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On the Overvoltage Theory of H. Eyring

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In a recent paper, Eyring, Glasstone and Laidler[1] developed a new overvoltage theory which, in my opinion, is open to serious objections. The present note is concerned with a brief consideration of the most essential of these.

Eyring proceeds from the theory of the retarded discharge, in which, however, he introduces a number of changes.

1. Eyring assumes that in all cases the reacting particle is a water molecule, whence, in his opinion, there follows the experimentally observed independence of the overvoltage upon the composition of the solution. Such a view, in accordance with which the overvoltage is independent of the hydrogen ion concentration in the solution, is shared by other authors[2], though it contradicts experimental data beyond all doubt. It is exactly in the simplest case from the theoretical point of view, that is, for solutions containing an excess of an indifferent electrolyte, that the overvoltage on mercury, upon decreasing the hydrogen ion concentration ten-fold, does not remain constant but increases by ca. 0.058[3]. Here, however, I will not go into a detailed consideration of this fact, since in reality Eyring's assumption leads to an entirely different result. If the reacting particle is a molecule of water, it is the potential of the cathode and not the overvoltage that remains constant with a change in the composition of the solution. The overvoltage, on the

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[1] Eyring, Glasstone and Laidler, J. Chem. Phys., 7, 1053 (1939).

[2] Bowden and Agar, Ann. Rep. Chem. Soc., **35**, 90 (1938).

[3] Lewina and Sarinsky, Acta Physicochimica URSS, 7, 486 (1937). Herasymenko and Šlendyk, Z. physik. Chem., **A 149,** 123 (1930).
According to the data of Wagner and Traud, Z. Elektrochem., **44,** 39 (1938), this shift is less (about 0.025).

other hand, defined as the difference between the potential of a reversible hydrogen electrode in the same medium and the potential of the cathode, should change as a result of a change in the former. The independence of the potential of the cathode upon the hydrogen ion concentration was actually observed by Lukowzew, Lewina and Frumkin[4] for the nickel electrode in alkaline solutions over a certain concentration interval. On the basis of this result, these authors arrived at the conclusion that the reacting particle in these solutions is a water molecule. From the constancy of the cathodic potential it follows, of course, that the overvoltage decreases with an increase in the concentration of the alkali.

Let V denote the potential difference between the cathode and the solution, and η the overvoltage. Then we obtain the following relations for the dependence upon the concentration at constant current strength:

(a) Hg in acid solutions in the presence of an indifferent electrolyte:

$$V = \text{const.} + \frac{2RT}{F} \ln [\mathrm{H}^{\cdot}]; \quad \eta = \text{const.} - \frac{RT}{F} \ln [\mathrm{H}^{\cdot}]; \tag{1}$$

(b) Hg in dilute acid solutions in the absence of an indifferent electrolyte:

$$V = \text{const.} + \frac{RT}{F} \ln [\mathrm{H}^{\cdot}]; \quad \eta = \text{const.}; \tag{2}$$

(c) Ni in alkaline solutions:

$$V = \text{const.}; \quad \eta = \text{const.} + \frac{RT}{F} \ln [\mathrm{H}^{\cdot}]. \tag{3}$$

The hypothesis which Eyring makes does not lead to equation (2), as he assumes, but to equation (3). This follows unambiguously from the very nature of his conclusion. A kinetic derivation in which the reverse reaction of the ionization of molecular hydrogen is not taken into account, in general cannot give a relation between the current strength and the overvoltage, but only between the current strength and the potential of the cathode, since the thermodynamic constants which characterize the product of the reaction — molecular hydrogen — must be present in the expression for the overvoltage. Since, in accordance with Eyring's assumption, the concentration of the reacting particle — the water molecule — is the same in all solutions, the relation obtained by calculation can only connect the current strength with the value of the cathodic potential, *i. e.*, must lead to equation (3), which is never obeyed in acid solutions where discharge of course actually occurs not on account of water molecules, but on account of hydrogen ions. The different nature of the result obtained by Eyring is explained by the fact that he assumes the interface potential in the double layer at the reversible potential to be always equal to zero. It is evident that if this hypothesis happens to be correct for some one concentration of hydrogen ions, it cannot hold for all the rest. The independence of the entropy of activation in acid solutions upon the nature of the metal in the case of mercury, gallium, Wood's metal, palladium and platinum, which follows from Eyring's computations and points to a similar mechanism of the process, deserves attention.

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

2. The second change which Eyring introduces into the theory of the retarded discharge consists in the following: According to Eyring the surface of a metal in aqueous solutions is covered with a monomolecular layer of water molecules which are firmly bound to the metal in the form of H-atoms and OH-groups. The slow stage in the discharge of a hydrogen ion is the transfer of a proton from a water molecule in the solution to a molecule bound to the electrode. The assumption of the existence of such a chemisorbed layer of water on a metal is, however, in contradiction with experimental data on the adsorption of water on metals. As is known, water vapour is but extremely weakly adsorbed on the surface of mercury, and in the case of platinum too it is only possible to observe reversible van der Waals adsorption of water[5].

3. The third special point in Eyring's theory is his explanation of the fractional value of the coefficient $\alpha = 0.5$ which appears in the formula for the current strength I:

$$I = I_0 e^{-\frac{\alpha VF}{RT}}.$$

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[5] Cassel u. Salditt, Z. physik. Chem., **A 155**, 321 (1931). Schaaff, Z. physik. Chem., **B 26**, 413 (1934).

According to Eyring, the value of the coefficient α, which is equal to 0.5, points to the fact that the decrease in potential between the initial and activated states amounts to one-half of the total decrease in potential — an assumption which was also made by Erdey-Gruz and Wick[6].

Horiuti and Polanyi[7], on the basis of the theory of the transition state, indicated the possibility of a different interpretation of the fractional value of α, connecting it with the problem of the relative position of the potential curves of the hydrogen ion and the adsorbed hydrogen atom. It is my opinion that a correct theory should take into consideration both effects simultaneously.

A number of other conceptions advanced in the work of the American authors, regarding, for example, the mechanism of the action of surface-active substances, the oxygen overvoltage, etc., are also extremely debatable. I confine myself, however, only to the above remarks.

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[6] Erdey-Gruz u. Wick, Z. physik. Chem., **A 162**, 53 (1931).

[7] Horiuti and Polanyi, Acta Physicochimica URSS, **2**, 505 (1935).