The Isotopic Exchange between Hydrogen and Water on Platinum. Relative Rates of Exchange of Isotopic Hydrogen Molecules

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The isotopic exchange between deuterium- and tritium-containing hydrogen and ordinary water vapor on platinum has been investigated using mass spectrometric and radiotracer techniques. A certain amount of HD is formed when D_2 exchanges with deuterium-free water vapor. The rate of HD formation shows that the exchange cannot be due to the interaction of a D_2 molecule, from the gas phase or from the van der Waals layer, with a chemisorbed hydrogen atom or hydroxyl radical. It is necessary to assume that both the hydrogen molecule and the water undergo a dissociative chemisorption on the surface. The ratio of the rates of chemisorption of HD and D_2 has approximately the value given by the simple collision theory for a reaction without activation energy. This points to the possibility that hydrogen is chemisorbed without activation energy on bare dual sites on the surface, formed by the desorption of water or hydrogen.

The isotopic exchange between water and hydrogen has been studied by a large number of investigators. Most of the work has been done with liquid water with a view to elucidating the phenomena involved in the electrolytic discharge of molecular hydrogen. During the war, the exchange reaction between water vapor and hydrogen acquired technical importance as the basis for a method of producing heavy water. The mechanism of the exchange reaction was extensively studied by Farkas in the middle of the thirties^{1,2}. From a comparison of the rates of the exchange reaction and the *para-ortho*-hydrogen conversion, Farkas concluded that the exchange must involve a dissociative chemisorption of the hydrogen as atoms. Later, doubts were cast on the correctness of this mechanism, based mainly on the high heats of chemisorption of hydrogen on clean metal surfaces, which seemed to preclude the occurrence of desorption near room temperature. Eley suggested a mechanism where the interaction of a hydrogen molecule from the gas phase or the van der Waals layer with a chemisorbed hydroxyl or hydrogen atom was responsible for the exchange³. Recently, the validity of the early measurements of the heat of adsorption of hydrogen on clean metal surfaces has been questioned,

and Rideal and Trapnell have been able to show that the heat of adsorption on tungsten falls to quite low values at full coverage of the surface, in contradiction to previous results⁴. Recent considerations of the effect of the electric double layer formed in chemisorption predict a large variation in heat of adsorption with coverage to be quite common, independent of any neighbour interactions⁵. These new findings make the arguments against Farkas's original mechanism appear less serious.

In the early work with deuterium exchange, heat conductivity measurements were generally used for the determination of deuterium. Since then, the mass spectrometer has become generally available. With it, much more detailed and accurate information about the composition of the hydrogen can be obtained than was possible before. The discovery of the radioactive tritium provides another important tool for investigations of this kind.

With these new experimental resources at hand, an investigation of the exchange reaction has been made in an attempt to test the correctness of the different mechanisms proposed. The rate of the tritium exchange has been used as a measure of the activity of the catalyst, thereby making it unnecessary to assume that the activity of the catalyst is unchanged between successive experiments. In this way the ratio of the exchange rates of D_2 and HD has been obtained, and this in turn makes possible a determination of the amount of HD formed when D_2 exchanges with an excess of light water. As shown below this provides important information about the mechanism of the exchange.

EXPERIMENTAL

Reaction apparatus

The exchange reaction was studied in a static system. To eliminate any influence of diffusion on the reaction rate the reacting gas was circulated over the catalyst. The apparatus is shown in Fig. 1. It contains about 50 ml of specially purified water and has a total volume of about 2 l. During an experiment, most of the water is at A in the figure. From A, the water flows through a capillary constriction to a heated piece of asbestos at B, where it is evaporated without risk for explosive boiling. The vapor passes to the jet at C, which it leaves with a high velocity, thus circulating the gas in the rest of the apparatus. Thermostated water circulates through the condensers. Most of the excess water vapor is condensed on the downward path of the gas and only a little in the lower part of the upward condenser. In the upper part of the latter, there is a constriction. Any water condensing above this constriction would have therefore been visible. The fact that no water was observed shows that the water vapor pressure of the gas, when it left the condensers, was the equilibrium pressure corresponding to the temperature of the water circulating through the condensers. After leaving the condensers, the gas enters the bulb D, which constitutes most of the volume of the reaction apparatus. It is inserted in a thermostat set at a temperature higher than that of the gas circulating through the condensers. On its way out from the bulb the gas comes into contact with the platinized platinum catalyst at E. A thermocouple inside the glass tube carrying the catalyst indicates the temperature at which the exchange reaction takes place. The stopcock F and the ground joint G are lubricated with apiezon L high vacuum grease which is considered to have an immeasurably low vapor pressure at room temperature. Before being installed, the reaction apparatus was heated in oxygen in an oven to 550 °C to burn out any organic impurities. The efficiency of the gas circulation was checked by cooling at E when the apparatus was running with about equal pressures of hydrogen and water vapor. A very rapid condensation took place and continued as long as the cooling was applied. This could not have been due to diffusion of water vapor through the hydrogen, but showed that the circulation in the apparatus was very efficient.

Fig. 1. Reaction apparatus. A: About 50 ml light water. B: Heated asbestos fabric. C: Jet nozzle. D: 1.5 l bulb. E: Platinized platinum catalyst and thermocouple. F: Stopcock. G: Ground joint.

Fig. 2. Gas analysis section. A: From reaction apparatus. B: Liquid air trap. C: Toepler pump. D: Sample storage bulbs. E: Ampoule for mass spectrometric deuterium determination. F: Proportional counter. G: To vacuum.

Materials

The catalyst consisted of a piece of platinum foil, $20 \times 10 \times 0.05$ mm, platinized by 60 mA, 2–3 min. After platinizing, the foil was purified using cathodically evolved hydrogen in a dilute sulfuric acid bath, carefully rinsed with distilled water and kept in doubly distilled water overnight before use.

The water used for the exchange experiments was purified by double distillation, and finally the vapor was passed through a quartz tube kept at 800°C to destroy any volatile organic impurities.

Commercial cylinder hydrogen was used and purified before use by passing through a pyrex tube filled with platinized asbestos at 500°C and a liquid air trap.

Deuterium was prepared by electrolysis of 99.6 % heavy water and purified as the hydrogen above. Deuterium was circulated over the platinized asbestos for three hours before the gas from the electrolysis cell was sent to the deuterium storage bulb.

Tritium, about 0.1 mC as hydrogen gas, was obtained from A.E.R.E., Harwell, England.

Determination of deuterium

Deuterium was determined in a 90° , Nier type mass spectrometer. The pressure before the leak was kept constant during all analyses. The spectrometer was calibrated with gas samples of known composition. These were prepared by diluting deuterium gas from the storage bulb with hydrogen. An aliquot of the gas was analyzed in the mass spectrometer and another part burned in dry oxygen and the deuterium content in the resulting water

determined by means of the gradient tube method. In this way a calibration for D_2 was obtained. Still another part of the gas mixture was equilibrated over a glowing platinum wire, previously outgassed by prolonged heating in a high vacuum, and then analyzed in the spectrometer. This gave a calibration curve for HD. There was very little mass 2 background in the spectrometer, and background on masses 3 and 4 from previous samples was never observed. In the range of HD and D_2 , percentages used it was found that peak heights and percentages were always proportional within experimental errors, when the 2 peak was corrected for background, so that there was no fractionation in the spectrometer. The percentage of HD and D_2 was consequently obtained directly from the peak heights on the recorder diagram. When the HD content of a sample was below 0.5 %, the value obtained was discarded and not used in the calculation of the reaction rate constant, since the spectrometer was not calibrated below this percentage. The standard deviation obtained when making repeated measurements on several samples taken from the same storage bulk was 3 % of the measured HD or D_2 percentage.

Determination of tritium

Tritium analyses were made in a proportional counter. The counter consisted of a 20 mm diam. copper tube, enclosed in a pyrex tube. The anode was a 0.05 mm tungsten wire. It hung freely and was stretched by a 20 g weight at the lower end, and could thus easily be removed. The distance between the sleeves, i. e. the active length of the wire, was 25 cm. The total volume of the counter was 200 ml. The high voltage was supplied by an EKCO power unit type 1033/7. The pulses were amplified in an EKCO amplifier type 1008 and counted with an EKCO scaler type 1009 A. The counter had a plateau with a slope of 4 % per 100 volt between 1 900 and 2 100 volt. When measurements were made, the sample gas was first allowed to expand into the previously evacuated counter. Ordinary hydrogen was then added to a total pressure of 40 mm Hg. Finally, methane was added to a total pressure of 200 mm Hg. The counter was left for 15 min. to allow the gases to mix completely. Counting was made at 4 to 5 different voltages with each sample. The precision of the method was tested by counting ten different mixtures of a gas of known activity and ordinary hydrogen. These samples underwent exactly the same treatment as the samples taken during exchange experiments. The standard deviation of the activity of the original T-containing gas was obtained as 3 % of the mean value. The counter did not show any detectable memory effects. After some use, the plateau became steeper and narrower, probably as a result of the deposition of hydrocarbon residues from the methane on the anode, caused by the discharges *. Replacement of the anode wire restored the original plateau.

Procedure

Before each experiment, the whole apparatus was evacuated by means of a mercury diffusion pump to less than 10^{-5} mm Hg. The water in the reaction apparatus was frozen in a solid CO_2 bath during the evacuation.

The stopcock leading to the reaction apparatus was closed, and the water heated and distilled to position A (Fig. 1). A constant flow of water passed through the capillary and entered the heated zone, where it was evaporated. When the vapor jet circulation was working, the predetermined mixture of tritium, deuterium and hydrogen was admitted *via* a liquid air trap. The mixing of the gases was performed in a special bulb and if desired the mixture could be equilibrated over a glowing platinum filament. After admission of the gas, the total pressure in the reaction apparatus was measured on a mercury manometer placed outside the apparatus while the stopcock was kept open. As mentioned above the water vapor pressure could be taken as the saturation pressure corresponding to the temperature of the water circulating through the condensers. The hydrogen pressure was obtained as the difference. The number of moles of water taking part in the exchange reaction was about 2 000 times the number of moles of hydrogen, so that the increase in deuterium and tritium content of the water after completed exchange could be neglected.

The exchange reaction was allowed to go on for 5 min. during which the liquid air trap (volume about 20 ml) was evacuated. Then the first sample was taken. After the

Fig. 3. Reaction of hydrogen containing tritium and a few per cent D₂ with light water vapor. (Exp. 6).

Fig. 4. Reaction of tritium containing, D₂-rich hydrogen with light water vapor. (Exp. 4).

water vapor had been frozen out, the sample was sent to a storage bulb *via* a Toepler pump. Four or five samples at intervals of about 10 min. were taken in each experiment.

From the sample storage bulb, part of the gas was forced into an ampoule, which was removed from the apparatus, and the gas contained submitted to mass spectrometric analysis.

The rest of the gas was forced into a gas burette by means of the Toepler pump, and the mercury adjusted to a constant marked level (Fig. 2). The pressure of the gas was then measured on the other arm of the manometer by means of a cathetometer. The temperature at the gas burette was noted. The gas was then allowed to expand into the counter, and the mercury level in the Toepler pump adjusted to the lower end of the outlet tube (B, Fig. 2). When corrected for temperature variations, the amount of hydrogen in the counter was thus proportional to the pressure of the gas in the burette. Counting was then done as described, and gave the relative specific activity of the gas. Absolute determination of the specific activity was of course not necessary.

RESULTS

All measurements were made at a water vapor pressure of 14 mm Hg, a hydrogen pressure of 22 mm Hg and a reaction temperature of 25 °C.

All successful experiments are reported in Table 1, where the apparent monomolecular reaction constants of the different hydrogen molecules are given. The plot of the logarithm of the tritium content in the hydrogen against time generally gave excellent straight lines, showing that the reaction was of first order. When a gas mixture containing a few per cent D₂ and very little HD was exchanged, the plot of $\log (D_2)$ vs. time was also strictly linear (Fig. 3). When hydrogen with a high D₂ content was exchanged, however, there seemed to be a tendency for the half life to decrease slightly as the deuterium content of the hydrogen decreased (Fig. 4). The number of samples taken is too small to allow anything more than a qualitative observation of this effect.

In a few experiments, first order kinetics were not obtained, instead the exchange tended to become slower with time. This was attributed to some impurity in the reaction gas, which caused poisoning of the catalyst. When this was observed, the reaction apparatus was heated in an oven to 500 °C for several hours to burn out any impurities, and the catalyst replatinized.

The D_2 , HD and HT concentrations were generally observed over a range of 10 or more. If four points are taken on each curve, and the logarithm of a concentration value is considered as derived from a sample taken from a normal distribution of concentration values with a coefficient of variation of 3 %, the ratio of the reaction constants of HD and D_2 is obtained from six experiments (5—10) with a coefficient of variation of 4 %. This means that in present case, where the ratio is near unity, there is only one chance in twenty that the obtained ratio is in error by more than 0.08.

DISCUSSION

Before undertaking a discussion of the mechanism of the exchange reaction it must be shown that the kinetics are not obscured by the influence of diffusion.

The adsorption of water on a blank platinum surface has been examined by Bowden and Throssell⁷. At the relative saturation of the water vapor used in the present experiments, they have found an adsorbed amount corresponding to as much as 50 molecular layers. By means of an optical method they found that the water was not uniformly distributed but must have been localized as microscopic droplets on certain contaminated parts of the surface. On almost the whole surface the adsorbed layer was only about 2 molecules thick. If it is still assumed for the moment that the water is adsorbed as a layer 50 molecules thick, the diffusion through this layer would approximately account for the observed reaction rates with a roughness factor of unity for the surface. However, from the measurements of Bowden and Rideal⁸, confirmed by numerous polarization measurements, it is evident that the roughness factor of platinized platinum is of the order of 10^3 . It is thus quite clear that diffusion through the adsorbed layer of water cannot have influenced the reaction rate in any way. As mentioned earlier the mixing of the reaction gases was very rapid, so that the gas could at all times be regarded as homogeneous and the water vapor as deuterium-free.

The various mechanisms proposed for the exchange reaction will now be discussed in the light of the experimental findings.

I. The fact that HD is formed during the exchange of D_2 with H_2O shows at once that the deuterium atoms are not transferred simultaneously to the water, so that the reduction of a surface oxygen atom by a hydrogen molecule cannot be responsible for the exchange.

II. The electrolytic mechanism proposed for the hydrogen electrode

where M means a surface metal atom, cannot be expected to occur in such a thin water layer as was present in these experiments. The incomplete solvation of the ions would increase the activation energy for the process considerably above the value in the presence of liquid water¹.

III. Rideal and Eley have suggested a mechanism for the *para-ortho*-hydrogen conversion where the interaction of a hydrogen molecule from the van der Waals layer and a chemisorbed hydrogen atom is the rate determining step⁹

Table 1.

Experiment No.	Initial content in hydrogen			k_{D_2} min ⁻¹	k_{HD} min ⁻¹	k_T min ⁻¹	$\frac{k_{D_2}}{k_T}$	$\frac{k_{HD}}{k_T}$
	% D ₂	% HD	% H ₂					
1	74.7	10.2	15.1	0.122		0.097	1.26	
2	83.4	7.5	9.1	0.063		0.051	1.23	
3	65.3	15.1	19.6	0.136		0.099	1.37	
4	66.6	13.9	19.5	0.099		0.078	1.27	
5	6.3	0.31	93.4	0.157		0.123	1.27	
6	4.7	0.26	95.1	0.081		0.066	1.24	
7	4.1	0.21	95.7	0.118		0.083	1.30	
8	0.03	3.0	96.9		0.187	0.163		1.15
9	0.04	3.9	96.1		0.085	0.078		1.09
10	0.04	3.8	96.2		0.094	0.083		1.14

It has been shown by Farkas¹ that the *p-o*-conversion and the exchange of deuterium occur with similar rates under conditions such as used here; the small difference in rate seems to be due to an isotopic effect. Therefore, if the *p-o*-conversion proceeds at all according to eqn. (2) it must be assumed that the chemisorbed D atom produced according to the same mechanism:

is rapidly transferred to the water. The chemisorbed hydrogen atoms would then consist exclusively of light hydrogen.*

In experiments 8—10 (Table 1), the ratio of the following two reaction constants were measured:

In experiments 5—7 the ratio k_1/k_3 was measured:

In these experiments there must be very little chemisorbed deuterium on the surface, and according to the above mechanism the reaction constants represent the rate of reaction of HD, HT and D₂ with chemisorbed H atoms.

If it is now assumed that the surface is free from chemisorbed deuterium even when pure D₂ is undergoing exchange, it is easy to calculate the concentration of HD in the hydrogen in terms of the remaining D₂ from the formulae for consecutive reactions, because the ratio of their reaction constants is known from experiments 5—10.

In experiment 4 (Fig. 4) the rate constant for D₂ is taken from the slope of the straight line of best fit for the experimental values of log (D₂). In Fig. 5 are shown the curves for the calculated (curve I) and actually observed (curve II) HD concentration. Curve III would be obtained if no HD formation

Fig. 5. The formation of HD in the exchange of D_2 with H_2O (Exp. 4).

from D_2 occurred. Clearly much smaller amounts of HD are formed than those required by the postulated mechanism.

If chemisorbed D atoms are actually present on the surface, the rates of D_2 and HD disappearance are governed by the following expressions:

$$-\frac{d(D_2)}{dt} = k_1(D_2) \sigma_H - k_4(HD) \sigma_D \quad (7)$$

$$-\frac{d(HD)}{dt} = k_2(HD) \sigma_H + k_4(HD) \sigma_D - k_1(D_2) \sigma_H - k_5(H_2) \sigma_D \quad (8)$$

Here σ_D = fraction of deuterium among the chemisorbed hydrogen atoms, σ_H = that for light hydrogen, σ_T = that for tritium.

$$\sigma_H + \sigma_D + \sigma_T = 1 \quad (9)$$

where, of course, $\sigma_T \ll 1$.

The ratio

$$\frac{-d(HD)/dt}{d(D_2)/dt} = \frac{k_1(D_2)\sigma_H - k_4(HD)\sigma_D + k_5(H_2)\sigma_D - k_2(HD)\sigma_H}{k_1(D_2)\sigma_H - k_4(HD)\sigma_D} \quad (10)$$

is seen to have its lowest value for $\sigma_D = 0$, which gives the above-mentioned curve I in Fig. 5. Consequently, for $\sigma_D > 0$, the HD concentration must at all times be *higher* than that given by curve I. The fact that the experimental curve is considerably below curve I definitely rules out a Rideal-Eley mechanism as the preliminary step in the exchange of molecular hydrogen with water.

IV. A mechanism suggested by Eley³ involves interaction between a D_2 molecule and a chemisorbed OH radical

which must be followed either by

or

In eqn. (13) the D atom in the hydroxyl group can then exchange rapidly with the water. If reaction (12) occurs, it gives rise to the same kinetics as mechanism III above and is thus excluded for the same reasons. The correct rate of HD formation from D_2 could, however, result if reactions (12) and (13) occurred simultaneously. As they must involve quite dissimilar transition states this is very unlikely. Besides, reaction (13) seems improbable as such, since it involves the simultaneous breaking and formation of three bonds. It is also unable to explain the exchange between hydrogen and alcohols, which occurs with about the same rate as with water¹.

V. Finally, Farkas has presented evidence for a mechanism in which the hydrogen is chemisorbed as hydrogen atoms on the platinum surface¹.

If the exchange occurs *via* chemisorption of hydrogen it is necessary that the chemisorption of water is also reversible. It is now generally agreed that chemisorption of simple hydrides involves a splitting of the bond between the central atom and a hydrogen atom³. In the case of water this leads to formation of hydroxyl radicals on the surface. If the hydroxyls are irreversibly adsorbed, they will eventually cover the surface completely if they are mobile, and the exchange comes to a standstill. If they are immobile on the surface, some isolated hydrogen atoms will be left which could be active in mechanisms III and IV but not in the one discussed here. As the former mechanisms have been shown to be inapplicable, the dissociative chemisorption of water must necessarily be reversible. It is then reasonable to assume that the chemisorbed hydrogen atoms are transferred to the water *via* desorption of a hydrogen atom and an adjacent hydroxyl radical. The disappearance of the various hydrogen molecules is then governed by the following equations:

$$\frac{-d(D_2)}{dt} = k_1(D_2) - k'_1\sigma_D^2 \quad (14)$$

$$\frac{-d(HD)}{dt} = k_2(HD) - k'_2\sigma_H\sigma_D \quad (15)$$

$$\frac{-d(H_2)}{dt} = k_3(H_2) - k'_3\sigma_H^2 \quad (16)$$

$$\frac{-d(HT+DT)}{dt} = k_4(HT) + k_5(DT) - k'_4\sigma_H\sigma_T - k'_5\sigma_D\sigma_T \quad (17)$$

The above equations involve two assumptions:

a) That the amount of chemisorbed hydrogen is independent of the isotopic composition of the molecular hydrogen. In view of what is now known about the generally occurring large variation in heat of adsorption with coverage it is very unlikely that the necessarily small difference in heat of adsorption between the different isotopes can give rise to any noticeable change in coverage.

b) That surface diffusion of the adsorbed hydrogen atoms is rapid compared with desorption, so that the composition of the desorbed hydrogen is statistically governed by the amount of the different hydrogen isotopes chemisorbed on the surface.

It is evident that by choosing a suitable value of the ratio k'_2/k_1 , this mechanism can be made to account for any observed rate of HD formation.

Using the above equations and some additional ones describing the chemisorption and desorption of the water on the surface, Farkas has calculated the composition of the adsorbate from a comparison of the rates of *p-o*-hydrogen conversion and deuterium exchange¹. He then had to assume that $k_1 = k_2 = k_3$ and $k'_1 = k'_2 = k'_3$.

If the preliminary step is the chemisorption of hydrogen molecules as atoms, and the exchange is made with water containing only light hydrogen, it is obviously correct to write:

Rate of transfer of chemisorbed deuterium to the water = net rate of exchange = $k_D\sigma_D$ (18)

whilst that for tritium = $k_T\sigma_T$ (19)

From eqns. (15) and (17) it is seen that, in the exchange of HD and HT with light water, first order kinetics will always be obtained since the amount of chemisorbed deuterium and tritium will be proportional to the fraction of HD and HT, respectively, in the hydrogen gas. In the exchange of D_2 with light water, on the other hand, eqn. (14) shows that the kinetics will not be simple first order. The deviation from first order kinetics depends on the ratio k'_1/k_1 . In all cases where the exchange of hydrogen with a high D_2 content was observed, there is in fact a slight downward curvature of the $\log(D_2)$ vs. time lines, as required by eqn. (14) (Fig. 4). However, the number of samples taken in each exchange experiment is too small to permit an evaluation of the σ_D^2 -term.

If a mixture of small amounts of almost HD-free D_2 with H_2 is undergoing exchange the disappearance of D_2 represents directly the rate of chemisorption of D_2 if assumption b) above is correct.

If HD in low concentration is present in the hydrogen, on the other hand, some HD will desorb from the surface. The probability of escape to the hydrogen gas of a chemisorbed D-atom will be constant as long as σ_D is small, resulting in first order kinetics. When the deuterium in the hydrogen gas is present as D_2 this probability is determined by measuring the rate of formation of HD. In experiments 5 to 7, the rate of HD formation was obtained from a knowledge of the mean value of the ratio of the reaction constants of D_2 and HD, obtained from experiments 5 to 10 as 1, 14. The probability of desorption of a D atom as HD enters the calculations as a parameter. If this probability is given the value 0.23, the experimental points give the best agreement with the theoretical curve. Evidently, then, the rate of chemisorption of HD is $1/1-0.23 = 1.30$ times larger than the actual rate of disappearance of HD. The ratio of the rates of chemisorption of HD and D_2 at equal concentration is then $1.30/1.14 = 1.14$.

If it is assumed for the moment that the probability of escape to the hydrogen as HT of a chemisorbed tritium atom is the same as that for deuterium as HD at low D concentrations, the relative rates of chemisorption of HD, D_2 and HT are obtained as 1.14:1:1.03. It is interesting to note that this is quite close to what would be expected from the simple collision theory for a process without activation energy (1.16:1:1).

It is now known that hydrogen is chemisorbed immeasurably fast on many clean metal surfaces even at liquid air temperatures, so that the energy of activation of the adsorption must be very low. This process may therefore well be a case where the assumption of equilibrium between reactants and activated complex in the theory of absolute reaction rates is not valid. The ratio of the adsorption velocities of different isotopic hydrogen molecules may then be expected to be equal to the ratio of the collision frequencies with the surface. If this is true the obtained ratios of adsorption velocities seem to indicate that the chemisorption of a hydrogen molecule on a bare dual site occurs without appreciable energy of activation even when the surface is largely covered with adsorbate.

If the relative rate of chemisorption of H_2 can be obtained analogously from the simple collision theory, the *p-o*-conversion of light hydrogen can be calculated to proceed 1.8 times faster than the deuterium exchange. Farkas¹ generally obtained a conversion rate 2—3 times higher than the exchange rate. If the disagreement is real, the explanation may be that there is a certain probability that a hydrogen molecule adsorbed on a dual site may desorb before the atoms are separated by surface diffusion. Assumption b) is then no longer valid, and the arguments based on it break down. Whether such an immediate desorption actually occurs could have been tested by observing the *ortho-para*-conversion of the unexchanged deuterium in the experiments with D_2 -rich gas.

In conclusion it has been shown that of the mechanisms so far suggested for the isotopic exchange between hydrogen and water vapor on platinum, the only one in agreement with the reported experimental results involves a simultaneous dissociative chemisorption of both hydrogen and water on the surface. This is followed by desorption of the same molecular species. The hydrogen is chemisorbed as atoms, the water as a hydrogen atom and a hydroxyl radical. The chemisorption of hydrogen probably occurs without any appreciable activation energy and its rate is governed by the production of bare dual sites on the surface by the desorption of water or hydrogen.

A consequence of this mechanism is that in order for a metal to be an efficient catalyst for the isotopic exchange between hydrogen and water, the heat of adsorption of hydroxyl radicals must be low. The heat of adsorption of hydroxyl should run roughly parallel to the tendency of the metal to combine with oxygen. Among the metals commonly used in hydrogen catalysis, platinum has the lowest affinity for oxygen, and it is thus not surprising to find that it is by far the most efficient catalyst for the exchange reaction¹⁰⁻¹².

Acknowledgement. The author wishes to thank professor Ole Lamm for his kind interest and supervision and Stockholms Superfosfatfabriks AB for a grant that made the work possible.

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Received February 7, 1956.