

## ISOTOPIC EXCHANGE OF DEUTERIUM WITH HYDROGEN OF SOME HYDRIDES

J. NOVÁKOVÁ, P. JÍRŮ and V. ZAVADIL

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

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Exchange of deuterium has been studied with commercial potassium and barium hydrides, hydrides of pure niobium and tantalum metals, yttrium hydride and with hydrides of rare earths metals. Non-stoichiometric composition of the hydrides made impossible a quantitative evaluation of the exchange mechanism. In most cases the ability to exchange deuterium with hydride hydrogen was found to be connected with the thermal stability of the hydrides.

In our previous communication<sup>1</sup> we have found that lattice hydrogen of some hydrides (Na, Ca, Zr) is exchanged with gaseous deuterium at relatively low temperatures. To determine the exchange mechanism relations were used, derived earlier for the exchange between gaseous oxygen isotope and the lattice oxygen of oxides<sup>2</sup>. Sodium hydride exchanged most of this hydrogen already at 100°C, the main part of the exchange being accomplished by mechanism R'', *i.e.*, by exchange of one deuterium molecule for two hydrogen atoms of the hydride in one step. With calcium hydride this type of exchange was not found which means that the exchange proceeded either by mechanism R' or was considerably affected by equilibration occurring in the gaseous phase. Mechanism R' denotes such type of exchange when one atom of the molecule of the gaseous phase is exchanged with one atom of the solid phase in one step (dissociative mechanism). The exchange between deuterium and calcium hydride proceeded at 300–400°C; at this temperature a considerable portion of the hydride hydrogen was already exchanged. With both the mentioned hydrides the exchange rate diminished in such a manner that could be explained by the effect of diffusion of the lattice hydrogen towards the hydride surface. Therefore we considered the possibility to apply the exchange of deuterium with hydride hydrogen for calculating the diffusion of the lattice hydrogen of hydrides. The exchange between deuterium and Zr hydride was considerably influenced by the non-stoichiometry of the sample: in the case that hydrogen was absorbed by the sample even during the exchange, a high exchange rate was observed already at 300°C. If the sample was saturated with hydrogen before the measurement, the exchange proceeded at a far lower rate. Exchange by mechanism R'' was not observed which might indicate that a sample saturated with hydrogen enhances its dissociation and consequently also its exchange. With Ti hydride, equilibration in the gaseous phase prevailed over the exchange with the hydride hydrogen.

To complement the study we have followed, in the present paper, the exchange with some further hydrides. Of the group of salt (ionic) hydrides we studied the exchange with K and Ba hydrides and of the group of metal hydrides those of Nb, Ta and Y. We further investigated the exchange of deuterium with hydrides of the rare

earths metals (Pr, Nd, Sm, Eu, Gd, Tm, and Lu). According to some authors<sup>3</sup>, the bond in bivalent hydrides is of metallic type while in the trivalent ones the bonds are rather of ionic character. The rare earths metal hydrides were chosen particularly with respect to their simple laboratory preparation.

### EXPERIMENTAL

Potassium hydride was supplied by the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences. The amount of hydrogen, found after decomposition of the sample in a closed vacuum apparatus, preceded by evacuation at room temperature, corresponded to the composition  $\text{KH}_{0.8}$ . Barium hydride (Schuchardt, München, GFR) had the declared content of 1.4% H (corresponds to  $\text{BaH}_2$ ); barium was of the purity 99%. Niobium and tantalum hydrides were prepared from sheets of metals of the purity 99.98% and 99.5, respectively. A ribbon, weighing about 0.1 g, was cut from the sheet of 0.05 mm thickness, spot-welded to molybdenum wire in the reaction vessel and heated in a vacuum of  $10^{-6}$  Torr to white glow for several hours in a previously evacuated and preheated apparatus. After heating of the metal ribbon the temperature was slowly lowered (within 2–3 days) and meanwhile hydrogen was led in to the pressure of several Torr. The pressure was measured by means of a McLeod manometer in a known volume (450  $\text{cm}^3$ ); the sample was protected by a freezing trap with liquid nitrogen. Metal stopcocks were used throughout.

Sorptions of hydrogen found under the above conditions were very small, corresponding to compositions  $\text{NbH}_{0.1}$  and  $\text{TaH}_{0.05-0.13}$ . After finishing the sorption the samples were sealed off under vacuum.

TABLE I

#### Conditions of Isotopic Exchange

$T_1$  Temperature at which the concentration of deuterium atoms decreased by more than 1%,  $T_2$  temperature of exchange measurements (decrease minimum 5%/h, equilibrated after 20 h), % of exchanged hydrogen atoms at  $T_2$  after 20 hours, – and + denote absence and presence of the mechanism  $R''$ , respectively,  $T_3$  temperature at which the equilibrium pressure over the metal attains  $10^{-4}$  Torr (see<sup>5</sup>).

Sample	$T_1$ , °C	$T_2$ , °C	%	$R''$	$T_3$ , °C
$\text{YH}_{1-2}$	380	800	16	–	1 157
$\text{PrH}_{1.7}$	280	600	100	–	1 150
$\text{NdH}_{1.5}$	240	520	80	–	1 062
$\text{SmH}_{1.3-2.1}$	60	120	100	+	573
$\text{EuH}_{1.2-1.5}$	200	600	100	–	480
$\text{GdH}_{1.5}$	150	240	100	+	1 175
$\text{TbH}_{1-2}$	400	500	60	–	1 150
$\text{TmH}_{1.1}$	100	200	22	+	680
$\text{LuH}_2$	200	500	6	–	950

Samples of the rare earths metals and of yttrium (Technasnabexport, Moscow, USSR) were of the following declared purities: Y 93.8%, Pr 96.25%, Nd 97.25%, Sm 95%, Eu 94.35%, Gd 95.8%, Tm 96.59%, Lu 96.51%. Purity of Tb was not given. Pieces of metals, weighing 0.03–0.1 g, were purified mechanically; metallic Eu and Pr were heated in vacuum in a quartz vessel to 800–1000°C, the remaining metals were heated in a tungsten coil sealed into the reaction vessel. Metallic Tb, Lu, Y and Nd were heated to white glow; Sm, Gd and Tm to dark red glow only, because they began to evaporate and form films on the walls of the vessel. After both the samples and the apparatus had been heated for two days, hydrogen was slowly led in within a few days at gradually decreasing temperature and the samples were evacuated, mostly at room temperature, to  $10^{-6}$  Torr for several hours. Then the samples were sealed off. Compositions of the obtained hydrides are summarized in Table I.

Hydrogen and deuterium were prepared by decomposing water with sodium in a vacuum apparatus and were filled into reservoirs through palladium tubes. Deuterium containers of the volume 500 cm<sup>3</sup> and 1 Torr pressure were used for studying the exchange.

The exchange of gaseous deuterium with hydride hydrogen was continuously followed by means of a mass spectrometer MCH 1302 (USSR). The deuterium reservoir was connected to the leak of the mass spectrometer by means of a breakable seal. The pressure of the gaseous mixture did not change during sampling into the mass spectrometer.

## RESULTS

Potassium hydride, after evacuation at room temperature, exchanged its hydrogen very slowly. Heating was accompanied, besides exchange, also by a considerable release of hydrogen from the hydride. Reproducible results were obtained with potassium hydride heated in vacuum at 100°C (Fig. 1); under these conditions the pressure of the reaction mixture remained practically unchanged. Minimum on curve 3 in Fig. 1 proves that at least a part of the exchange proceeds *via* mechanism R". The exchange rate was not of the first order (Fig. 1, curve 3), probably because of the effect of diffusion. Using the relation of Klier and Kučera<sup>4</sup> the value of the diffusion coefficient of lattice hydrogen at 100°C was calculated to be  $D/R^2 = 3.5 \cdot 10^{-5} \text{ m}^{-2}$ ; here  $R$  is the particle radius. Under the mentioned conditions practically all potassium hydride hydrogen participates in the isotopic exchange.

With barium hydride deuterium exchange proceeds even at room temperature with a sample, previously evacuated at the same temperature. With increasing temperature also the hydride hydrogen is released in addition to the exchange reaction. At 200°C almost all atoms of the hydride hydrogen are exchanged. Mechanism R" was not found.

Under the conditions given in Experimental both hydrides of Nb and Ta could be prepared only in a very low H : Me ratio, actually it is rather a solution of hydrogen in the respective metal. In spite of this, the exchange did proceed, namely with niobium hydride at 400°C (above 500°C hydrogen was released) and with tantalum hydride at 500–550°C; in the latter case 25% of the total content of hydride hydrogen was exchanged after 60 hours. In neither of these cases the mechanism R" was observed.

Hydrides of the rare earths metals and yttrium hydride of definite stoichiometric compositions could not be prepared. Hydrogenation under the conditions, described in Experimental, yielded hydrides of the composition about  $\text{MeH}_{1.5}$  (Table I). The exchanges were performed in such a way that the composition of the gaseous phase of the first sample was followed analytically in dependence on the increasing temperature. The values  $T_1$  and  $T_2$  (see Table I) give a rough picture of the exchange ability of the hydrides. Precise measurements could not be carried out because of the insufficient amount of the samples. The behaviour of Y, Pr, Nd, Tb and Lu hydrides in the exchange with deuterium was similar. A small portion of deuterium was exchanged at lower temperatures, 200–300°C, the main part above 500°C where still no decomposition of hydrides took place. Eu hydride differed slightly in its exchange ability; a part of hydrogen was exchanged practically to equilibrium at relatively low temperatures: at 200°C 1% of the lattice hydrogen, at 400°C 11% was exchanged and at 600°C the exchange was practically complete (Fig. 2). With none of these hydrides the R" mechanism was found. The properties of Sm, Gd and Tm hydrides were different from the above mentioned. First of all, the metals evaporated at low temperatures, so that the hydrides could be prepared in the form of evaporated films. However, these did not differ as to their exchange ability from powder hydrides, prepared from metals heated to lower temperatures. Lower evaporation temperature of Sm and Tm is in accordance with the tabellated data<sup>5</sup>. Exchange tem-

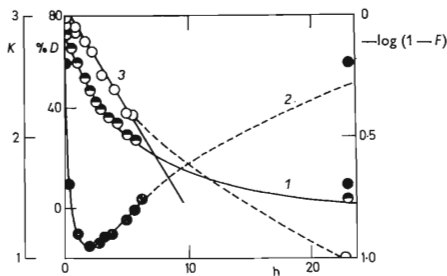


FIG. 1

Time Course of the Exchange between Deuterium and Potassium Hydride at 100°C

1 Atomic Concentration of deuterium in the gaseous phase, 2 ratio  $K = [\text{HD}]^2 : [\text{H}_2][\text{D}_2]$ , expressing the deviation from equilibrium in the gaseous phase, 3  $F$  degree of exchange, expressed as  $c_0 - c/c_\infty - 0.2$  (concentration of atomic deuterium in the gaseous phase:  $c_0$  initial,  $c$  in time  $t$ ,  $c_\infty$  equilibrium, 0.2 natural deuterium concentration).

peratures of these three hydrides are surprisingly low and with all of them the presence of R'' mechanism was observed.

## DISCUSSION

Isotopic exchange of the gaseous phase with the respective isotope in the solid phase involves adsorption, the exchange itself with the dissociation of gas molecules (dissociation affects the exchange rate only if mechanism R or R' is operative) and desorption of the exchanged gas. Applicability of the isotopic exchange to the calculation of the diffusion coefficient of the lattice isotope is limited to those cases when all the above mentioned processes are faster than the diffusion itself. A commonly used criterion of the effect of diffusion on the exchange rate is the deviation from the 1st order of the reaction (related to atomic concentration of the isotope). Since in most of the hydrides studied the pressure was not quite constant during the measurement, the deviations from the 1st order could not be unambiguously assigned to diffusion and thus the diffusion coefficient could not be evaluated. Only with Na, Ca and K hydrides the decrease of exchange rate was attributed to diffusion. The calculated value of the diffusion coefficient of potassium hydride at 100°C was twice as great as with sodium hydride, assuming the same size of particles in both cases.

In view of the non-stoichiometry of the samples different kinds of exchange mecha-

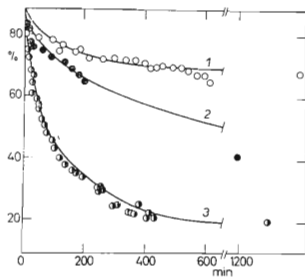


FIG. 2

Time Course of Deuterium Atomic Concentration in the Exchange With Europium Hydride

1 200°C, 2 400°C, 3 600°C.

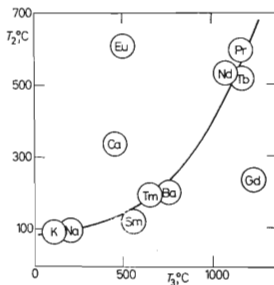


FIG. 3

Dependence of the Exchange Temperature  $T_2$  on the Temperature of Vacuum Evaporation of the Respective Metal,  $T_3$

nism could not be calculated, either. It can be stated qualitatively that in most hydrides the exchange proceeded as a dissociation process. Only with Na, K, Sm, Gd, and Tm the effect of R" mechanism could be detected which in the first two of them prevailed over the R' mechanism.

A conceivable dependence of the lattice oxygen on the strength of the oxide lattice was found in the case of oxides. Winter found<sup>8</sup> that within the same crystallographic structure the ability to exchange increases with increasing dimensions of the oxide lattice. A fair correlation was obtained between the higher exchange ability and the lower melting point of the oxides<sup>7</sup>. Mechanism R" was established particularly with oxides whose metallic cations were inclined to valence changes.

Correlation of the ability of hydrides to exchange hydrogen with their melting points could not be carried out, as most of them dissociated at temperatures lower than are their melting points. Therefore the values of the dissociation pressures of hydrides were calculated for the temperatures of the exchange measurements. These values range between  $10^{-2}$ – $10^{-5}$  Torr where also the exchange of oxygen with oxides takes place. The exchange of hydride hydrogens is consequently connected with their thermal stability. Thermal stability of the hydrides of rare earths metals increases with increasing atomic number<sup>3</sup>. However, the dissociation pressures<sup>3</sup> of Sm, Tm and Gd hydrides would reach, at the temperatures of exchange, values lower than  $10^{-10}$  Torr. We have therefore tried to find out whether the physical properties of these three metals did not show any anomalies. First ionization potentials<sup>8</sup>, electronic structures and radii of the respective metal cations change monotonously<sup>3</sup>, the crystallic structure of the hydrides of rare earths metals is planar cubic centered with bivalent hydrides (except for Eu and Y, see<sup>3</sup>), densities and melting points increase monotonously with atomic number<sup>9</sup>. The only deviation are the low evaporation heats of Sm and Tm (see<sup>5</sup>). According to our results also Gd evaporates at relatively low temperatures. The dependence of the evaporation temperatures of metals on the temperature of exchange, complemented by previous results (see Fig. 3) is satisfactory with the exception of Gd, Eu and Ca. The deviation of Gd might be eliminated by a correction for the different evaporation temperature as compared with paper<sup>5</sup>. On the other hand it cannot be excluded that the lowering of the evaporation temperature of the Gd sample used in our experiments might be caused by admixtures, especially Cu, Fe, Ca or by traces of Y, Tb and Sm. Eu and Ca differ in their crystallographic structure from the other hydrides, shown in Fig. 3. On the other side barium which has the same (orthorhombic) structure as Eu and Ca, complies with the above dependence. It should be pointed out that this dependence involves in fact also thermal stabilities of the hydrides and consequently the substitution of dissociation pressure for the evaporation heat of the metal can smooth out only the deviations in the case of Sm, Tm or possibly also Gd hydrides. The assumption of the dependence of the exchange ability of the hydrides on their evaporation heat is not clear; it is possible that the exchange is merely made easier by the lower cohesivity of the

metal which is not entirely saturated with hydrogen — the hydrides had not the stoichiometric composition  $MH_2$ .

It can be concluded that hydrides exchange their lattice hydrogen at temperatures lower than those of their decomposition. Most of the hydrides studied show an increase of the exchange ability with their decreasing stability, with the exception of Gd, Tm and Sm hydrides.

#### REFERENCES

1. Nováková J., Jirů P., Zavadil V.: *This Journal* 36, 520 (1971).
2. Klier K., Nováková J., Jirů P.: *J. Catal.* 2, 479 (1963).
3. Mueller W., Blackledge J. P., Libowitz G. W.: *Metal Hydrides*. Acad. Press., New York 1968.
4. Klier K., Kučera E.: *J. Phys. Chem. Solids* 27, 1087 (1968).
5. *Handbook of Thin Film Materials*. Sloan Materials Division.
6. Winter E. R. S.: *J. Chem. Soc. A* 1968, 2889.
7. Nováková J.: *Cat. Rev.* 4, 77 (1970).
8. Larsen E. M.: *Transitional Elements*, p. 170. Benjamin, Amsterdam 1965.
9. Mac Kay K. M.: *Hydrogen Compounds of the Metallic Elements*, p. 59. Spon, London 1966.

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