The Mechanism of the Hydrogen Electrode Process. II. The Electrochemical Mechanism. The Existence of Hydrogen Molecule Ions on the Surface of the Electrode.

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Okamoto and one of the present authors⁽¹⁾ have previously suggested that it was the neutralization of hydrogen molecule ion adsorbed on the electrode-solution interface which governed the rate of the hydrogen electrode process on the mercury electrode. The proposed mechanism which was called the electrochemical mechanism has since been worked out and established by formulating the rate of the governing reaction by the statistical mechanical method, by deriving therefrom quantitative conclusions on the behavior of the hydrogen electrode process and by confirming latters by experimental data.⁽²⁾ Especially Tafel's empirical relation⁽³⁾ between electrolytic current i and the overvoltage η, i.e.

$$\log i = -0.5\frac{F\eta}{RT} + \text{const.}\,,$$

and its range of validity was quantitatively derived from the theory.⁽²⁾

The present article deals with an experimental confirmation of one of direct conclusions from the theory i.e. the experimental verification of the existence of hydrogen molecule ion at the electrode-solution interface.

From the premise that the neutralization of hydrogen molecule ion is the slowest step it follows that hydrogen ions $(H^+)_{ads.}$ and hydrogen molecule ions $(HH^+)_{ads.}$ adsorbed on the interface must be at the partial equilibrium with each other and with ions H^+ in the bulk of the solution,

or $$(HH^+)_{ads.} \rightleftarrows (H^+)_{ads.} + H^+ + \ominus\,,$$

where $\ominus$ denotes metal electrons. Assuming the simple mass action law the electrical work required to transpose one mol of the reactant to the resultant is given by

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(1) Horiuti and Okamoto, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **28** (1936), 231.

(2) Hirota and Horiuti, to be published in a near future.

(3) Tafel, *Z. physik. Chem.*, **34** (1900), 200; **50** (1905), 649.

$$F\eta = -RT \ln \frac{n_{\mathrm{HH}^+}}{n_{\mathrm{H}^+} \cdot c_{\mathrm{H}^+}} + \text{const.} \qquad (1),$$

from the condition that the total work should vanish at the equilibrium, where n_{HH^+} and n_{H^+} are respective numbers of the adsorbed elementary systems per unit area of the interface and c_{H^+} the concentration of H^+ in the bulk of the solution. It follows from Eq. (1)

$$\frac{n_{\mathrm{HH}^+}}{n_{\mathrm{H}^+}} \propto e^{-\frac{F\eta}{RT}} \qquad (2),$$

i.e. n_{HH^+} increases with negative polarization rapidly compared with n_{H^+}. By a more detailed statistical mechanical calculation taking the mutual interaction of $(\mathrm{HH}^+)_{\mathrm{ads.}}$ among themselves and with H^+ into account, $\frac{n_{\mathrm{HH}^+}}{n_{\mathrm{H}^+}}$ assumes the form,

$$\frac{n_{\mathrm{HH}^+}}{n_{\mathrm{H}^+}} = \kappa e^{-\frac{F\eta + u^{\mathrm{H}^+}_{\mathrm{HH}^+} \cdot \frac{n_{\mathrm{H}^+}}{Z} - u^{\mathrm{HH}^+}_{\mathrm{H}^+} \cdot \frac{n_{\mathrm{HH}^+}}{Z} + u^{\mathrm{HH}^+}_{\mathrm{HH}^+} \cdot \frac{n_{\mathrm{HH}^+}}{Z}}{RT}} \qquad (3),$$

where κ is a constant independent of n_{HH^+}, n_{H^+} and of η.(4) Z is the

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(4) In a separate work which will be published in a near future (Reference 2), the present authors have formulated and evaluated the constant κ with the result:

$$\kappa = Q_{\mathrm{HH}^+} \Big/ Q_{\mathrm{H}^+} \cdot \sqrt{\frac{Q_{\mathrm{H}_2}}{n}} = 1.0 \times 10^{-6}.$$

n is the number of hydrogen molecules per unit volume of the hydrogen gas of the hydrogen electrode to which the potential η is referred and Q_{H_2} the summation of states of a free hydrogen molecule expressed by

$$Q_{\mathrm{H}_2} = \frac{(2\pi m_{\mathrm{H}_2} kT)^{\frac{3}{2}} 2\pi^2 I_{\mathrm{H}_2} kT}{h^5 \sinh \left(1 - \frac{x}{2}\right) \cdot \frac{h\nu_0}{2kT}} e^{-\frac{\varepsilon^0_{\mathrm{H}_2}}{kT}},$$

where m_{H_2} is the mass, I_{H_2} the moment of inertia, 6.21×10^{-21} g. cm.^{2}, ν_0 the harmonic frequency 4417.2 cm.$^{-1}$, x the anharmonicity constant 0.0297, and $\varepsilon^0_{\mathrm{H}_2}$ the potential energy at the equilibrium position −109.12 kcal., numerical values being due to Jeppesen (*Phys. Rev.*, **44** (1933), 165).

Q_{H^+} and Q_{HH^+} are summation of states of respective elementary systems housed between a mercury atom and a water molecule at the interface being expressed by

$$Q_{\mathrm{H}^+} = \int \frac{A^2}{h^2} \frac{1}{2} \left(\sinh \frac{h\nu_{\mathrm{H}^+}}{2kT} \right)^{-1} e^{-\frac{\varepsilon_{\mathrm{H}^+}}{kT}} d\sigma,$$

and

number of metal atoms per unit area of the metal surface and $u^{\mathrm{H}^+}_{\mathrm{HH}^+}$ is the potential exerted upon an adsorbed HH^+ by surrounding H^+ when $n_{\mathrm{H}^+}=Z$. $u^{\mathrm{HH}^+}_{\mathrm{HH}^+}$ and $u^{\mathrm{HH}^+}_{\mathrm{H}^+}$ have similar meanings. $u^{\mathrm{HH}^+}_{\mathrm{HH}^+}$, for instance, was calculated by summing up quantum mechanical repulsive potentials⁽²⁾ among HH^+ of interest and another HH^+ resting on one of surrounding metal atoms. Details of the calculation are left to the original paper.⁽²⁾ Numerical values thus obtained are

$$u^{\mathrm{HH}^+}_{\mathrm{HH}^+} = 0.35 \text{ e.v.}\,, \quad u^{\mathrm{H}^+}_{\mathrm{HH}^+} = u^{\mathrm{HH}^+}_{\mathrm{H}^+} = 0.09 \text{ e.v.}$$

From the above result the followings can be deduced for the variation of population of HH^+ and H^+ with increasing cathodic potential.

At a sufficiently low cathodic potential charged particles at the interface consist almost exclusively of H^+. As the cathodic polarization is gradually increased, a point is reached when n_{HH^+} is no more negligible compared with n_{H^+}. From simplified Eq. (2) one sees that at room temperature a raise of cathodic polarization by 0.2 volts is sufficient to convert the ratio $\frac{n_{\mathrm{HH}^+}}{n_{\mathrm{H}^+}}$ from 10^{-2} to 10^2. Taking the mutual interaction of HH^+ and H^+ into account according to Eq. (3) another effect is expected at this turning point which can be subjected to an experimental verification.

Replacing the interface with the simplified model of Helmholtz's double layer and neglecting the concentration of negative ions on the cathode, the charge of the condenser $\epsilon(n_{\mathrm{H}^+} + n_{\mathrm{HH}^+})$ and its potential $\eta + \eta_0$ are related to each other by the formula,

$$-C(\eta+\eta_0) = \epsilon(n_{\mathrm{H}^+}+n_{\mathrm{HH}^+}) \tag{4}$$

where η_0 is the absolute potential of the reference electrode, ϵ elementary charge and C the capacity of the double layer per unit area.

$$Q_{\mathrm{HH}^+} = \int \frac{\sqrt{2\pi I_{\mathrm{HH}^+} kT}}{h} \frac{1}{2^5} \prod_i^{1\ldots5} \left(\sinh \frac{h\nu_i}{2kT}\right)^{-1} e^{-\frac{\mathcal{E}_{\mathrm{HH}^+}}{kT}} d\sigma\,,$$

where $d\sigma$ is the elementary volume of the coordinate space of the water molecule's centre. Quantities in integrals, which are, in general, functions of σ, have the following meanings:

A : the phase integral of the motion of H^+ perpendicular to the axis through the centres of the mercury atom and the water molecule.

ν_{H^+} : the harmonic frequency of the vibration along the axis.

ν_i : the normal vibrational frequencies of the hydrogen molecule ion housed between the mercury atom and the water molecule.

I_{HH^+}: the moment of inertia of hydrogen molecule ion belonging to the single rotational degree of freedom around the $\mathrm{Hg-H_2O}$ axis.

$\mathcal{E}_{\mathrm{H}^+}$ and $\mathcal{E}_{\mathrm{HH}^+}$: the potential energies at equilibrium positions.

The total amount of charge required to create a unit area of new surface, E, is given by⁽⁵⁾

$$E = \epsilon (n_{\mathrm{H}^+} + 2n_{\mathrm{HH}^+}) \qquad (5).$$

When H^+ at the interface is replaced by HH^+ the charge required to create a unit area would increase by Eq. (5), the charge of the condenser being assumed to remain constant. But since an increase of HH^+ is associated with more or less decrease of H^+ due to repulsion, the increase in E due to neutralization to form H^+ might possibly be overcompensated by the decrease of the number of adsorbed H^+. Assuming C to be 19 microfarads according to Frumkin,⁽⁶⁾ E could be expressed as the function of η by solving Eqs. (3), (4), and (5) simultaneously as shown by the dotted line in Fig. 1. The ordinate gives the number of elementary charge required to create a unit area and the absissa polarization referred to the decinormal calomel electrode. As was expected the curve shows a marked dip at the polarization where $(H^+)_{\mathrm{ads.}}$ are replaced by $(HH^+)_{\mathrm{ads.}}$.

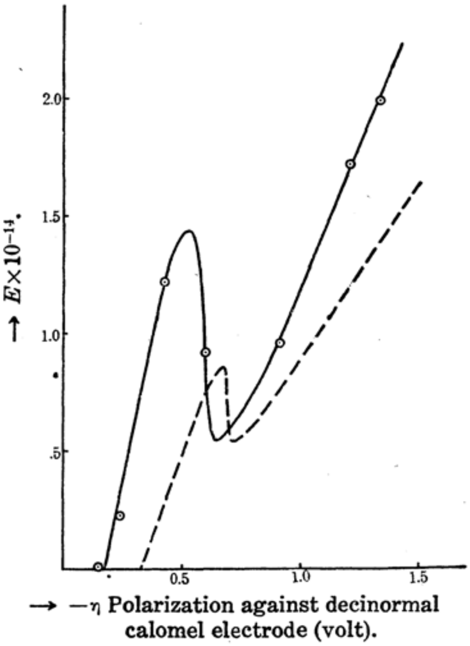

Fig. 1.

The above theoretical conclusion was subjected to an experimental investigation by the following procedure. Cathodically polarized mercury was slowly dropped into N/10 HCl solution, the current flowing was followed by an oscillograph and analysed to obtain the amount of charge E experimentally.

Fig. 2 shows the apparatus used. B is a burette of 60 cm. length and of 0.8 cm. diameter through its lower orifice of 0.3 mm. width mercury being dropped into the solution. S is a big mercury surface against which mercury drop is polarized at a constant potential. R is the switch which allows us to vary the potential stepwise. Solutions are combined with siphons packed with glass wool. The rate of dropping was varied from

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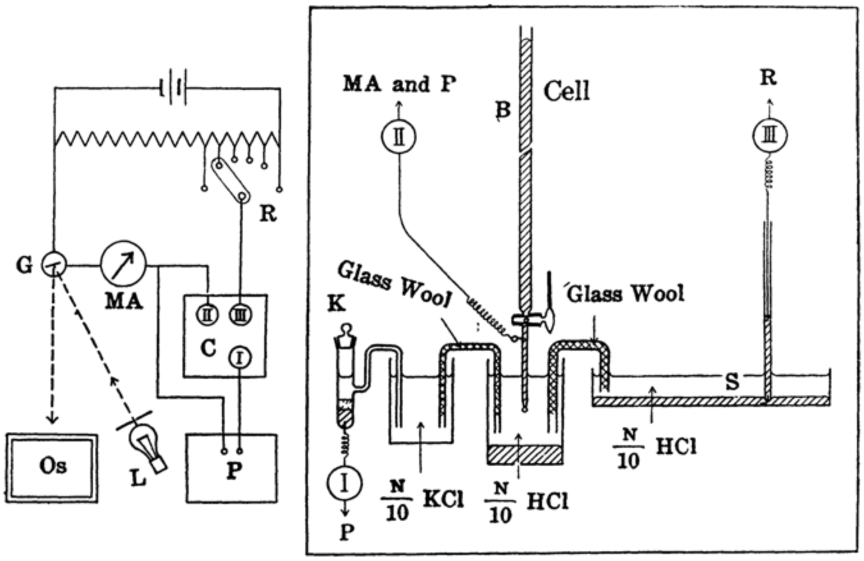
(5) HH^+ requires another elementary charge for neutralization.

(6) Frumkin, *Z. physik. Chem.*, A, **164** (1933), 121.



MA : Microammeter. Os : Oscillograph. P : Potentiometer. G : Galvanometer.
C : Cell. K : Decinormal calomel electrode. L : Light source. R : Switch.

Fig. 2.

once per 2 sec. to once per 10 sec. Full size of a drop as determined by weighing was 0.0020 c.c. which was found independent of the rate of dropping but slightly of the polarization. Polarization was varied from -0.15 to -1.35 volts against decinormal calomel electrode at an interval of about 0.2 volts.

An oscillograph record was taken at a constant dropping rate but raising the polarization stepwise for every two or three drops. Here are shown two such ones taken both at 19°C. and respectively at the dropping rate once per 2.2 sec. and once per 7.1 sec. One sees that the current increases rapidly at first when a drop begins to grow but more and more slowly afterwards until the drop leaves the orifice when the current returns to the zero line to start a new course again.(7) Irregular discontinuities on the figure are due to switching from a polarization to another.

The record thus obtained being apparently contaminated with steady electrolytic currents the quantity of charge E in question was separated from the latter by the following analysis. The observed current at a given polarization and at a certain definite drop magnitude was plotted against the rate of increase of drop's area. The inclination of the straight line

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(7) Instantaneous minus value of the current is due to the momentary diminution of the area after the mercury drop has been torn off at the orifice.

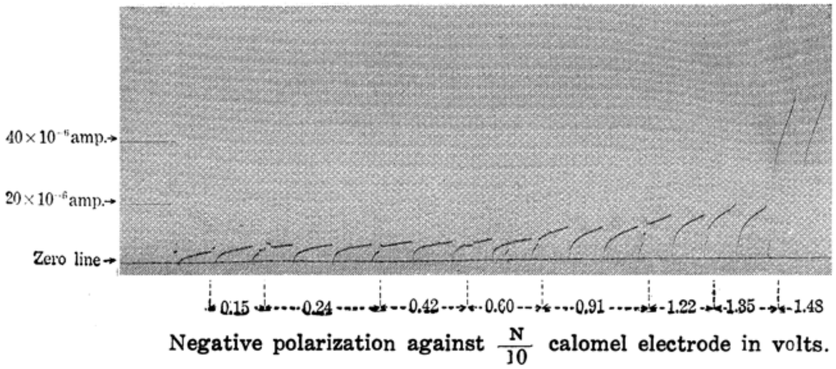

Fig. 3. Oscillograph record I. Dropping rate: Once per 7.1 sec.

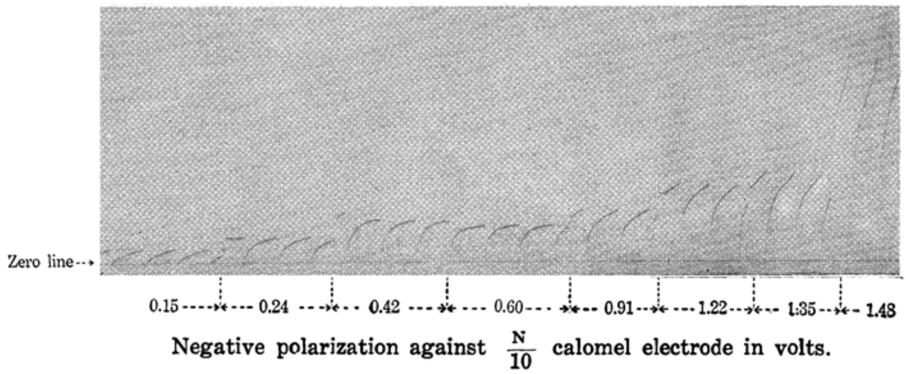

Fig. 4. Oscillograph record II. Dropping rate: Once per 2.2 sec.

gives the charge in question while its intercept at zero rate of increase of drop's area the electrolytic current which is a constant at a given polarization and at a definite surface area.

Experimental value of charge E expressed by the number of elementary charges per unit area was plotted against the polarization and shown by the full line in Fig. 1, the drop area being 0.159 cm.^{2} throughout.

One sees that the experiment satisfactorily confirms the strong dip on the theoretical curve derived from the claimed existence of hydrogen molecule ion at the interface. Quantitative disagreement would rather be shifted to the inaccuracy of *a priori* quantum mechanical calculation of interatomic potentials.

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