

ISOTOPIC EXCHANGE OF GASEOUS DEUTERIUM WITH LATTICE HYDROGEN OF HYDRIDES

J. NOVÁKOVÁ, P. JÍRŮ and V. ZAVADIL

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

Received March 26th, 1970

Isotopic exchange of gaseous deuterium with saline hydrides (lithium, sodium and calcium) and metal hydrides (titanium and zirconium) was studied in the temperature range of 20–400°C. The homophase equilibration was found to take place in the case of the lithium and titanium hydride; in the case of the other hydrides studied the heterophase exchange, *i.e.* the exchange with lattice hydrogen took place in addition to the homophase-exchange. The treatment used in the study of oxygen isotopic exchange with oxides was applied to the deuterium exchange with hydrides.

The isotopic exchange of a labelled gas with one component of a solid (*e.g.* O₂ with lattice oxygen of oxides, N₂ with lattice nitrogen of nitrides, D₂ with lattice hydrogen of hydrides) can provide valuable information on the mobility of this solid component in the surface as well as in the bulk of the solid. In certain cases it is also possible to compute the diffusion coefficient of the exchanging particle.

Sometimes, especially at low temperatures, the exchange with the element in the lattice does not proceed, but an equilibration of gaseous isotopic species may take place on the solid surface (*e.g.* H₂ + D₂ ⇌ 2 HD). According to the classification introduced previously¹ this reaction is called the homo-phase equilibration (R).

The hetero-phase exchange (exchange with the lattice component) may take place either by an exchange of a gaseous molecule with one atom of the solid phase in one elementary act (R'), or by an exchange of one gaseous molecule with two atoms of the solid phase in one elementary act (R''). Both these mechanisms cause an equilibration of the gaseous mixture, but — in contrast with the pure homo-phase equilibration — with the participation of atoms of the solid.

Mechanisms R' and R'' can be easily distinguished when performing the exchange with an initially equilibrated isotopic mixture; in the case of the pure R' mechanism the ratio (HD)²/(H₂)(D₂) does not change during the exchange, while in the case of the R'' mechanism the time dependence of the ratio (HD)²/(H₂)(D₂) exhibits a minimum. Usually, however, either two or all three mechanisms take place in the exchange, and it is difficult to determine their relative importance. In such cases a computer analysis may be conveniently used to establish the participation of the individual mechanisms R, R', and R''.

Many papers have been devoted to the study of isotopic exchange of labelled oxygen with oxides and the behaviour of these systems was described using the above mentioned mechanisms²⁻⁴. Most papers on isotopic exchange of oxygen with solids that appeared before 1968 were reviewed in¹. However, only a small number of papers was devoted to the kinetics of exchange of labelled nitrogen with nitrides, and of deuterium with hydrides^{5,6}. A comparison between the isotopic exchange of gaseous oxygen with oxides and that of gaseous deuterium with hydrogen of hydrides, and the possibility of using the same relations for both systems was one of the reasons of the study of deuterium exchange with hydrides as reported in this paper. Another reason was the interest in the behaviour of hydride hydrogen itself.

Large number of papers, reviews⁷⁻⁹, and also books¹⁰⁻¹³ appeared on hydrides. Hydrides are interesting from many points of view, both theoretical (bonds in simple compounds) and practical (source of pure hydrogen, moderators in nuclear reactors *etc.*) The mobility of hydrogen of hydrides is regarded as a characteristic property of various hydrides, especially of the hydrides of the so called metallic group (Pd_2H , hydrides of the elements of groups V and VI, and possibly TiH_2 , ZrH_2). The hydrogen mobility in hydrides was computed theoretically¹⁴, measured by magnetic proton resonance¹⁵, in electrical fields¹² *etc.* However, isotopic exchange kinetic of deuterium with hydrogen of hydrides was not often used to determine the hydrogen mobility.

We plan to undertake a larger study concerning the isotopic exchange of gaseous deuterium with the lattice hydrogen of some pure hydrides representing the main groups of hydrides: the saline, metal, and covalent group. In this paper we report on preliminary results on deuterium exchange with several hydrides of the saline group (lithium, sodium and calcium) and the metal group (titanium and zirconium); exchange with lithium-aluminium hydride is mentioned, too. The results can be regarded as preliminary only, as we did not prepare the samples ourselves in high vacuum, but rather used commercially available hydrides.

EXPERIMENTAL

The same experimental technique was used as in the measurements of oxygen exchange with oxides⁴. The hydride sample (0.2 g) was evacuated at constant temperature overnight. The pressure was then of the order of 10^{-5} Torr, if no dissociation took place. The sample was protected by a trap cooled by liquid nitrogen. In some experiments hydrogen was admitted and the sample heated up to 400°C under the pressure of 10 Torr for 12 hours. The sample was then slowly cooled to the room temperature, and hydrogen was pumped away until the pressure was 10^{-5} Torr. The hydride sample was then sealed off and connected by means of a breakable seal with a 500 cm³ reservoir filled with deuterium at 4 Torr. The sample with the reservoir were then joined to a mass spectrometer (MCh 1302, production USSR). The exchange was followed continuously. The hydride was kept in a furnace at a constant temperature (deviations less than $\pm 2^\circ\text{C}$).

Deuterium and hydrogen were prepared under vacuum by decomposition of water with an excess of sodium (purified *in vacuo*).

Hydrides of lithium, sodium, calcium and lithiumaluminium hydride were commercially available reagents (Lachema). Hydrides of titanium and zirconium were prepared by Dr Kříž (Institute of Inorganic Synthesis, Czechoslovak Academy of Sciences) by a direct synthesis from the metal and hydrogen. No other gaseous components except hydrogen were observed by means of a mass spectrometer when the samples were heated up to 400°C. The surface areas of sodium hydride and calcium hydride were measured by the BET method using argon (cross section

16.6 \AA^2). Surface areas $2.1 \text{ m}^2/\text{g}$ and $3.7 \text{ m}^2/\text{g}$ were found for sodium hydride and calcium hydride, respectively.

RESULTS

First, the behaviour of lithium, sodium and calcium hydrides evacuated at room temperature was investigated when the samples were heated. All the samples released hydrogen at elevated temperatures (from 50°C up). Experiments were then carried out at 150°C in order to find out whether the hydrogen release could be suppressed by admitting to the sample hydrogen at various pressures (1–5 Torr). It turned out that it was impossible to suppress in this way the hydrogen release in the case of lithium hydride. Some suppression effect was observed in the case of calcium hydride, and the evolution of hydrogen was suppressed from sodium hydride by hydrogen pressure of 2 Torr. In the case of lithium hydride and calcium hydride probably adsorbed hydrogen was involved. Samples of lithium hydride and calcium hydride evacuated at 400°C for 12 hours did not release any hydrogen at temperatures up to 400°C . Therefore, exchange experiments were performed with lithium hydride and calcium hydride heated overnight at 400°C beforehand, sodium hydride was used after an overnight evacuation at room temperature.

It was found that lithium hydride did not exchange its lattice hydrogen up to 400°C ; a small part may be exchanged between 400 and 600°C . The homo-phase equilibration ($\text{H}_2 + \text{D}_2 = 2\text{HD}$) proceeded in the presence of lithium hydride from 150°C up.

The exchange of deuterium with lattice hydrogen of sodium hydride is shown in Fig. 1. The upper part of the figure shows the time dependence of the atomic deuterium concentration in the gas phase, in the middle part the results are plotted in the semilogarithmic scale; this function should be linear, if no diffusion occurred. If we assume that the theoretical equilibrium concentration is reached when all hydrogen atoms of sodium hydride are exchanged ($c_\infty = 6.3\%$, after 140 hours this situation was actually achieved), the results indicate that the exchange is influenced by a diffusion process (curve 1). Up to the concentration of 25 atomic percent of deuterium the first order of the reaction is preserved (see curve 2). In the lower part of the figure, the time dependence of the ratio $(\text{HD})^2/(\text{H}_2)(\text{D}_2)$ is shown. A minimum can be seen on this curve which is caused by the participation of the mechanism R'' in the exchange¹.

Using the relations derived by Klier and Kučera¹⁶ for exchange reactions between fluids and solids with tracer diffusion, the value D/r^2 was calculated for this system; D is the diffusion coefficient and r the radius of the particles (the spherical model is assumed here).* The ratio D/r^2 calculated for sodium hydride at 100°C was $1.83 \cdot 10^{-5} \text{ min}^{-1}$.

* The model of this diffusion theory assumes that the diffusion occurs as an exchange reaction between monoatomic iso-concentration layers of the solid.

Calcium hydride was evacuated at 400°C overnight, prior to the experiment. The results of the exchange experiments with deuterium at 300, 360, and 400°C are shown in Fig. 2. After a fast start, the reaction proceeded very slowly up to the point, where

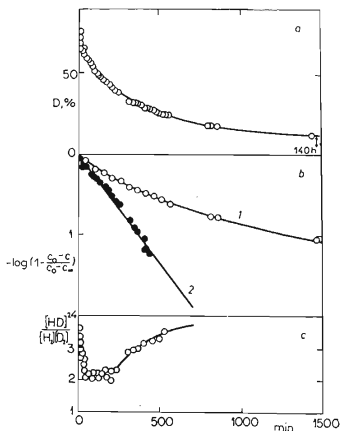


FIG. 1

Exchange of Deuterium with NaH at 100°C (0.2 g NaH) evacuated overnight at room temperature, 4 Torr of D_2

Time functions of: *a* atomic deuterium concentration; *b* $\log [1 - (c_0 - c)/(c_0 - c_\infty)]$, where c_0 , c , and c_∞ means concentration at time 0, t , and ∞ , respectively; *c* the ratio $(HD)^2/(H_2)(D_2)$.

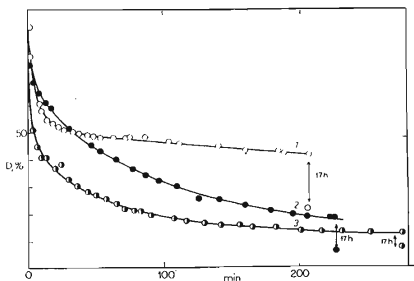


FIG. 2

Exchange of Deuterium with CaH_2

0.2 g CaH_2 evacuated overnight at 400°C, 4 Torr of D_2 ; 1, 2 and 3 at 300, 360, and 400°C respectively.

all hydride hydrogen was exchanged. The semilogarithmic plot of the dependence exchanged fraction time (Fig. 3) shows that the process is diffusion controlled. The ratio D/r^2 calculated with the use of the relations derived by Klier and Kučera¹⁶ is $6.9 \cdot 10^{-5} \text{ min}^{-1}$ for calcium hydride at 400°C . The equilibrium ratio $(\text{HD})^2 : (\text{H}_2)(\text{D}_2)$ did not change during the exchange. The homo-phase equilibration on calcium hydride was found to start at about 200°C ; this equilibration plays probably an important role in the temperature range of $300-400^\circ\text{C}$. Because of this reason, it was impossible to decide, without extensive computations, which of the mechanisms of the hetero-phase exchange participated. The R-mechanism might completely mask the R'' mechanism.

The samples of lithium-aluminium hydride were evacuated overnight at room temperature. Up to 100°C no deuterium exchange was observed, at higher temperatures the samples decomposed.

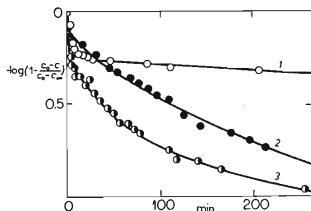


FIG. 3

Exchange of Deuterium with CaH_2

Time function of $\log[1 - (c_0 - c)/c_0 - c_\infty]$ for samples from Fig. 2.

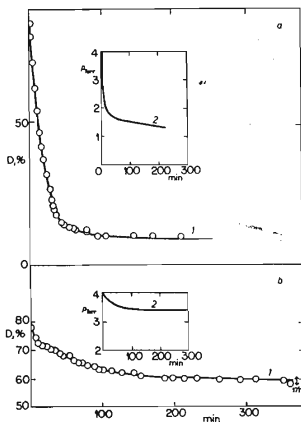


FIG. 4

Exchange of Deuterium with ZrH_2 at 300°C

0.2 g ZrH_2 : a evacuated overnight at 300°C , 4 Torr of D_2 ; b sample used in a kept overnight at 400°C under 10 Torr of H_2 , evacuated at room temperature, 4 Torr of D_2 . Time functions: 1 atomic deuterium concentrations; 2 the gas pressure during exchange.

Both titanium and zirconium hydrides were evacuated at room temperature prior to the first exchange experiment. After deuterium was admitted, the composition of the gas phase was followed as a function of increasing temperature. Both hydrides were releasing hydrogen: the onset was at 250°C and 170°C with titanium and zirconium hydride, respectively.

In the case of the titanium hydride, the homo-phase equilibration between the evolved hydrogen and the deuterium mixture began at 250°C. If the titanium hydride was evacuated overnight at 400°C, the homo-phase equilibration started at about 190°C. No heterophase exchange was observed up to 400°C.

If the zirconium hydride was evacuated at room temperature, both exchanges took place — the homo-phase equilibration with evolved hydrogen as well as the heterophase exchange with lattice hydrogen of the solid. Samples of zirconium hydride evacuated overnight at 400°C consumed within a few minutes all admitted deuterium after the start of the exchange at 300°C. Samples of zirconium hydride evacuated at 300°C overnight consumed considerable amount of hydrogen, too, but the exchange was still measurable; the time dependence of the atomic deuterium concentration from this experiment is shown in Fig. 4a. Also, the pressure decrease during the reaction is plotted. The same sample was then heated overnight in hydrogen (pressure 10 Torr) at 400°C, then slowly cooled to the room temperature and evacuated. The same experiment as described above was then carried out with this sample. The result is shown in Fig. 4b. The exchange proceeded slower than in the first case, the equilibrium concentration was higher, and the decrease of pressure during the measurement (due to the absorption of the isotope mixture) was smaller. The number of exchanged hydrogen-atoms of the solid was $1.5 \cdot 10^{21}$ in the first case and $6.7 \cdot 10^{19}$ in the latter (assuming all atoms of the gaseous phase were exchanged, including the absorbed ones). Supposing that the stoichiometric composition of the hydride is Zr_2H , the sample used contained $2.6 \cdot 10^{21}$ atoms of hydrogen.

In both experiments shown in Fig. 4 the homophase equilibration played an important role, and started at a much lower temperature than the heterophase exchange. Therefore, it was not easy to decide which one of the two possible mechanisms of heterophase exchange — R' or R'' — took place.

By a mistake, one sample of the zirconium hydride evacuated earlier at 400°C was kept in a mixture of hydrogen and air (rather than in pure hydrogen) at 400°C overnight. After this gaseous mixture was pumped away and no exchange was found to proceed up to 400°C.

With all samples (hydrides of lithium, sodium, calcium, lithium, aluminium, titanium and zirconium — all evacuated at room temperature overnight) the possibility of a reaction with a small amount of ethylene (40 μ mol) was studied. Up to 400°C (with lithium aluminium up to 140°C) no change in the gas composition — besides evolution of hydrogen — was observed.

DISCUSSION

Although considerable amount of experimental and theoretical work on hydrides has been carried out, many interesting questions remain. We believe that the mobility and inner diffusion of lattice hydrogen of various hydrides is one of them. According to our opinion, the results of the isotopic exchange of labelled gaseous hydrogen with the lattice hydrogen of hydrides give valuable information on both these quantities.

The first results obtained on the deuterium exchange with saline hydrides are of interest. It was generally assumed that the saline hydrides had an ionic character with hydrogen acting as the anion, and that they had practically stoichiometric composition⁹ at temperatures in which we investigated them in our experiments. Therefore, the occurrence of lattice hydrogen exchange in sodium hydride and calcium hydride at relatively low temperatures seems to be somewhat surprising. Taking into account the dissociation pressures of lithium, sodium and calcium hydrides, the participation of the heterophase exchange in the case of sodium hydride may be explained: using the equation $\log p = -A/T + B$ with the data of McKay¹², we obtain the following dissociation pressures: $3.3 \cdot 10^{-4}$ for lithium hydride, $8 \cdot 10^{-4}$ for sodium hydride, and $5.3 \cdot 10^{-3}$ for calcium hydride (in Torr at 300°C). The value of the dissociation pressure of calcium hydride was obtained by extrapolation of the experimental data of Galatnionova¹¹; it has to be noted that McKay's data for A and B give rather different pressure values.

The behaviour of the titanium and zirconium hydride in the deuterium exchange experiments is more difficult to explain. The selfdiffusion of hydrogen in the titanium hydride was calculated¹⁴ and measured by the proton resonance method¹⁵ at the room temperature. The dissociation pressure⁷ of the titanium hydride is sufficiently high at 300°C (it is at least comparable to that of saline hydrides, and those exhibit some heterophase exchange). In contrast with these facts we found no heterophase exchange of deuterium with the hydrogen of the titanium hydride. The occurrence of the heterophase exchange with lattice hydrogen of the zirconium hydride is very surprising: zirconium hydride is supposed to be very stable at high temperatures, its dissociation pressure is of the order of 10^{-7} Torr at 300°C (data on the dissociation pressure of zirconium hydride vary widely; this is presumably due to oxygen contamination of the surface of the hydride⁷). We observed the exchange of deuterium with most of the hydrogen of the zirconium hydride sample at a relatively low temperature, at 300°C (our sample had probably a lower content of hydrogen than would correspond to the stoichiometric composition ZrH_2). The decrease of the exchange rate after the heat treatment of the sample in the hydrogen atmosphere, and the decreased amount of the adsorbed gas phase might be explained by filling of the hydrogen vacancies of the sample during the heating in hydrogen. If one compares the exchange data with the hydrogen-absorption (Fig. 4), it can be seen that the exchange proceeds mainly during the absorption of hydrogen. A strong effect of poisoning

both the homophase equilibrium and the heterophase exchange found after the heat treatment of samples in the presence of air indicates that the original sample was not substantially contaminated.

REFERENCES

1. Nováková J.: *Catalysis Rev.* 4, 77 (1970).
2. Klier K., Nováková J., Jirů P.: *J. Catal.* 2, 479 (1963).
3. Muzykantov V. S., Popovskij V. V., Boreskov G. K.: *Kinetika i Kataliz* 4, 624 (1964).
4. Muzykantov V. S., Jirů P., Klier K., Nováková J.: *This Journal* 33, 829 (1968).
5. Cheselske F. J., Wallace W. E., Hall W. K.: *J. Phys. Chem.* 63, 505 (1959).
6. Hall W. K., Wallace W. R., Cheselske E. J.: *J. Phys. Chem.* 65, 128 (1961).
7. Libowitz G. G.: *J. Nucl. Mat.* 2, 1 (1960).
8. Samsonov G. V.: *Ž. Neorgan. Chim.* 8, 685 (1963).
9. Libowitz G. G.: *Advan. Chem. Ser.* 39, 66 (1963).
10. Gibb T. R. P. jr in the book: *Progress in Inorganic Chemistry* (F. A. Cotton, Ed.), Vol. 3, p. 315. Interscience 1962.
11. Galatnionova N. A.: *Vodorod v Metallach*. Metallurgizdat, Moscow 1959.
12. McKay K. M.: *Hydrogen Compounds of the Metallic Elements*. Spon, London 1966.
15. Mueller W. M., Blackledge J. P., Libowitz G. G.: *Metal Hydrides*. Academic Press, New York 1968.
14. Coogan G. K., Gutowski H. S. j.: *J. Chem. Phys.* 36, 110 (1962).
15. Stalinski B., Coogan C. K., Gutowski H. S.: *J. Chem. Phys.* 34, 1191 (1961).
16. Klier K., Kučera R.: *Phys. Chem. Solids* 27, 1087 (1966).

Translated by Z. Herman.