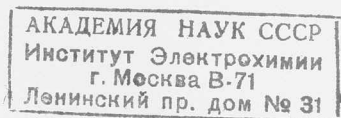


On the Mechanism of Hydrogen Electrode Process: A Reply to Prof. Horiuti

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[Introduced by Juro HORIUTI.]

I shall deal separately with the metals mercury, nickel, and platinum:

1. *Mercury.* In order to explain the fact that τ (using the notations of Horiuti) is ca. 0.5 on the basis of the "electrochemical" theory of Horiuti, we must assume that the ratio $n_{\text{HH}^+}/n_{\text{H}^+}$ is large compared with unity. In this case the experimental value of the capacity of the mercury electrode in acid solutions would be increased twice as compared with the capacity in neutral or alkaline solutions where the double layer is formed by normal cations like K^+ or Na^+ . This follows immediately from Eqs. (4) and (5) of the paper of Hirota and Horiuti.⁽¹⁾ Solving simultaneously Eqs. (3), (4), and (5) of this paper we obtain a relation between the "total charge" E and the polarization $-\eta$. Using the value $Z = 10^{15}$, the values of K , $w_{\text{HH}^+}^{\text{H}}$, $w_{\text{HH}^+}^{\text{HH}^+}$ and C as given by Hirota and Horiuti, and making use like Hirota and Horiuti of the assumption that $E = 0$ at the potential of the normal hydrogen electrode⁽²⁾ we find that according to the "electrochemical" theory the electrode capacity had to double its normal value of 19 microfarads between $\eta = -0.6$ and $\eta = -0.75$. Hirota and Horiuti obtain from the same equations another relation between the charge and the polarization. This is expressed by the dotted curve on Fig. 1 of their paper, which shows in the same potential interval a maximum and a minimum. I think that their

(1) *Bull. Chem. Soc. Japan*, **13** (1938), 228. Any experimental determination of the capacity gives the derivative of what Hirota and Horiuti call "the total amount of charge E " by the potential, $\frac{\partial E}{\partial \eta}$.

(2) The latter is incorrect, the zero point of E corresponding really to a polarization of ca. 0.57 against a decinormal calomel electrode, but this shift of the zero point does not influence very much the results of the calculations.

calculations must contain some error, as it follows directly from their Eqs. (4) and (5) that E must steadily increase with increasing $-\gamma$:

$$E = -C(\gamma + \gamma_0) + \varepsilon n_{\text{HH}^+}.$$

The experimental determination of the capacity (Borissowa and Proskurnin) and of the charge (Barclay and Butler, *Trans. Farad. Soc.*, **36** 1940, 130) of the mercury electrode in acids reveal no signs of the appearance of HH^+ in the overvoltage region. In fact the "total charge" of a mercury electrode in the overvoltage region, for instance at a polarization of 1 V against a calomel electrode, is within the limits of experimental error identical with the charge observed at the same potential in a neutral solution of KCl.⁽³⁾ This is demonstrated with still greater exactness by the coincidence of the cathodic branches of electrocapillary curves in equally concentrated solution of HCl and KCl. The surface concentration of HH^+ ions, if they really exist at the mercury solution interface, must be therefore very small as compared with the surface concentration of H^+ . Under these conditions it is impossible to derive from the "electrochemical" theory the correct value of $\tau \sim 0.5$ and this theory must be therefore rejected. Horiuti quotes unpublished measurements of Mituya who observed an increase of τ with current densities as small as $10^{-9} \sim 10^{-11}$ amp/cm². The measurements of overvoltage according to ordinary methods with current densities below 10^{-8} present exceedingly great difficulties and

(3) Hirota and Horiuti carried some measurements of the charge of cathodically polarized dropping mercury and obtained results which from their point of view confirm the theoretical curve of Fig. 1 of their paper. Their experimental curve giving the relation between charge and polarization has an anomalous form never observed by other authors. I should give the following tentative explanation for the appearance of this anomaly. The measurements have been carried out as shown by Fig. 2 on p. 232 of their paper in a vessel from which air was not excluded. Under these conditions a "polarographic maximum" due to the reduction of dissolved oxygen is observed with a dropping mercury electrode. As the current in the "polarographic maximum" is not independent of the rate of dropping, the procedure used to separate the faradaic and the non-faradaic currents by Hirota and Horiuti could not be effective. This explanation is proposed of course only as a tentative one, but it is certain that the charge measurements given in the paper of Hirota and Horiuti are vitiated by some experimental error. Namely, the zero value of the charge E in $N/10$ HCl would otherwise be observed as it is known from innumerable experiments with dropping electrodes at a polarization of 0.57 against a decinormal calomel electrode, whereas the experimental value of Hirota and Horiuti is ca. 0.16 V.

Horiuti does not mention how these have been overcome. According to Bowden and Grew (quoted by Bowden and Agar, *Ann. Rep. Chem. Soc.*, **35**, 96) who used a completely enclosed cathode and polarized it through the glass walls the ordinary theoretical relationship is obeyed down to currents of 10^{-10} amp/cm².

Moreover an increase of τ at low current densities cannot be considered as an argument in favour of the interpretation given by Horiuti. This increase as it follows from the theory developed by Frumkin (*Acta Physicochimica URSS*, **7**, 1937, 782) would be quite compatible with the assumption that at higher current densities the slowest step is the $H^+ \rightarrow H$ reaction.

2. *Nickel.* The overvoltage phenomena observed with nickel electrodes are rather complex and I do not think there exists at the present moment a theory which could be applied to the behaviour of nickel in all solutions. It is not my aim to discuss the whole of this question in this paper as I am awaiting the results of some experiments which are carried out at the present moment in the Karpov Institute and I shall confine myself to one side of the problem only. Lukowzew, Lewina, and Frumkin,⁽⁴⁾ as well as Legran and Lewina⁽⁵⁾ have found that the overvoltage strongly depends on the concentration of the solution. According to Horiuti this effect is an apparent one, and is caused by the unequal distribution of the current on the surface of the electrode in solutions of low concentrations. It is easy to show that this conclusion is incorrect. Let us denote by r the resistance of a tube of flow which envelops, a surface element of the electrode of a definite small area σ starting from the orifice of the side tube; r will of course vary with the position of this element on the electrode surface. Although it is difficult to evaluate the distribution of the current on a cathode of an irregular shape, we may estimate that in the case of the apparatus used by us, the ratio $r_{\max} : r_{\min}$ certainly did not exceed 4. Even at the extreme case of a poorly conducting solution the ratio between the maximum and the minimum current density on the electrode surface could not exceed the same value of 4, and the ratio between the maximum and the average current density 2 or 2.5. The latter ratio represents certainly an upper limit. As the potential of the electrode was measured at

(4) *Acta Physicochimica URSS*, **11** (1939), 21.

(5) *Ibid.*, in course of publication.

a point where the current density reaches approximately its maximum value, whereas the current density was calculated assuming a uniform distribution, the upper limit of the possible error in the overvoltage measurement is ca. $0.10 \log_{10} 2$ or 0.030 V. The actual lowering of overvoltage observed with increasing concentration is according to the data of Lukowzew and Lewina and of Legran and Lewina at least 0.12 both in acid and alkaline solutions, even if we confine ourselves to concentrations below $N/1$. We obtain still more convincing results if we calculate the possible error for definite values of the current density. For instance, the difference between the overvoltages in 0.013 N and in 0.15 N HCl with a current density of 10^{-5} A/cm² amounts to 0.065. The error due to the unequal distribution of current may amount in the more dilute solution to 3~4 mV; and in the more concentrated one it is ca. ten times smaller. Horiuti arrived at the conclusion that the influence of the unequal distribution of current must have been large under the conditions of our experiments choosing for his calculations the most dilute solution ($3 \cdot 10^{-4}$ N HCl) among those which were investigated. Actually, the results obtained with this solution have not been used in drawing the theoretical conclusions in the paper of Lukowzew, Lewina, and Frumkin.

According to Horiuti there exists a relation between the conductivity of our solutions and the observed current density at a given overvoltage, which points to an ohmic origin of the effects observed. I think that the curves drawn by Horiuti refute by themselves this suggestion. As the current density observed with the same solution increases ca. ten times when we pass from $\eta = 0.15$ to $\eta = 0.25$, the bend on the curves drawn by Horiuti should be shifted with increasing overvoltage towards higher values of $\log \kappa$. Between $\eta = 0.15$ and $\eta = 0.25$ the shift should amount to one unity. In reality the position of the bend as shown by the drawing remains unchanged. This excludes an ohmic origin of the effect. In the case of LaCl_3 it was shown by special experiments that the effect cannot depend on a change of conductivity as the addition of an equivalent amount of KCl leaves the overvoltage unchanged. To close this section I shall mention that the overvoltage measurements of Lukowzew, Lewina, and Frumkin have been checked recently by Lukowzew who determined the overvoltage at very low current densities in the neighbourhood of the reversible potential under conditions when the influence of the

ohmic drop was certainly nil, and by Lewina who measured in the same solutions the kinetics of the exchange reaction with D_2 . The results of both investigations which shall soon be published in *Acta Physicochimica* are in a good agreement with the data obtained earlier and show the same strong decrease of overvoltage with increasing alkalinity. The reality of this effect seems to me therefore beyond any doubt. The real reason for the discrepancy between our data and the data of Horiuti and his collaborators consists probably in a different pretreatment of the nickel surface, which yields a surface with quite different properties. This side of the question needs further investigation.

3. *Platinum.* The kinetics of the discharge of hydrogen ions on platinum has been investigated recently in this laboratory by Dolin and Ershler with the help of an entirely new method. Their results will soon be published in *Acta Physicochimica*. It appears from this investigation that the rate determining step for the lower cathodic polarizations is (using the notations of Horiuti) $\frac{H^+}{H} \rightarrow \frac{H}{H}$ and for the higher polarizations $H^+ \rightarrow H$.

These conclusions are in some respects similar to the conclusion of Horiuti and Ikusima,⁽⁶⁾ but I do not think that the molecular hydrogen ion $\frac{H}{H^+}$ which plays an important rôle as an intermediate step in the scheme of Horiuti and Ikusima really exists on the surface of the platinum electrode. As shown by many authors who have investigated the adsorption of electrolytes on the platinum electrode⁽⁷⁾ the hydrogen ions in the double layer of this electrode are readily exchanged against other cations. This behaviour would be very difficult to explain if these ions were present in the form of H_2^+ ions.

(6) HORIUTI and IKUSIMA: *Proc. Imp. Acad. Tokyo*, **15** (1939), 39.

(7) FRUMKIN and DONDE: *Ber. Dtsch. chem. Ges.*, **60** (1927), 1816; KOLTHOFF and KAMEDA: *J. Am. Chem. Soc.*, **51** (1929), 1888; SLYGIN, FRUMKIN, and MEDWEDOWSKY: *Acta Physicochimica URSS*, **4** (1936), 911; FRUMKIN and SLYGIN: *Ibid.*, **5** (1936), 819.

