THE ELECTRODEPOSITION OF HYDROGEN AND DEUTERIUM AT THE DROPPING MERCURY CATHODE[1]

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Received December 12, 1938

The high reproducibility of the polarographic current–voltage curves obtained with the dropping mercury cathode allows one to follow the phenomenon of hydrogen overvoltage in great detail. In this way it was established that the potential of a mercury cathode at which hydrogen is being evolved changes with current density and with the concentration of ions in a manner differing from that of a reversible hydrogen electrode. The old definition of overvoltage as the difference between the potential of the metal being examined and that of a reversible hydrogen electrode in the same solution has no precise meaning.

Overvoltage must be defined by its dependence on the current density and must be referred to the standard potential of a non-polarizable electrode (in this work the decinormal calomel electrode). The first empirical equation defining the overvoltage, π, at the dropping mercury cathode was deduced by Heyrovský (9, 10) and Herasymenko (7, 8) in the form:

$$\pi = 2RT/F \log [\mathrm{H}^+]_s - 3RT/2F \log i + K$$

where $[\mathrm{H}^+]_s$ is the concentration of hydrogen ions in the surface layer at the mercury cathode in the solution of the strong acid in the presence of excess electrolyte (potassium chloride) and i is the current. Since the average areas of the mercury drops are constant, the current density is taken to be proportional to the current. If concentration polarization at the cathode is taken into account,

$$[\mathrm{H}^+]_s = k(i_d - i)$$

where i_d is the limiting (or "diffusion") current due to the deposition of hydrogen ions, we obtain, according to Tomeš (17), the overvoltage relationship in the form

$$\pi = 2RT/F \log (i_d - i) - 3RT/2F \log i + K$$

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[1] Presented before the Division of Physiological and Inorganic Chemistry at the Ninety-fifth Meeting of the American Chemical Society, held at Dallas, Texas, April 18–22, 1938.

This formula does not hold exactly for very small currents or for very rapid dropping of mercury, in which case the factor 3/2 decreases towards unity. Moreover it does not hold for a slow rate of dropping, since in this case the factor 3/2 increases towards 2.

Heyrovský (11), in correlating the observations of Müller, Novák, and Tomeš, corrected the above formula to

$$\pi = 2RT/F \log (i_d - i) - RT/F \log (1 + \omega i)i + K \qquad (1)$$

where ω is the "adsorption coefficient" of the freshly formed hydrogen molecules at the cathodic interface.

When the rate of dropping is great, adsorption of the molecules is hindered by the rapid renewal of the mercury surface, and ω is small. Under these conditions ωi is small compared to unity, and equation 1 takes the form

$$\pi = 2RT/F \log (i_d - i) - RT/F \log i + K'$$

This form of the equation also holds for very small currents, since here again ωi is small compared to 1.

For a small dropping speed, ω is so large that 1 is small compared to ωi. The overvoltage relationship then takes the form

$$\pi = 2RT/F \log (i_d - i) - 2RT/F \log i + K''$$

This equation must hold for infinitely slow dropping speed, i.e., for the overvoltage at a steady mercury surface. This has been well established (3, 5, 6).

Mathematical analysis of equation 1 shows that it agrees with the course of the overvoltage current–voltage curve (11), particularly as regards the position of the so-called "half-wave" potential (see figure 1).

It is significant for the mechanism of the deposition of the different hydrogen isotopes that equation 1 holds just as well for the electrodeposition of deuterium from solutions of deuterium chloride or deuterium sulfate in heavy water, where the adsorption coefficient is approximately eight times greater than in light water and the constant K is more negative.

Figure 1 shows a comparison of the polarographic current–voltage curves in light and in heavy water. These curves were obtained under identical conditions of dropping, temperature, concentration, and galvanometer sensitivity. Utmost care was taken to keep the 99.6 per cent heavy water protected from light water. The coefficient of log i, which is 0.102 in light water near the "half-wave" potential, becomes 0.133 in heavy water. In mixtures of light and heavy water the values of this coefficient, b, as well as those of the "adsorption coefficient," ω, vary as given in table 1.

The experimental results in table 1 were obtained in careful polarographic investigations by Novák (14). This same author obtained the important result that the overvoltage in heavy water decreases at high

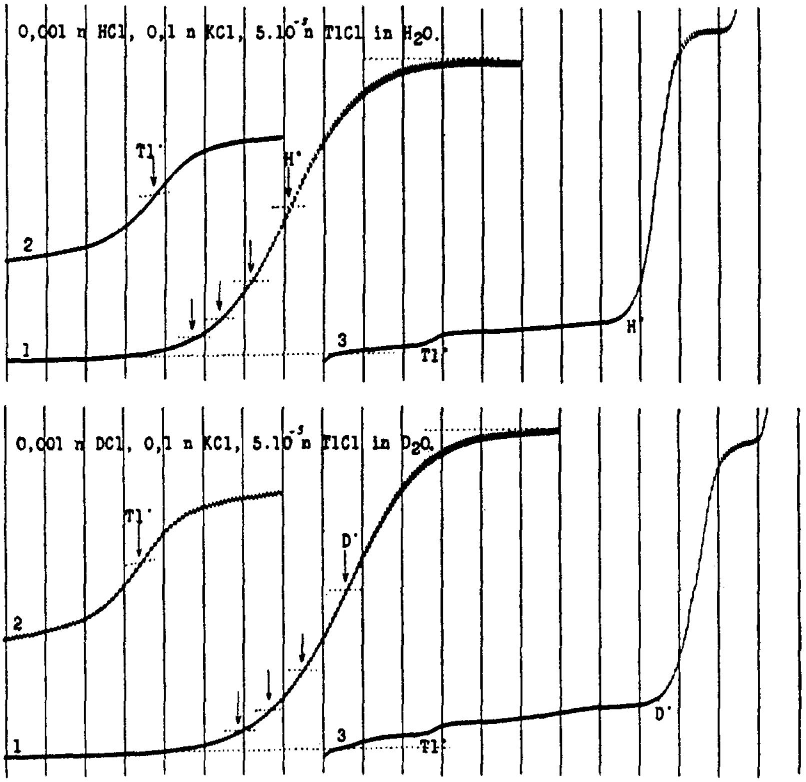

FIG. 1. Comparison of the polarographic current-voltage curves in light and in heavy water. Upper polarogram: 0.001 *N* hydrochloric acid, 0.1 *N* potassium chloride, and 5×10^{-5} *N* thallous chloride in light water. Curve 1: 50 millivolts per complete rotation, from 1.3 volts E.M.F., sensitivity 1/100. Curve 2: 50 millivolts per complete rotation, from 0.35 volt E.M.F., sensitivity 1/2. Curve 3: 200 millivolts per complete rotation, from 0 volt E.M.F., sensitivity 1/100. Lower polarogram: 0.001 *N* deuterium chloride, 0.1 *N* potassium chloride, and 5×10^{-5} *N* thallous chloride in heavy water. Curve 1: same E.M.F. and sensitivity as curve 1 in upper polarogram. Curve 2: same E.M.F. and sensitivity as curve 2 in upper polarogram. Curve 3: same E.M.F. and sensitivity as curve 3 in upper polarogram.

temperature more than in light water. At 60°C. the coefficients, *b*, are in the ratio 0.116/0.111, whereas at 20°C. the ratio is 0.113/0.102. Thus at higher temperatures the overvoltage in heavy water approaches that in light water.

The significant feature of the current–voltage curves in mixtures of light and heavy water is that they show only one homogeneous bend without a trace of double-wave formation (see figure 2). This proves that the isotopic hydrogen ions are deposited at the same rate at the same potential. In other words, the deposition potentials of hydrogen ion and deuterium ion do not differ materially. The difference of 87 millivolts between the evolution of hydrogen from light and from heavy water is large enough to make a double wave quite evident, providing this difference were really that of the deposition potentials. The polarographic curve of a mixture of radium and barium shows a double wave even though the deposition potentials differ by only 60 millivolts (13).[2]

The fact that there cannot exist different deposition potentials for the hydrogen isotopes refutes any theory which ascribes the greater overvoltage of deuterium to a slower rate of deposition of its ions. The theory of Erdey-Grúz and Volmer (5), which assumes the discharge of hydrogen ions to be the slowest process in the cathodic evolution of hydrogen, is disproved by the fact that heavy hydrogen is evolved more slowly than light hydrogen. This theory, originated by Smits (16), postulates a slow rate of deposition of hydrogen ions owing to their dehydration. In heavy water the ions are somewhat less hydrated than in light water, owing to the smaller free energy and smaller dielectric constant of deuterium oxide, and the evolution of deuterium should be facilitated; this is in disagreement with experimental results.

TABLE 1

Differences in overpotentials at the "half-diffusion current" observed with 0.001 N hydrochloric acid, at 20°C., in mixtures of heavy and light water and in pure light water

POLAROGRAM NO.	$\overset{x}{D_2O}$	$\pi_{\frac{1}{2}}-\pi'_{\frac{1}{2}}$ (OBSERVED)	b	[illegible] i	$\pi_{\frac{1}{2}}-\pi'_{\frac{1}{2}}$ (CALCULATED)
		volts			*volts*
12	0.996	0.087	0.113	8.33	0.081
15	0.986	0.078	0.111	7.60	0.077
16	0.946	0.063	0.111	4.80	0.063
17	0.765	0.031		2.50*	0.035
18	0.498	0.015	0.104	1.41	0.017
33	0	0	0.102	1.07	

* Value interpolated from the graph.

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[2] In the theoretical discussion which follows the reader must distinguish clearly between the process of "deposition (or discharge) of hydrogen ions," which means the cathodic formation of atomic hydrogen in the nascent state, and the evolution of hydrogen, which means the total process of hydrogen molecule formation.

The polarographic results of Novák (14; see also figure 1) show that the deposition of thallous and zinc ions proceeds in heavy water at slightly more positive potentials than in light water Heyrovský (11) suggests that this is also the case for deuterium ions and for hydrogen ions and that the rate of formation of molecular deuterium from nascent deuterium is slower than that of hydrogen. Electrolytic hydrogenation which does not include molecule formation (e.g. the electroreduction of fumaric and maleic acids in acid solution) proceeds at the dropping mercury electrode reversibly without overvoltage. A somewhat greater positive potential is obtained in heavy water than in light water for such processes. On the

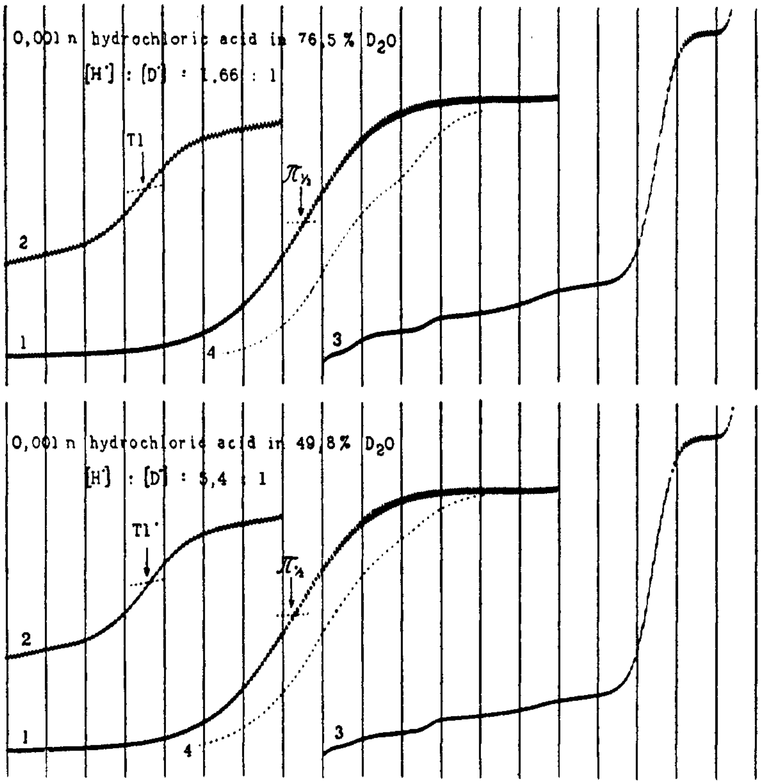

FIG. 2. Polarographic curves of 0.001 *N* hydrochloric acid. Upper polarogram: in a mixture of 76.5 per cent heavy water and 23.5 per cent light water. Lower polarogram: in a mixture of 49.8 per cent heavy water and 50.2 per cent light water. Curve 1, with sensitivity 3/50 from 1.3 volts E.M.F.; curve 2, with sensitivity 1/2 from 0.35 volt E.M.F.; curve 3, with sensitivity 3/50 from 0 volt; curve 4, expected, if deposition potentials of isotopes were different.

other hand, the electroreduction of hydrogen peroxide takes place in an alkaline solution in heavy water at a potential which is 87 millivolts more negative than in light water. This must be due to the process of discharge of deuterium ions from alkaline solution and suggests that the ion product constant of deuterium oxide is responsible for the large overvoltage in this case.

The above considerations led Heyrovský (11) to the following theory of overvoltage in light and heavy water and to the deduction of the electrolytic separation coefficients of the hydrogen isotopes.

Hydrogen isotopes are discharged reversibly and at the same potential, forming at the mercury cathode highly active amalgams of atomic hydrogen, potentials of which are given by the following equation:

$$\pi_{\mathrm{H}} = -RT/F \log \frac{P_{\mathrm{H}}}{[\mathrm{H}^+]} k = -RT/F \log \frac{P_{\mathrm{D}}}{[\mathrm{D}^+]} k = -RT/F \log \frac{P_{\mathrm{H}} + P_{\mathrm{D}}}{[\mathrm{H}^+] + [\mathrm{D}^+]} \tag{2}$$

in which P_{H} and P_{D} denote the activities of atomic hydrogen and atomic deuterium at the cathode. (Drucker (4) has shown recently that the reversible electrode potentials of hydrogen and of deuterium are nearly identical.)

The rate of formation of molecular hydrogen by combination between atoms is very slow on a mercury surface, so that the rate is determined by the reaction (10)

$$\mathrm{H} + \mathrm{H}^+ \rightarrow \mathrm{H}_2^+$$

The subsequent neutralization of the particle H_2^+ by an electron at the cathode is supposed to be very rapid. The magnitude of the current is proportional to the product $P_{\mathrm{H}}[\mathrm{H}^+]$. In an acid solution of light and heavy water

$$i = k[P_{\mathrm{H}} + P_{\mathrm{D}}]\,([\mathrm{H}^+] + [\mathrm{D}^+])$$

To express the kinetic activity of hydrogen ions in mixtures of light and heavy water, let us use the Grotthuss idea of constant interchange of hydrogen ions with water. Water molecules dissociate at a rate which must be equal to that of the rate of recombination of their ions. The latter is given by the product

$$k'([\mathrm{H}^+] + [\mathrm{D}^+])([\mathrm{OH}^-] + [\mathrm{OD}^-])$$

where k' is independent of the composition of the mixture, as it is governed only by the electrostatic properties of the isotopic ions. The above product is equal to the sum of the four ionic products of light and heavy water, which in the mixture is equal to

$$K_1C_{H_2O} + K_1'C_{HOD} + K_2'C_{HOD} + K_2C_{D_2O} = a$$

where C_{H_2O}, C_{HOD}, and C_{D_2O} denote mole fractions of the species H_2O, HOD, and D_2O, so that

$$C_{H_2O} + C_{HOD} + C_{D_2O} = 1$$

a denotes the rate of dissociation of water molecules in the mixture. Then

$$k''a([H^+] + [D^+])$$

expresses the rate of exchange of hydrogen ions in the mixture, and this is the kinetic reactivity with which they impinge on the cathode interface. Therefore in the kinetic formula for the magnitude of current, $k''a$ must be substituted for k, and

$$i = k''a(P_H + P_D)([H^+] + [D^+])$$

Correction for the adsorption of freshly formed hydrogen molecules at the cathodic interface by the theory of Langmuir leads to

$$i = k''a(P_H + P_D)([H^+] + [D^+])/(1 + \omega i)$$

Substitution in equation 2 gives

$$\pi = 2RT/F \log ([H^+] + [D^+]) - RT/F \log [i(1 + \omega i)/a] + K$$

which is the general formula of overvoltage for any mixture of light and heavy water.

The difference in overvoltage in pure water and in pure deuterium oxide of the same acidity is accordingly

$$\pi - \pi' = RT/F \log \frac{a_1}{a_2} \cdot \frac{1 + \omega_2 i}{1 + \omega_1 i}$$

According to Schwarzenbach, Epprecht, and Erlenmayer (15) $a_1 = 10^{-14}$, $a_2 = 0.185 \times 10^{-14}$, $\omega_1 i$ from the coefficient 0.012 is 1.07, and $\omega_2 i$ from the coefficient 0.113 is 8.33. Hence we calculate

$$\pi - \pi' = RT/F \log \frac{10^{-14}}{0.185 \times 10^{-14}} \cdot \frac{1 + 8.33}{1 + 1.07} = 0.081 \text{ volt}$$

The observed value is 0.087 volt. It should be mentioned that the only results of overvoltage in deuterium oxide published besides those discussed here are the data of Bowden and Kenyon (2). They obtained in 0.1 *m* deuterium sulfate a difference of 130 millivolts from that in light water, while the coefficient, b, in heavy water $= 2RT/F = 0.116$ volt, just as in light water. The latter value is in perfect agreement with the theory given here for stable electrodes. The difference of 130 millivolts, although much larger than that observed polarographically, is quite compatible with the formula in view of the great increase of adsorption, ω, at a stable mercury electrode.

The agreement between the overvoltage differences calculated and observed in mixtures of heavy and light water, as shown in table 1, is still better. The concentration of HOD had to be calculated. Equations worked out by Heyrovský (11, 12) in his original publication on the overvoltage of heavy water give

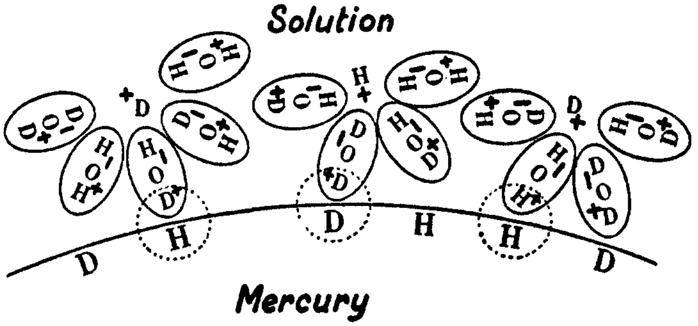

Fig. 3. The slowest step in the formation of molecules of hydrogen evolved at a cathode under overvoltage. The interaction of the electrodeposited hydrogen and deuterium atoms with water molecules in a mixture of light and heavy water to form the particles H_2^+, HD^+, and D_2^+.

$$[H^+][OD^-]/C_{HOD} = K_1' = 0.5 \times 10^{-14}$$

$$[D^+][OH^-]/C_{HOD} = K_2' = 0.0925 \times 10^{-14}$$

$$K_1K_2/K_1'K_2' = C_{HOD}/C_{H_2O} \cdot C_{D_2O} = 4$$

$$C_{HOD} = 2x(1 - x);\ C_{H_2O} = (1 - x)^2;\ \text{and}\ C_{D_2O} = x^2$$

for any mixture made up of x volumes of heavy water and $(1 - x)$ volumes of light water. From the above picture that molecules of hydrogen are formed by the interaction of deposited atoms with hydrogen ions of the solution (see figure 3) the electrolytic separation coefficient of the hydrogen isotope, α,

$$(H)/(D) = \alpha(1 - x)/x$$

may be derived. (H) and (D) denote the numbers of hydrogen and deuterium atoms in the electrolytically evolved hydrogen. Their ratio must be proportional to

$$(2i_{H_2} + i_{HD})/(2i_{D_2} + i_{HD})$$

where i_{H_2}, i_{HD}, and i_{D_2} are the components of the current which caused the evolution of the molecules H_2, HD, and D_2, respectively. The rate of formation of hydrogen molecules, which is proportional to i_{H_2}, is given by

$$d(H_2)/dt = i_{H_2} = kP_H([H^+] + [D^+])\cdot(K_1C_{H_2O} + K_1'C_{HOD})$$

since the rate at which isotopic ions exchange with light hydrogen ions resulting from H_2O and HOD dissociations is given by the product of the last two terms in brackets. Similarly we obtain

$$i_{D_2} = kP_D([H^+] + [D^+])\cdot(K_2'C_{HOD} + K_2C_{D_2O})$$

$$i_{HD} = kP_H([H^+] + [D^+])\cdot(K_2'C_{HOD} + K_2C_{D_2O}) + kP_D([H^+] + [D^+])(K_1C_{H_2O} + K_1'C_{HOD})$$

$$i_{H_2} = kP_H([H^+] + [D^+])(K_1C_{H_2O} + K_1'C_{HOD})$$

Substituting into the relation

$$(2i_{H_2} + i_{HD})/(2i_{D_2} + i_{HD}) = \alpha(1 - x)/x$$

we obtain

$$\alpha = 2K_1'/K_2 = K_1/2K_2' = K_1/K_2 = 5.4$$

This result has been derived without considering the adsorption of hydrogen molecules at the cathode and hence is valid only for very small current densities. For larger currents the factor $1/(1 + \omega i)$ must be introduced; this changes the value of α.

In practically pure light water we find

$$\alpha_{H_2O} = \frac{K_1}{K_2}\cdot\frac{1}{1 + \omega i} = 2.7$$

and in practically pure heavy water

$$\alpha_{D_2O} = \frac{K_1}{K_2}(1 + \omega i) = 50$$

In a 50 per cent mixture

$$\alpha_{HOD} = 7$$

The separation coefficient on mercury in mixtures containing mainly light water has been found to lie between 2.7 and 2.8 and is well known to increase considerably at very high concentrations of heavy water.

It should be emphasized that the evolution of hydrogen discussed in the present article is that obtained in polarographic studies with very small current densities, not more than 0.001 ampere per square centimeter, so that no visible evolution of bubbles takes place. The cathodic interface is, therefore, probably not supersaturated with molecular hydrogen. When bubbles become visible, no strict rules may be expected to hold.

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