami, K. Funato and J. Nakamura, *Vacuum*, 46 (1995) 1145.