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Title	STATES OF HYDROGEN CHEMISORBED ON ZINC OXIDE AT LOW TEMPERATURE
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 26(2), 63-78
Issue Date	1978-10
Doc URL	<a href="https://hdl.handle.net/2115/25044">https://hdl.handle.net/2115/25044</a>
Type	departmental bulletin paper
File Information	26(2)_P63-78.pdf



## STATES OF HYDROGEN CHEMISORBED ON ZINC OXIDE AT LOW TEMPERATURE

By

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(Received March 14, 1978; in revised form September 5, 1978)

### Abstract

Rates of adsorption and desorption of hydrogen and deuterium were measured on zinc oxide below room temperature. Three states, I, O and L, of chemisorbed hydrogen were found at  $-195^{\circ}\text{C}$ . The activation energy of adsorption was nearly zero and kinetic isotope effect was absent for adsorption from  $22^{\circ}\text{C}$  to  $-195^{\circ}\text{C}$ , while a large isotopic shift of peaks was observed in the thermal desorption spectra at low temperature. The three states of hydrogen are concluded to be formed on Zn-O pair sites and to be distinguished by different extents of interaction with hydroxyl groups on ZnO surface. The fact that the peak temperature of state O hydrogen shifts to a higher temperature in the thermal desorption, when the adsorption temperature is changed from  $-78^{\circ}\text{C}$  to  $-195^{\circ}\text{C}$ , is explained in terms of a transition of state O hydrogen formed at  $-78^{\circ}\text{C}$  into state L and a modified state O hydrogen. Thermal desorption spectra of  $\text{H}_2$  and  $\text{D}_2$  are analyzed by Redhead's method, resulting in 19, 15 and 11 Kcal/mol of activation energies of desorption or the heats of adsorption of states I, O and L hydrogen, respectively. The activation energies for deuterium are higher by about 0.5 Kcal/mol than those mentioned above.

### Introduction

Baranski and Galuszka<sup>1)</sup> have found recently a new chemisorbed state of hydrogen on ZnO by means of thermal desorption below  $0^{\circ}\text{C}$ , and named it as state O hydrogen, as its peak in thermal desorption spectra appeared at lower temperature side of the so-called state I hydrogen peak. However, hydrogens of states I and O were not distinguished by IR measurement by Kokes *et al.*<sup>2)</sup> State I hydrogen has been investigated by many researchers<sup>1-6)</sup> and found to be active for IR absorption, for hydrogenation of ethylene and to show large kinetic and thermodynamic isotopic effects on adsorption below room temperature. In the present paper, the kinetic behavior of hydrogen on ZnO was investigated in detail below room temperature with special reference to isotopic effects on rates of adsorption and desorption of state O hydrogen.

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### Experiment

Kadox 25 (New Jersey Co.) was used as a ZnO sample and applied the same thermal treatment as done by Dent and Kokes,<sup>4</sup> that is, Kadox 25 was evacuated at 400°C for 3 to 4 hr. after a pre-evacuation at 150°C for 2 hr. In a case where the amount of adsorbed hydrogen or deuterium decreased, the sample was heated in oxygen at 400°C. The vacuum system is of a usual type made of Pyrex glass as schematically shown in Fig. 1 and able to be evacuated to  $5 \times 10^{-7}$  Torr. Hydrogen or deuterium gas of 99.5% purity ( $N_2 < 0.01\%$ ,  $H_2 < 0.40\%$ ) was purified by passing it through a Pd-Ag thimble. Helium or oxygen gas with nominal purity of 99.999% or 99.95%, respectively, was used after being passed through a liquid nitrogen trap.

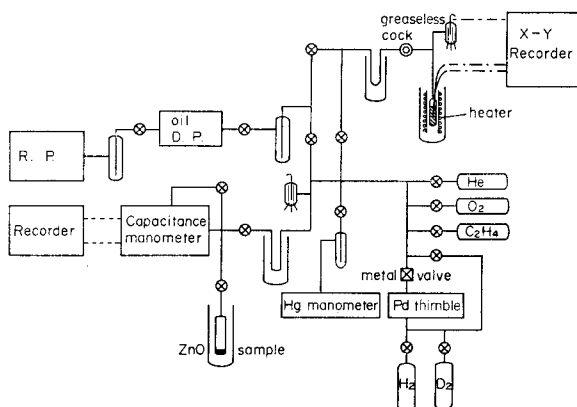
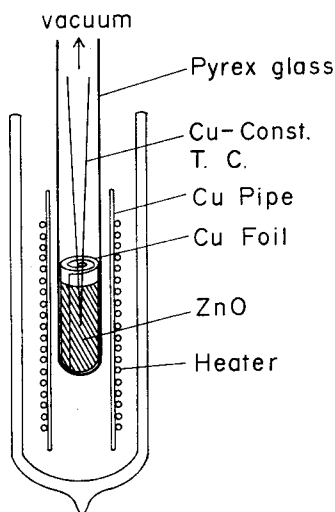


Fig. 1. Vacuum system used for measurements of the rate and amount of adsorption of  $H_2$  and  $D_2$ , and the thermal desorption.

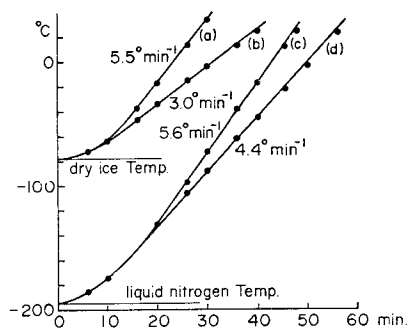
Rates of adsorption and amounts of adsorbed hydrogen or deuterium were measured by observation of pressure with a capacitance manometer (Granville Phillips). The adsorbent without being pressed was placed in the bottom of a catalyst vessel of 30 mm diameter. Prudent treatments of ZnO sample were required for measurements of adsorption rate on account of its powdered form and poor thermal conductivity. Observed adsorption rates depended upon an amount of Kadox-25 used and procedure of its cooling before measurements. To observe fast and reproducible adsorption rates, the adsorbent must be of less than 4 g and cooled in helium gas.

The thermal desorption spectra were obtained by the use of a B-A gauge and a cell shown in Fig. 2 especially devised with respect to the poor thermal conductivity of the adsorbent. The adsorbent of 0.35 g rolled with

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**Fig. 2.** Cell of the thermal desorption measurement.



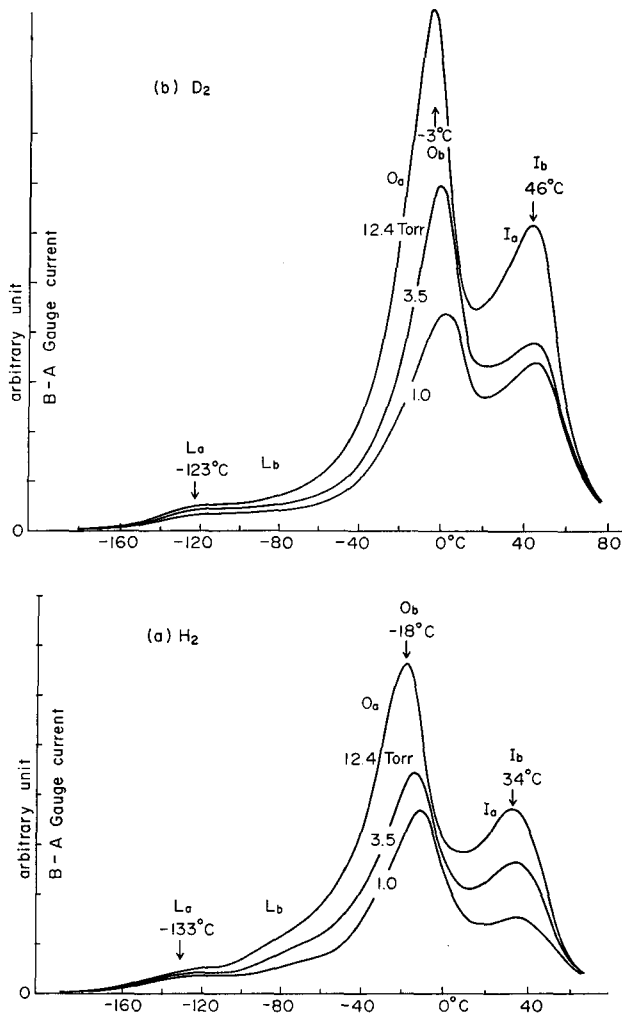
**Fig. 3.** The temperature-time relation in the thermal desorption measurement.

a Cu foil was set in a Pyrex glass tube of 0.8 cm diameter and a Cu-Const. thermocouple (Cu wire: 0.1 mm; Const. wire: 0.2 mm in diameter) was attached to the Cu foil. A desorption peak temperature observed with a Cu foil rolled three fold was higher by  $8^\circ$  than that observed with a foil rolled eight to ten fold. A Cu foil rolled ten fold was used for the thermal desorption measurements. The sweep of temperature was started with replacement of the Dewar vessel containing cryogen to an empty one. The rate of temperature rise was changed from  $3^\circ/\text{min.}$  to  $6^\circ/\text{min.}$ ; linear rise of temperature was secured except the initial stage as shown in Fig. 3. The slow rate of temperature change at the initial stage arises from the large heat capacities of the cell and Cu pipe of heater. Peaks of desorption spectra were scarcely affected by the present sweep rates: a peak temperature in the case (b) of Fig. 3 is lower by  $1.5^\circ$  than that in the case (a), which was comparable with the experimental error caused by the use of different cells. Peak temperatures of hydrogen desorption agreed with those observed by Baranski *et al.*, who have used a gas chromatographic method with temperature controlled carrier gases. The pressure at a peak of desorption spectrum was of an order of  $10^{-4}$  Torr, while the back ground pressure was  $2 \times 10^{-6}$  Torr.

### Experimental Results

Figure 4 shows the thermal desorption spectra of  $\text{H}_2$  and  $\text{D}_2$  adsorbed at  $T_a = 22^\circ\text{C}$  and evacuated at  $T_e = -195^\circ\text{C}$ . Results with another cell and  $T_a = T_e = -195^\circ\text{C}$  are shown in Fig. 5. Comparing the results of Figs. 4(a)

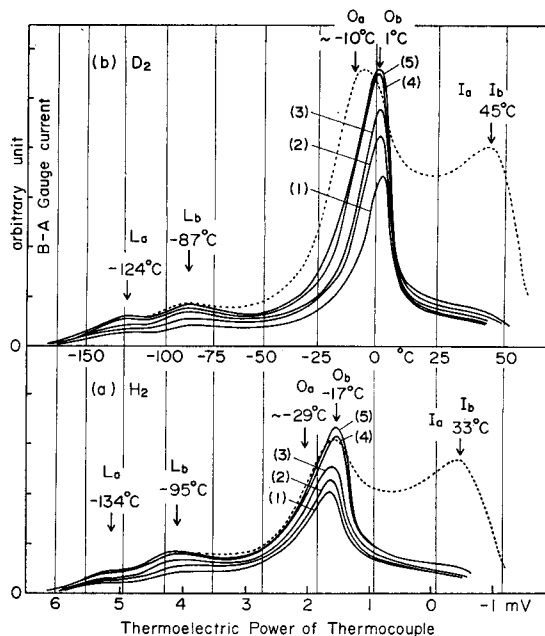
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**Fig. 4.** Thermal desorption spectra of H<sub>2</sub> (a) and D<sub>2</sub> (b) with  $T_a=22^\circ\text{C}$  and  $T_e=-195^\circ\text{C}$ . The ZnO is exposed to H<sub>2</sub> or D<sub>2</sub> gas at  $T_a=22^\circ\text{C}$  for 10 min. and evacuated at  $T_e=-195^\circ\text{C}$  for 5 min.

and 5 (a) for H<sub>2</sub> with those of Baranski *et al.*, we identified the peak around room temperature and the large peak at the peak temperature of  $T_p = -17^\circ\text{C}$  to state I and state O hydrogen, respectively. In Fig. 5, the amount of state I hydrogen with  $T_a = T_e = -195^\circ\text{C}$  is so small that the spectra are lack of the corresponding peak. Newly observed peaks at  $T_p = -95$  and  $-134^\circ\text{C}$  are named as L<sub>a</sub> and L<sub>b</sub>, respectively. Figure 6 shows spectra with  $T_a =$

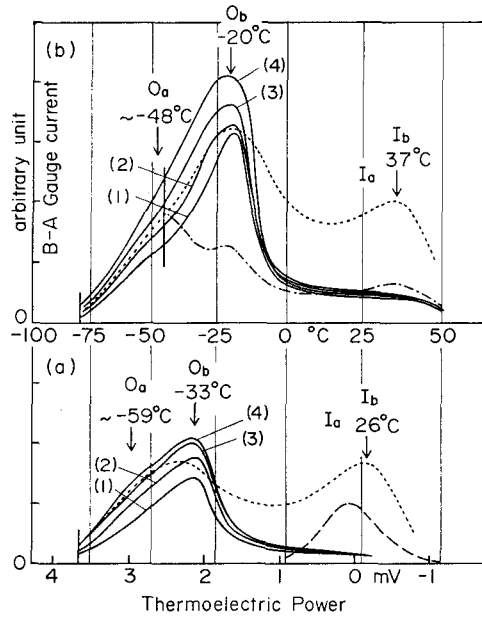
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**Fig. 5.** Thermal desorption spectra of  $\text{H}_2$  (a) and  $\text{D}_2$  (b). The ZnO is exposed to  $\text{H}_2$  or  $\text{D}_2$  gas at  $T_a = -195^\circ\text{C}$  for 10 min. and evacuated at  $T_e = -195^\circ\text{C}$  for 5 min. Gas pressures introduced are: (1) 0.8 Torr, (2) 2.6 Torr, (3) 4.4 Torr, (4) 8.1 Torr, (5) 12.0 Torr. Dotted curves (.....) show the spectra with  $T_a = 22^\circ\text{C}$  and  $T_e = -195^\circ\text{C}$  for gas pressure  $p = 9.1$  Torr.

$T_e = -78^\circ\text{C}$  and those with  $T_a = 22^\circ\text{C}$  and  $T_e = -78^\circ\text{C}$  and  $T_a = T_e = -45^\circ\text{C}$ , and furthermore, a spectrum of water desorbed from the same adsorbent with  $T_a = T_e = 0^\circ\text{C}$ . The broken curve in Fig. 6(a) illustrates a quite symmetric spectrum obtained by the present method for physisorbed water. Peaks of state O hydrogen in Figs. 4, 5 and 6, on the other hand, are asymmetric, indicating that this peak consists of, at least, two sub-states,  $O_a$  and  $O_b$ , which are obvious as given by dotted curve in Fig. 5(b) and dot-dash curve in Fig. 6(b), where amount of  $O_a$  is comparable with that of  $O_b$ . Baranski *et al.* have also found for states I and O two sub-states,  $I_a$ ,  $I_b$  and  $O_a$ ,  $O_b$ , respectively. State O hydrogen is a main species in a case of  $T_a$  below  $-78^\circ\text{C}$ . Peak height of state I hydrogen was not changed during evacuation period of 5 to 30 min, at  $T_e = -78^\circ\text{C}$  or  $-195^\circ\text{C}$ . This indicates that state I hydrogen is stable. Peak temperatures and areas in desorption spectra of  $\text{D}_2$  were higher than those of  $\text{H}_2$ . As shown in Table I, the isotopic shifts

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**Fig. 6.** Thermal desorption spectra of H<sub>2</sub> (a) and D<sub>2</sub> (b) with  $T_a = T_e = -78^\circ\text{C}$  (solid curves, (—)),  $T_a = 22^\circ\text{C}$  and  $T_e = -78^\circ\text{C}$  (dotted curves (.....)) for  $p = 8.1$  Torr and  $T_a = T_e = -45^\circ\text{C}$  (dot-dash curve (-·-·-)) for  $p = 8.1$  Torr. (1) 1.7 Torr, (2) 4.4 Torr, (3) 8.1 Torr, (4) 12.0 Torr. A desorption spectrum of weakly adsorbed water with  $T_a = T_e = 0^\circ\text{C}$  and  $p = 4.1$  Torr is given by broken curve (-·-·-).

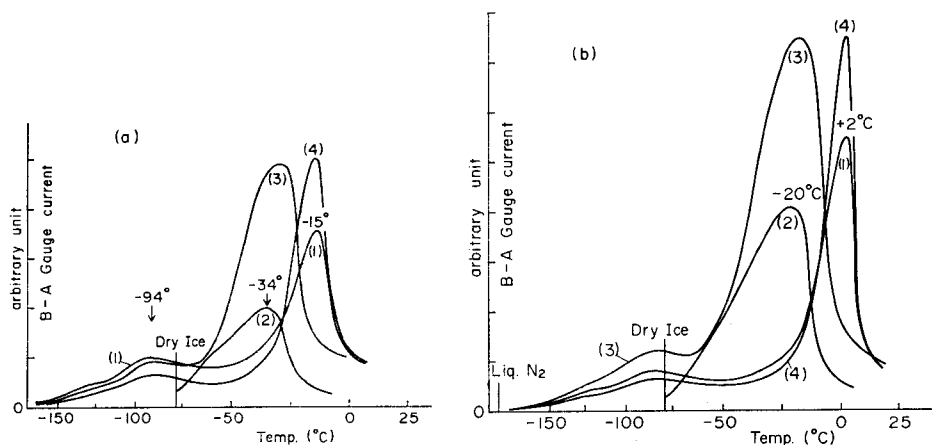
**TABLE I** Peak temperature  $T_p$  of the thermal desorption spectra of H<sub>2</sub> and D<sub>2</sub>.  $T_p$ 's of I<sub>a</sub> peak can not be determined in the present experiment, and those of O<sub>a</sub> are roughly determined.  $T_a$ : adsorption temperature,  $T_e$ : evacuation temperature.

$T_a$ (°C)	$T_e$ (°C)	state I, $T_p$ (°C)			state O, $T_p$ (°C)					state L, $T_p$ (°C)						
		H <sub>2</sub>		isotopic shift I <sub>b</sub>	H <sub>2</sub>		D <sub>2</sub>		isotopic shift O <sub>a</sub> O <sub>b</sub>	H <sub>2</sub>		D <sub>2</sub>		isotopic shift L <sub>a</sub> L <sub>b</sub>		
		I <sub>b</sub>	I <sub>b</sub>		O <sub>a</sub>	O <sub>b</sub>	O <sub>a</sub>	O <sub>b</sub>		L <sub>a</sub>	L <sub>b</sub>	L <sub>a</sub>	L <sub>b</sub>			
22	-78	26	37	11	~-59	-33	~-48	-20	~-11	13						
22	-195	33	45	12	~-29	-17	~-10	+1	~-19	18	-134	-95	-124	-87	10	8
-78	-78				~-59	-33	~-48	-20	~-11	13						
-195	-195				~-29	-17	~-10	+1	~-19	18	-134	-95	-124	-87	10	8

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of  $T_p$  were  $9^\circ$  for state L,  $11^\circ$  for state I, and  $13^\circ$  or  $18^\circ$  for state O with  $T_a = -78^\circ$  or  $-195^\circ\text{C}$ , respectively.

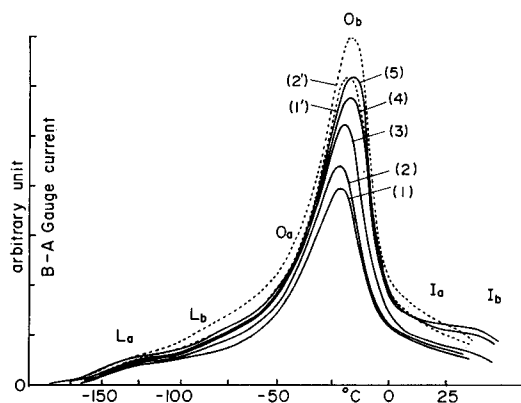
Peak temperature  $T_p = -17^\circ\text{C}$  of state  $O_b$  hydrogen observed with  $T_a = T_e = -195^\circ\text{C}$  (Fig. 5(a)) shifted to  $-33^\circ\text{C}$  in a case of  $T_a = T_e = -78^\circ\text{C}$  (Fig. 6(a)); a similar shift of state  $O_b$  deuterium from  $1^\circ$  to  $-20^\circ\text{C}$  was observed (Figs. 5(b) and 6(b)). These shifts of  $T_p$  are summarized in Table I. In order to elucidate these shifts, experiments shown in Figs. 7(a) and 7(b) were carried out. Curves (1) and (2) are references obtained with  $T_a = T_e = -195^\circ\text{C}$  and  $T_a = T_e = -78^\circ\text{C}$ , respectively. In the case of curve (3), adsorbent was brought into contact with  $\text{H}_2$  at  $T_a = -78^\circ\text{C}$  for 19 min., evacuated for 3 min. and then cooled down to  $-195^\circ\text{C}$  in contact with He gas and thermal desorption was applied after evacuation for 5 min. Curve (4) was obtained by the same process carried out more deliberately, *i. e.*, after adsorption of  $\text{H}_2$  at  $-78^\circ\text{C}$ , the sample was evacuated for 30 min., cooled down to  $-195^\circ\text{C}$ , evacuated again for 20 min. and then thermal desorption was applied. Peak temperature of  $O_b$  hydrogen in curve (3) is in the middle of those of curves (1) and (2), while the peak in curve (4) agreed with that in curve (1). This fact shows that a slow transition of the state of O hydrogen formed with  $T_a = T_e = -78^\circ\text{C}$  took place at  $-195^\circ\text{C}$  and completed during the evacuation for 20 min. at  $T_e = -195^\circ\text{C}$ . A similar transition was observed with  $\text{D}_2$  as seen in Fig. 7(b). Such shifts of  $T_p$  were not observed for a change of  $T_a (= T_e)$  from  $-183^\circ\text{C}$  to  $-195^\circ\text{C}$  or from  $-45^\circ\text{C}$  to  $-78^\circ\text{C}$ , respectively



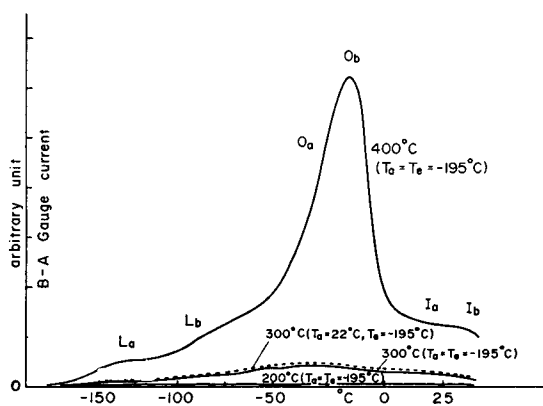
**Fig. 7.** Transitions of state O peaks of  $\text{H}_2$  (a) and  $\text{D}_2$  (b). (1)  $T_a = T_e = -195^\circ\text{C}$ , (2)  $T_a = T_e = -78^\circ\text{C}$ , (3)  $T_a = T_e = -78^\circ\text{C}$ , cooled down to  $-195^\circ\text{C}$  and evacuated at  $T_e = -195^\circ\text{C}$  for 5 min., (4)  $T_a = T_e = -78^\circ\text{C}$  cooled down to  $-195^\circ\text{C}$  and evacuated at  $T_e = -195^\circ\text{C}$  for 20 min.

(Figs. 8 or 6 (b)), that is, the transition takes place at a temperature between  $-78^{\circ}\text{C}$  and  $-183^{\circ}\text{C}$ . We see, furthermore, in Fig. 7 that a part of state O hydrogen can easily transit into state L.

The dependence of amounts of state I, O and L hydrogens on the degree of dehydration of adsorbent in its preparation process was investigated by thermal desorption of  $\text{H}_2$  (Fig. 9). It was found that adsorption sites for hydrogen of every state, I, O and L, was formed simultaneously by evacuation of the adsorbent above  $300^{\circ}\text{C}$ . Water was desorbed continuously during evacu-



**Fig. 8.** Thermal desorption spectra of  $\text{H}_2$  at  $T_a = T_e = -195^{\circ}\text{C}$  (solid curves) and  $T_a = T_e = -183^{\circ}\text{C}$  (dotted curves). (1) 1.7 Torr, (2) 2.5 Torr, (3) 4.4 Torr, (4) 8.1 Torr, (5) 12.4 Torr, (1') 4.4 Torr, (2') 8.1 Torr.



**Fig. 9.** Thermal desorption of  $\text{H}_2$  at various stages of the thermal treatment of the ZnO. The adsorbent is kept at a given temperature for 90 min. The pressure of introduced  $\text{H}_2$  is 12.0 Torr.

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TABLE II Adsorbed amounts of  $H_2$  and  $D_2$  on ZnO measured by the volumetric method. The unit  $10^{18}$  molecules/g is equal to  $1.04 \times 10^{13}$  molecules/cm<sup>2</sup>. The values in the last line are the adsorbed amounts realized under the condition of thermal desorption with  $T_a = 22^\circ C$  and  $T_e = -195^\circ C$ , which are determined from peak heights of the thermal desorption and the adsorbed amounts given in this table. The values in the bracket are the items for the three species.

$H_2$ ( $10^{18} \frac{\text{molecules}}{\text{g}}$ )	$D_2$ ( $10^{18} \frac{\text{molecules}}{\text{g}}$ )	adsorption temp. $T_a$ ( $^\circ C$ )	Pressure (Torr)
2.6	2.6	22	14
4.1	4.5	-78	12
5.5	6.2	-183	12
8.1	11.0	-195	12
8.4	8.9	22 (with $T_e = -195$ )	12
$\left( \begin{array}{l} N(I) = 2.6 \\ N(O) = 4.6 \\ N(L) = 1.2 \end{array} \right)$	$\left( \begin{array}{l} N(I) = 2.9 \\ N(O) = 5.1 \\ N(L) = 0.9 \end{array} \right)$		

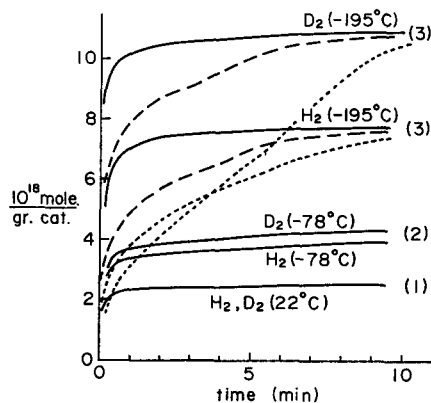


Fig. 10. The rates of adsorption of  $H_2$  and  $D_2$  at  $T_a = 22^\circ C$ ,  $-78^\circ C$  and  $-195^\circ C$ . The equilibrium pressure is about 6 Torr except dotted curves, where it is about 1 Torr. Solid curves (—) are obtained when the ZnO (3.5 g) is sufficiently cooled by He gas. Broken curves (---), when the ZnO (3.5 g) is cooled only by immersing it in liquid nitrogen for 60 min. Dotted curves (.....), when the ZnO (14.0 g) is cooled only by immersing it in liquid nitrogen for 60 min.

ation of adsorbent from 80°C to 400°C and predominantly above 300°C. The desorbed water condensed in a dry ice trap amounted to  $14 \times 10^{18}$  molecules/g, which exceeded the total amount of state I, O and L hydrogens as shown in Table II.

Figure 10 shows that the rates of adsorption of  $H_2$  and  $D_2$  were nearly the same in a range of adsorption temperature from 22°C to -195°C, in spite of the significant difference of thermal desorption spectra between  $T_a = 22^\circ\text{C}$  and  $-195^\circ\text{C}$  as shown in Fig. 5. The initial rates were faster than those observed by Dent *et al.*<sup>4)</sup> and Naito *et al.*<sup>5)</sup> with pressed ZnO samples. Amounts of adsorbed  $H_2$  and  $D_2$  are summarized in Table II. As seen in Table II and Fig. 10, isotopic effects on adsorbed amount (thermal isotope effect: TIE) are obvious at low temperature, while isotopic effects on the rate of adsorption (kinetic isotope effect: KIE) are negligible even at  $-195^\circ\text{C}$ . On the other hand, Kokes *et al.* have observed large KIE at low temperature by means of IR. The present results given by dotted and broken lines in Fig. 10 show that in a case with large amount of adsorbent and, hence, with insufficient cooling, apparently large KIE are observed. The existence of a small KIE is made significant by plots in Fig. 11, where the time courses

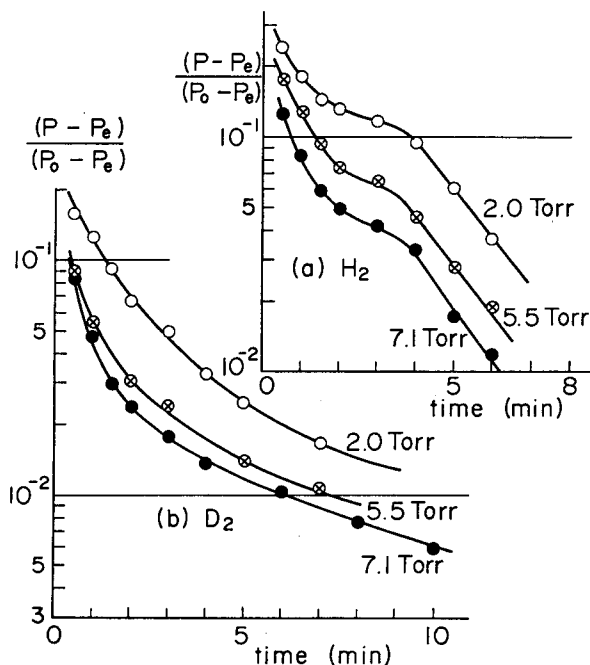
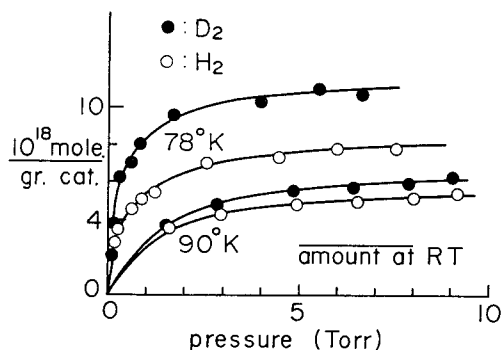


Fig. 11. The Langmuir plot for the rates of adsorption of  $H_2$  (a) and  $D_2$  (b) at  $T_a = -195^\circ\text{C}$ .

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of  $\ln(p-p_e/p_0-p_e)$  are plotted according to the Langmuir kinetics,  $\ln(p-p_e/p_0-p_e)=-kt$ , where  $p_0$  is the initial pressure and  $p_e$ , the equilibrium pressure.

Adsorption isotherms of  $H_2$  and  $D_2$  at  $-195^\circ\text{C}$  and  $-183^\circ\text{C}$  are shown in Fig. 12. The amount of  $D_2$  is larger than  $H_2$  by 38% or 17% at  $-195^\circ\text{C}$  or  $-183^\circ\text{C}$ , respectively.



**Fig. 12.** Adsorption isotherms of  $H_2$  and  $D_2$  at  $T_a = -195^\circ\text{C}$  and  $T_a = -183^\circ\text{C}$ . The unit  $10^{18}$  molecules/g is equal to  $1.04 \times 10^{13}$  molecules/cm<sup>2</sup>.

### Discussion

Thermal desorption from ionic crystals has not been widely attempted due to the difficulty of homogeneous rising of temperature of samples. The present method of experiment is a new attempt in this field, showing to be useful on account of its reasonable and reproducible results. The thermal desorption spectra show the presence of three states, I, O and L, of hydrogen chemisorbed on ZnO below room temperature; each state is composed of the two sub-states,  $I_a, I_b$ ;  $O_a, O_b$  and  $L_a, L_b$ . State I hydrogen is obvious with  $T_a = 22^\circ\text{C}$ , but little with  $T_a$  below  $-78^\circ\text{C}$  (Figs. 5 and 6); however, the activation energy of adsorption was absent irrespective of the states (Fig. 10). These facts suggest that hydrogen in states O and L prevents the formation of state I hydrogen at low temperatures; in addition, state I hydrogen seems not to transform to state O or L as the peak of thermal desorption was not changed by a prolonged evacuation below  $-78^\circ\text{C}$ .

The amount ratio  $N(I)/N(O)$  of state I to state O is approximated by the ratio of peak heights of  $I_b$  and  $O_b$  given in Fig. 4 and we have  $N(I)/N(O) = 0.56$  at 12 Torr of the initial pressure of hydrogen, where the adsorption was nearly saturated. We have similarly  $N(L)/N(O) = 0.25$  and 0.17

for hydrogen and deuterium, respectively, according to Fig. 5; thus,  $N(I) : N(O) : N(L) = 0.56 : 1.0 : 0.25$  or  $0.56 : 1.0 : 0.17$  for  $H_2$  or  $D_2$ , respectively, for the saturated adsorption at  $-195^\circ\text{C}$ . State I hydrogen and deuterium reversibly formed at  $22^\circ\text{C}$  was  $N(I) = 2.6 \times 10^{18}$  molecules/g as shown in Table II, which is conserved at  $T_a = -195^\circ\text{C}$ , though it increases a little. Referring to this value and a TIE given in Table II, that is, the ratio  $N(D_2)/N(H_2) = 1.1$  at  $-78^\circ$  and  $-183^\circ\text{C}$  (the ratio is 1.4 at  $-195^\circ\text{C}$ , which includes large numbers of physisorbed  $H_2$  and  $D_2$ ),<sup>7,8)</sup> we estimated the amounts of hydrogen and deuterium in the three states as given in Table II. The evaluated total amounts of  $H_2$  and  $D_2$  are comparable to that of water dehydrated from the adsorbent.

The adsorbent without pre-evacuation was inactive for hydrogen adsorption probably due to hydroxyl groups saturated its surface, and their small part, as high as 15%, is to be able to desorb by the pre-evacuation as estimated below. According to Dent and Kokes,<sup>4)</sup> the surface active for hydrogen adsorption is closed-packed (0001) surface, where the distance of O-O nearest neighbour is 3.3 Å and the area of a Zn-O pair is  $9.4 \text{ Å}^2$ . Approximating the surface area of a Zn-O pair as  $10 \text{ Å}^2$ , we have  $1.0 \times 10^{15}/\text{cm}^2$  as the density of Zn-O pair. Water evacuated from the catalyst with surface area of  $9.6 \text{ m}^2/\text{g}$  was  $1.5 \times 10^{14}$  molecules/ $\text{cm}^2$ , *i. e.*, 15% of Zn-O pairs. The large amount of hydroxyl groups not evacuated may give rise to some interactions with hydrogen adsorbed on bare Zn-O pairs.

Adsorption sites for state I hydrogen are established to be Zn-O pairs.<sup>2,3,4)</sup> Baranski *et al.*<sup>1)</sup> have attributed peaks  $I_a$  and  $I_b$  to Zn-H and O-H hydrogen, respectively, on the basis of the results of IR measurements. Infrared absorption bands of OH and ZnH appeared simultaneously, when ZnO was exposed to  $H_2$  gas. Adsorption potential for hydrogen atom of O-H is deeper and more steep ( $3487 \text{ cm}^{-1}$ ) than that of Zn-H ( $1705 \text{ cm}^{-1}$ ), so that hydrogen may desorb separately from O-H and Zn-H in thermal desorption. According to this point of view, equal amounts of hydrogen should come out from O-H and Zn-H, in conflict with the results shown in Figs. 4, 5 and 6, where amounts of  $I_b$  and  $O_b$  hydrogen are clearly more than  $I_a$  and  $O_a$ , respectively, and similarly  $N(L_b) > N(L_a)$ . This disagreement can be elucidated by a surface migration of the hydrogen on Zn sites onto more stable O sites, as suggested by Dent and Kokes for state I hydrogen at room temperature. Kokes *et al.*<sup>2)</sup> have observed IR spectra of stable Zn-H and O-H in the range of temperature from room one to  $-195^\circ\text{C}$ . However, the most of hydrogen adsorbed at  $T_a = T_e = -78^\circ\text{C}$  or  $-195^\circ\text{C}$  are in states O and L (Figs. 5 and 6). This fact suggests that states O and L hydrogen are also adsorbed on Zn-O pair sites.

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The present results on state I, O, and L hydrogens are summarized as follows. (1) Adsorption sites for the three states of hydrogen are simultaneously formed by evacuation of the adsorbent above 300°C; about 85% of the surface is still covered with OH groups. (2) The total number of adsorbed hydrogen is  $8.4 \times 10^{18}$  or  $8.9 \times 10^{18}$  molecules/g for H<sub>2</sub> and D<sub>2</sub>, respectively, while the number of bare Zn-O pair sites is  $14 \times 10^{18}$ /g, as estimated from the amount of desorbed water. (3) The rate of adsorption is almost the same at temperature ranged from room one to -195°C. (4) Isotopic shift of  $T_p$  of every peak in the desorption spectra is different, suggesting that every peak corresponds to different adsorbed state. (5) The adsorption sites for state O and L hydrogens are Zn-O pair sites as well as those of state I hydrogen and the three states may be distinguished by the extent of interaction with hydroxyl groups on the surface.

The activation heats of desorption or those of adsorption for every state of hydrogen were evaluated as follows. The rate of desorption is expressed according to the Redhead method<sup>9)</sup> as

$$-\frac{dn_d}{dt} = \nu_m n^m \exp(-E_d/kT), \quad (1)$$

where  $n$  is the number of adatoms per cm<sup>2</sup>,  $\nu_m$  the pre-exponential factor of rate constant in  $m$ th order desorption reaction, and  $E_d$  the activation energy of desorption, which is equal to the heat of adsorption of H<sub>2</sub> or D<sub>2</sub> on ZnO because of the absence of activation energy for adsorption. The order,  $m$ , of desorption was surmised from the dependence of  $T_p$  upon the coverage. The  $T_p$ 's shifted to higher with decrease of coverage in most of cases as seen in Figs. 4, 5(b) and 6, with only one exception as shown in Figs. 5(a) and 8 for hydrogen with  $T_a = T_e = -195^\circ\text{C}$ , where the  $T_p$ 's shifted slightly to lower temperature when the coverage decreased, which was possibly due to a large change in the amount ratio of O<sub>a</sub> to O<sub>b</sub>. The second order desorption ( $m=2$ ) can be concluded for the present results according to the Redhead method. Migration of adsorbed hydrogen is presumed in this kinetics. Applying a linear sweep of temperature with time, *i. e.*,  $T = T_0 + \beta t$ , to Eq. (1), we have

$$\frac{E_d}{kT_p^2} = \frac{n_0 \nu_2}{\beta} \exp\left(-\frac{E_d}{kT_p}\right), \quad (2)$$

where  $n_0$  is the initial coverage. This equation is numerically solved for  $E_d$ , as shown in Table III, using the values,  $\beta = 5.5^\circ \text{ min}^{-1}$ ,  $n_0 = 4 \times 10^{13}$  molecules/cm<sup>2</sup> and  $\nu_2 \sim 1 \times 10^{-2} \text{ cm}^2/\text{sec. molecule}$  or  $\nu_2 \sim 1/\sqrt{2} \times 10^{-2} \text{ cm}^2/\text{sec. molecule}$  for hydrogen or deuterium, respectively. The values of  $\nu_2$  are determined

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TABLE III Activation energies of desorption  $E_d$  calculated from Eq. (2) with use of  $T_p$  values in Table I

$T_a$ (°C)	$T_e$ (°C)	state I, (Kcal/mol)				state O, (Kcal/mol)				state L, (Kcal/mol)			
		H <sub>2</sub>		D <sub>2</sub>		H <sub>2</sub>		D <sub>2</sub>		H <sub>2</sub>		D <sub>2</sub>	
		I <sub>a</sub>	I <sub>b</sub>	I <sub>a</sub>	I <sub>b</sub>	O <sub>a</sub>	O <sub>b</sub>	O <sub>a</sub>	O <sub>b</sub>	L <sub>a</sub>	L <sub>b</sub>	L <sub>a</sub>	L <sub>b</sub>
22	-78	—	18.8	—	19.3	13.3	14.9	13.8	15.7	—	—	—	—
22	-195	—	19.2	—	19.7	15.2	16.0	16.3	16.9	8.5	11.0	9.2	11.4
-78	-78	—	—	—	—	13.3	14.9	13.8	15.7	—	—	—	—
-195	-195	—	—	—	—	15.2	16.0	16.3	16.9	8.5	11.0	9.2	11.4

from the hopping model of migrating atoms.<sup>10</sup> If a model of the two dimensional free gas is taken for migrating atoms,  $\nu_2$  is an order of  $10^{-3}\text{cm}^2/\text{sec}$ . molecule.<sup>10</sup> The numerical calculation shows that  $T_p$  is primarily affected by variation of  $E_d$  and less susceptible to variation of  $\nu_2/\beta$ , so that the mass difference (factor of  $1/\sqrt{2}$  in  $\nu_2$ ) and the difference in  $\nu_2$  for the two models of adatoms do not matter for the evaluation of  $E_d$ . The mass difference is only influential for the vibrational energy level in adsorbed states. Table III reveals such energy differences being about 0.5 Kcal/mol for states I and L, and state O with  $T_a = -78^\circ\text{C}$ , and about 1 Kcal/mol for state O with  $T_a = -195^\circ\text{C}$ , suggesting the adsorption potential at  $-195^\circ\text{C}$  is considerably different from the other states. In Table III,  $E_d$ 's are about 19, 15 and 11 Kcal/mol for hydrogen in states I, O and L, respectively, as compared with 20 Kcal/mol at desorption temperature around  $10^\circ\text{C}$ , 13 Kcal/mol around  $-38^\circ\text{C}$  and 10 Kcal/mol around  $-65^\circ\text{C}$  obtained by Kubokawa,<sup>11</sup> while Baranski *et al.* obtained 4.8 Kcal/mol, which has been estimated from the gradient of  $\ln(T_p^2/\beta)$  versus  $1/T_p$  plotted according to Eq. (2) with varying  $\beta$ . In this case one needs not assume  $\nu_2$  value. This value is, however, unreasonably as small as that of physically adsorbed hydrogen.

The remarkable shifts of  $T_p$  shown in Fig. 7 is now considered in detail. In the analysis of thermal desorption, it is generally presumed that a sample is always in thermal equilibrium at each temperature during the thermal desorption,<sup>12</sup> as seen in the usual analysis based on the Polanyi-Wigner theory. According to this presumption, the phenomenon shown in Figs. 5, 6 and 7 seems to suggest two equilibrium states for state O hydrogen (or deuterium), conflicting with the conclusion of thermodynamics. To interpret this curious phenomenon we assume that the state of hydrogen with  $T_a = -195^\circ\text{C}$  (we denote it as state O(LT)) differs from that with  $T_a = -78^\circ\text{C}$  (denoted as state O(HT)), and state O(HT) transits to state O(LT) and state L at the low temperature. A structure change of the adsorbate phase

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including surface hydroxyl groups but not of the adsorbent surface is probable, as ZnO is a very stable crystal. It is supposed that O (HT) formed at  $T_a = -78^\circ\text{C}$  is a state of adsorbed hydrogen being considerably mobile; with lowering temperature the migration in the state O (HT) becomes difficult resulting in a separation of this state into state L phase with a large amount of hydroxyls and state O (LT) phase with less hydroxyls, just like a phase separation of a binary alloy or compound. A surface migration of hydroxyl groups was confirmed by line widths of NMR measurement of proton in adsorbed hydrogen and OH groups on ZnO.<sup>19</sup> When the thermal desorption is started from  $-195^\circ\text{C}$ , state L hydrogen desorbs first, and consequently state O (LT) hydrogen can not transit to state O (HT), even though the temperature goes over the transition temperature. It is reasonable that state O (HT) with  $T_p = -33^\circ\text{C}$  is separated into more stable state O (LT) ( $T_p = -17^\circ\text{C}$ ) and less stable state L ( $T_p = -95^\circ\text{C}$ ). It should be noted that state I hydrogen and deuterium also show small shifts of  $T_p$ 's, as seen in Table I, when  $T_a$  is changed from  $-78^\circ\text{C}$  to  $-195^\circ\text{C}$ . These shifts may be caused by the phase transition of state O hydrogen. Baranski *et al.* demonstrate that  $T_p$ 's of states I and O hydrogen are sensitive to heat treatments of the adsorbent and conditions of thermal desorption, which implies that OH groups on the surface interact with adsorbed hydrogen resulting in shifts of the  $T_p$ 's.

### Conclusion

The three kinds of chemisorbed hydrogen, *i. e.*, states I, O and L are realized on zinc oxide below room temperature. Adsorption sites of states O and L are concluded to be Zn-O pair sites similar to those of state I hydrogen. They are tentatively distinguished by the extent of interaction with OH groups remaining on the surface: state I hydrogen is specified as the adsorbed state with almost no interaction with OH groups and poor surface migration below  $-78^\circ\text{C}$ , while state O is specified by presence of a strong interaction with OH groups and a frequent migration below room temperature. State O hydrogen at  $-78^\circ\text{C}$  is supposed to exist in a phase, which gives rise to the phase transition at the lower temperature in forming state L phase and a modified state O phase at  $-195^\circ\text{C}$ , in which OH concentration may be lower than that in state O at  $-78^\circ\text{C}$ . The absence of KIE in the adsorption process and the clear isotopic shifts of  $T_p$  in the thermal desorption are also emphasized among the present results.

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### Acknowledgements

The author wishes to express his sincere appreciation to Professor K. Miyahara for his valuable comments and critical reading of the present manuscript. He also thanks Mrs. R. Wake and Miss A. Hiratuka for helping preparation of the manuscript.

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