Letters to the Editor

The Exchange Reaction between Deuterium and Hydrogen on Nickel

By *S. Lewina*

Numerous attempts have been made to use the data on the kinetics of exchange between deuterium and hydrogen on electrodes as a function of various factors to clear up the mechanism of hydrogen overvoltage as well as the mechanism of the processes on the hydrogen electrode[1].

Recently Horiuti and Ikusima[2] derived a relation between the overvoltage and the exchange currents. The same authors also made an experimental study of the kinetics of isotopic exchange on platinum both at different polarizations and in solutions of different compositions. The data for platinum point to a marked dependence of the exchange rate on the composition of the solution.

Horiuti and Okamoto[3], in studying the exchange reaction on nickel in potassium hydroxide solutions of different concentrations, found that this process is independent of the alkali concentration. The authors interpret this fact as proof of the catalytic mechanism of hydrogen overvoltage on nickel.

Investigations on the kinetics of the exchange reaction on nickel carried out in our laboratory lead to different results. In Table 1 data are given for the exchange rate on nickel in NaOH solutions of different concentrations at 80° C. A nickel wire 0.3 mm. in diameter with a total apparent surface of 200 cm.^{2} served as the electrode. Before each experiment it was subjected to the following treatment: washing with a hot aqueous solution of alkali, heating to a temperature of 100° C in air, at which it was kept for

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[1] Horiuti a. Polanyi, Nature, **132**, 931 (1933); **133**, 142 (1934); Eley a. Polanyi, Trans. Farad. Soc., **32**, 1385 (1936); Calvin, Trans. Farad. Soc., **32**, 1428 (1936); Calvin and Dyas, Trans. Farad. Soc., **33**, 1492 (1937); Bennett and Polanyi, Trans. Farad. Soc., **34**, 377 (1940).

[2] Horiuti and Ikusima, Proc. Imp. Acad. Tokyo, **15**, 39 (1939).

[3] Horiuti and Okamoto, Bull. Chem. Soc. Japan, **13**, 216 (1938); Horiuti, Sci. Pap. Inst. Phys. Chem. Res., **34**, 450 (1940).

a period of one hour, and, finally, heating to a temperature of 450° C in a hydrogen atmosphere at which it was kept for a period of two hours[4].

In the Table K is the rate constant of the monomolecular reaction,

$$K = \frac{1}{t} 2{,}3 \lg \frac{D_0}{D_t} ,$$

where D_0 is the deuterium concentration at the beginning of the experiment and D_t is the deuterium concentration after a certain time t (expressed in hours).

As can be seen from the Table, the value of K increases with an increase in the alkali concentration.

The values of K, the rate constant of the isotopic exchange reaction on the one hand, and the values of exchange currents on the other increase with an increase in the alkali concentration according approximately to the same law as the rate constant of exchange reaction.

Table 1

Composition of solution	0.2 N NaCl	0.005 N NaOH and 0.2 N NaCl	0.02 N NaOH and 0.2 N NaCl	0.18 N NaOH	0.53 N NaOH
$K \times 10^2$	1.223	2.193	2.843	5.284	6.347

The exchange currents were calculated by extrapolating the linear parts of the curves showing the dependence of hydrogen overvoltage on the logarithm of current density[5], up to the value of the reversible hydrogen electrode potential. In the present work the values of the exchange currents were taken from the polarization curves obtained at room temperature. In the future, for comparison of the absolute values of the true isotopic exchange rates with the rates calculated from the exchange currents, it is intended to take the latter from polarization curves obtained with electrodes whose surfaces have been subjected to the same preliminary treatment and under the same temperature conditions, *i. e.*, at 80° C, under which the rate of the isotopic exchange on nickel was determined. At present a study is also being made of the isotopic exchange of hydrogen on platinum.

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The Karpov Institute of Physical Chemistry,
Laboratory of Surface Phenomena,
Moscow.

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[4] A detailed description of the method will shortly appear in another paper.

[5] Lukowzew, Lewina and Frumkin, Acta Physicochimica URSS, **11**, 21 (1939).