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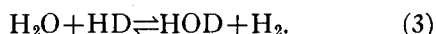
# The Equilibrium $\text{H}_2\text{O} + \text{HD} = \text{HOD} + \text{H}_2$ and Its Rôle in the Separation of the Hydrogen Isotopes

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WHENEVER hydrogen is liberated from an aqueous solution containing heavy water a separation of the isotopes occurs, i.e., the isotopic composition of the gas is not the same as that of the liquid.

To interpret this behavior the following equilibria have to be taken into consideration.



These equations define the D-content of hydrogen evolved from a solution of given D-content under equilibrium conditions.

To simplify the treatment we will take the relative concentrations of the molecular species  $\text{H}_2$ ,  $\text{HD}$ ,  $\text{D}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HOD}$ , and  $\text{D}_2\text{O}$  to be the same in the liquid and in the gas phase, i.e., we will neglect the difference in the vapor pressure of light and heavy water and the possible difference in the solubility of light and heavy hydrogen.

The equilibrium constant of the reaction (1) is well known theoretically<sup>1</sup> and experimentally<sup>2, 3</sup> and is  $K_1 = (\text{HD})^2/(\text{H}_2)(\text{D}_2) = 3.27$  at  $20^\circ\text{C}$ . The equilibrium constant  $K_2 = (\text{HDO})^2/(\text{H}_2\text{O})(\text{D}_2\text{O})$  has been calculated by Topley and Eyring<sup>4</sup> to be 3.27 at  $20^\circ\text{C}$ . Both  $K_1$  and  $K_2$  are nearly independent of temperature.

According to Bonhoeffer and Rummel<sup>5</sup>  $K_3$  is 3.8 at  $20^\circ$ . We have also obtained the same value at this temperature and about 2 at  $100^\circ\text{C}$ .<sup>6</sup>

In a number of processes when hydrogen is evolved from aqueous solutions we could actually

observe that the establishment of these equilibria does in fact occur and is, in these cases, the only cause for the separation of the hydrogen isotopes: the observed "separation factor" defined by

$$s = \frac{\text{H-content in the hydrogen}}{\text{D-content in the hydrogen}} : \frac{\text{H-content in water}}{\text{D-content in water}}$$

is practically equal to the equilibrium constant  $K_3$ . (As a simple calculation shows  $s$  would be identical with  $K_3$  if  $K_1 = K_2 = 4$ .)

Some examples of such processes are (1) the electrolysis of water,<sup>7</sup> (2) the decomposition of sodium formate by palladium black or *B. coli*,<sup>8</sup> (3) the evolution of hydrogen from water by the reaction  $\text{K}_4\text{Co}(\text{CN})_6 + \text{H}_2\text{O} = \text{K}_3\text{Co}(\text{CN})_6 + \text{KOH} + \frac{1}{2}\text{H}_2$ .<sup>9</sup>

In the case of electrolysis this equilibrium is not always established but only under certain conditions, e.g., on activated platinum electrodes.

The separation for the hydrogen isotopes according to the equilibria (1), (2) and (3) will furthermore occur when a mixture of light and heavy steam is decomposed at high temperatures, e.g., with iron or in the water-gas reaction or when oxides such as  $\text{CuO}$  are reduced by hydrogen. At temperatures when all the components  $\text{H}_2$ ,  $\text{HD}$ ,  $\text{D}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HOD}$  and  $\text{D}_2\text{O}$  are present together (in equilibrium) a sample on removal from the reaction chamber will reveal an isotopic fractionation since in general the concentration of D in the water molecules will not be equal to that in the hydrogen.

It is obvious also that in other cases when the establishment of the equilibria (1), (2) and (3), especially that of (3) [the equilibrium defined by (2) is always established in the liquid] is not

<sup>1</sup> Urey and Rittenberg, *J. Chem. Phys.* **1**, 137 (1933).

<sup>2</sup> Rittenberg, Bleakney and Urey, *J. Chem. Phys.* **2**, 48 (1934).

<sup>3</sup> A. and L. Farkas, *Nature* **132**, 894 (1933); *Proc. Roy. Soc. A* **144**, 467 (1934).

<sup>4</sup> Topley and Eyring, *J. Chem. Phys.* **2**, 217 (1934).

<sup>5</sup> Bonhoeffer and Rummel, *Naturwiss.* **22**, 45 (1934); *Zeits. f. Elektrochem.* (in print).

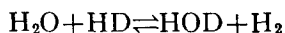
<sup>6</sup> A. and L. Farkas, *Proc. Roy. Soc. A* (1934) (in print).

<sup>7</sup> A. and L. Farkas, *Proc. Roy. Soc. A* (1934) in print.

<sup>8</sup> Farkas, Farkas and Yudkin, *Proc. Roy. Soc. B* (1934) in print.

<sup>9</sup> This experiment was suggested to us by Dr. J. Weiss and is of some interest since the liberation of hydrogen takes place from the homogeneous liquid.

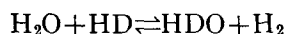
attained as for instance in electrolysis in general or in the dissolution of metals in water or in acids<sup>10-13</sup> the exchange reaction



may be operative to a certain extent thus modifying the primary separation of the hydrogen isotopes caused, e.g., in the electrolysis, by the different rate of discharge of the  $\text{H}^+$  and  $\text{D}^+$  ions or by the different rate of recombination of the H and D atoms.

It is hard to tell the extent of this exchange reaction in a particular case. That it really exists is shown by the fact that even the exchange between molecular hydrogen and water is catalyzed by different substances especially by metals.<sup>14</sup> This reaction is also clearly operative, e.g., on the surface of a metal electrode or on the surface of other metals since the high reactivity of hydrogen in nascent state is well known.

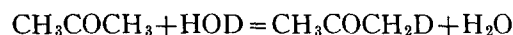
Qualitatively we can state that when the evolved gas contains more light hydrogen than is defined by the concentration determined by the equilibrium constant  $K$  the primary separation of the hydrogen isotopes is larger than the observed separation factor since the equilibrium reaction



tends to bring about a separation factor equal to  $K_3$ . On the other hand if the D-content of the gas liberated is higher than determined by the equilibrium the primary separation will be still smaller than the observed. The former behavior is shown when metals, such as zinc, iron, etc., are

dissolved in dilute acids or in the electrolysis of water, the latter in the dissolution of alkalis or alkaline earths in water. It is thus clear that the rate-determining steps are different in these processes since the separation factor in one of them is smaller, in the other, larger than the equilibrium constant.<sup>15</sup>

In this connection it may be pointed out that for the natural distribution of light and heavy hydrogen such equilibria between hydrogen compounds will play an important rôle. Natural hydrogen should have a D-content 1:15,000 to 1:20,000<sup>16</sup> and also other hydrogen compounds will reveal a different D-content compared with water. Halford, Anderson and Bates<sup>17</sup> have shown that the equilibrium constant of the exchange reaction between heavy water and acetone



is about 2, i.e., the heavy hydrogen is preferentially present in the acetone. It is most probable that this is also true for other organic compounds and this circumstance may explain the fact that water obtained from vegetable or animal material proves to be "heavy" compared with water.<sup>18</sup>

We are very much indebted to Professor E. K. Rideal, F.R.S. for his interest in our work and to the Central British Fund for German Jewry for a financial grant.

<sup>10</sup> A. and L. Farkas, *Nature* **133**, 139 (1934). *Proc. Roy. Soc. A* **144**, 16 (1934).

<sup>11</sup> Hughes, Ingold and Wilson, *Nature* **133**, 291 (1934), *J. Chem. Soc.* **1934**, 493.

<sup>12</sup> Horiuti and Szabo, *Nature* **133**, 327 (1934).

<sup>13</sup> Davis and Johnston, *J. Am. Chem. Soc.* **56**, 492 (1934).

<sup>14</sup> Horiuti and Polanyi, *Nature* **132**, 819 (1933).

<sup>15</sup> Discussion on heavy hydrogen held in The Chemical Soc. London, May 17, 1934. E. K. Rideal and A. Farkas.

<sup>16</sup> Bradley and Urey (*Phys. Rev.* **40**, 889 (1932)), have found that the D-content of hydrogen from He-bearing natural gases is the same as of normal water. Obviously this hydrogen was not in equilibrium with water.

<sup>17</sup> Halford, Anderson and Bates, *J. Am. Chem. Soc.* **56**, 491 (1934).

<sup>18</sup> Emeleus, James, King, Pearson, Purcell and Briscoe, *J. Chem. Soc. London*, in print.