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ON THE DISCONTINUOUS CHANGE WITH ELECTRODE POTENTIAL OF CHARGE REQUIRED TO INCREASE UNIT AREA OF HYDROGEN ELECTRODE OF MERCURY.

By

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(1). Introduction.

T. HONDA[1] has observed a discontinuous change of electric charge required to build up new surface of hydrogen electrode of mercury kept at a definite potential as shown in Fig. 1. Hydrogen electrode process on mercury proceeds acording to HORIUTI et al[2]. through the electrochemical mechanism,

$$2H^{+}(b) \rightleftarrows \left.\begin{matrix} 2H^{+}(a) \\ + \\ 2\varepsilon \end{matrix}\right\} \rightleftarrows H_2^{+}(\mathrm{a}) + \varepsilon \mathrel{\wedge\!\!\!\!\rightarrow} H_2, \qquad (1)$$

i. e. through the sequence, adsorption of hydrogen ion $H^{+}(b)$ in solution to form adsorbed ion $H^{+}(a)$, the combination of the latter with metal electron ε on the electrode resulting in adsorbed hydrogen-molecule-ion $H_2^{+}(a)$ and its neutralization to complete hydrogen molecule; the latter process determines the rate leaving the former two in partial or preliminary equilibrium.

The $H^{+}(a)$ and $H_2^{+}(a)$ being two possible intermediates adsorbed on the electrode surface in partial equilibrium with each other and with $H^{+}(b)$, it might be suggested with HONDA that the observed discontinuity has to do with the abrupt change of coverage along with the variation of the electrode potential, from $H^{+}(a)$ rich to $H_2^{+}(a)$ rich one, the latter being half-neutralized state of $2H^{+}(a)$.

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[1] T. HONDA: "Syokubai", Hokkaido Univ., No. 3, 39. (1948), (Printed in Japanese).

[2] J. HORIUTI &G. OKAMOTO: Sci Pap. I.P.C.R. Tokyo, 28, 231. (1936)
J. HORIUTI, T. KEII & K. HIROTA: J. Res. Inst. Catalysis, Hokkaido Univ. 2, No. 1, 1. (1951)

It was observed by HORIUTI and MITUYA[3] however that the curve of logarithm of the cathodic current i versus electrode potential η has a break at $\eta = -0.035$ volt as shown in Fig. 2, Tafel's constant $-\frac{RT}{F}\frac{\partial \ln i}{\partial \eta} = \tau$ (F: Faraday) being 1.3 or 0.3 above or below the point respectively.

According to the theoretical result arrived at by HORIUTI, KEII and HIROTA[2], τ is a proper function α+unity at higher η, where $H_2^+(a)$ population is small enough to leave the interaction amoung $H_2^+(a)$ negrigible, whereas simply α at lower η where the population is large enough to cause appreciable interaction which practically prevents its further increase with decreasing η.

It follows that the population of $H_2^+(a)$ was already appreciable around the electrode potential of the HONDA's discontinuity, much lower than that of the break and hence such transition as of the $H_2^+(a)$ rich to $H_2^+(a)$ rich coverage responcible for the observed discontinuity is very impossible. The propriety of the picture was questioned in the present paper by studing whether the discontinuity could afterall at the observed η and in the range compatible with the observed change of E and, if at all, the quantities, especially the abundance of the intermediates and the interaction energy amoung them relevant

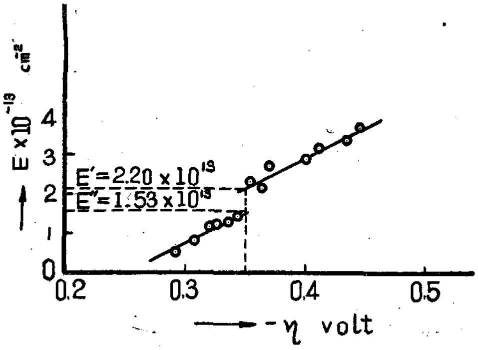

Figure 1.

The number E of elementary charges required to build up new surface of hydrogen electrode of mercury kept at definite electrode potential η. (T. HONDA.)

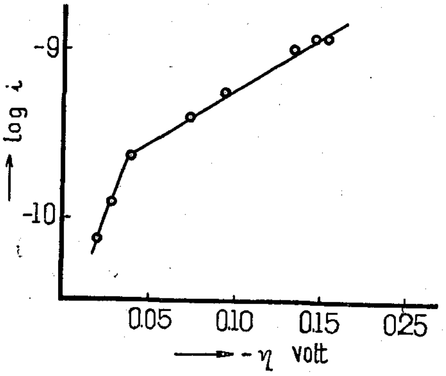

Figure 2.

The dependence of the cathodic current of hydrogen electrode of mercury on electrode potential η. (J. HORIUTI & A. MITUYA.)

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[3] J. HORIUTI & A. MITUYA: ibid, 2, No. 1, 79. (1951)

to the theoretical description of the discontinuity, of their consistency and adequancy.

(2). Existence of Discontinuity.

The problem of the project was investigated by approximating (I) the interaction energy according to BRAGG and WILLIAMS and assuming (II)$H^+(a)$ and $H_2^+(a)$ of being exclusive constituents of the positive side of the HELMHOLTZ's double layer without diffuse potential at the electrode surface.

From the equilibrium relations in the electrochemical mechanism (1) it follows that,

and
$$\left.\begin{aligned} p^{A(a)} &= p^{A(b)} \\ p^{B(a)} &= (p^{A(b)})^2 p^{\varepsilon} = (p^{A(b)})^2 p_0^{\varepsilon} e^{\frac{e\eta}{kT}}, \end{aligned}\right\} \qquad (2)$$

where $\eta = V - V_0$

is the electrode potential refered to that of the reversible hydrogen electrode and p^A or p^B the BOLTZMANN factor of the chemical potential of A or B respectively, which stands respectively for H^+ orH_2^+, notations (a) or (b) designating the adsorbed state or that in solution respectively and suffix 0 quantity appropriate the reversible hydrogen electrode. The p^{δ} is generally expressed in terms of the BOLTZMANN factor q^{δ} of the reversible work required to bring up δ, which represents A or B, from its reference state onto a preriminarily evacuated adsorption site σ for δ and the probability $\Theta_{\sigma(\delta)}$ and $\Theta_{\sigma(0)}$ of σ being occupied by δ or altogether empty, as[4],

$$\frac{q^{\delta}}{p^{\delta}} = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(0)}}. \qquad (3)$$

We have from (2) and (3) the adsorption isotherm,

$$\frac{q_0^{A(a)}}{p^{A(b)}} = \frac{\theta_A}{1-\theta} \exp\left(\frac{w_{AB}}{kT}\theta_B\right) \quad \text{for } H^+ \qquad (4)$$

and
$$\frac{q_0^{B(a)}}{(p^{A(b)})^2 p_0^{\varepsilon}} \exp\left(-\frac{e\eta}{kT}\right) = \frac{\theta_B}{1-\theta} \exp\left(\frac{w_{AB}\theta_A + w_{BB}\theta_B}{kT}\right) \quad \text{for } H_2^+, \qquad (5)$$

where $\theta_A = \Theta_{\sigma(A)}, \quad \theta_B = \Theta_{\sigma(B)},$

$$\theta = \theta_A + \theta_B \qquad (6)$$

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[4] J. HORIUTI: ibid., 1, No. 1, 13, (1948) § 5.

and hence $1-\theta = \Theta_{\sigma(0)}$.

The $q_0^{A(a)}$ (or $q_0^{B(a)}$) is the BOLTZMANN factor of the portion of the reversible work for A (or B) not due to the mutual interaction, $w_{AB}\theta_B$ (or $w_{AB}\theta_A$) the part, in accordance with approximation (I), due to the interaction with B (or A) in the surroundings except the electrostatic part already allowed for in terms of the HELMHOLTZ's double layer and $w_{BB}\theta_B$ the part of the reversible work for B due to surrounding B's: w_{AB} or w_{BB} is hence the value of $w_{AB}\theta_B$ or $w_{BB}\theta_B$ at $\theta_B=1$ respectively: w_{AA} similarly defined vanishes, the relevant interaction being purly electrostatical.

The $p^{A(b)}$, p_0^{ε}, $q_0^{A(a)}$ and $q_0^{B(a)}$ may be taken all constant determined by the experimental condition.

Differenciating the logarithms of (4) and (5) by E, the number of the elementary charges required to build up new surface of hydrogen electrode of mercury per unit area, we obtain,

$$0 = \frac{1}{\theta^A}\frac{\partial\theta^A}{\partial E} + \frac{1}{1-\theta}\frac{\partial\theta}{\partial E} + \frac{w_{AB}}{kT}\frac{\partial\theta_B}{\partial E} \tag{7}$$

and
$$-\frac{e}{kT}\frac{\partial\eta}{\partial E} = \frac{1}{\theta_B}\frac{\partial\theta_B}{\partial E} + \frac{1}{1-\theta}\frac{\partial\theta}{\partial E} + \frac{w_{AB}}{kT}\frac{\partial\theta_A}{\partial E} + \frac{w_{BB}}{kT}\frac{\partial\theta_B}{\partial E}. \tag{8}$$

We have, moreover, two relations according to (4) and (5) at the discontinuity ($\eta_c = -0.35$ volt),

$$\frac{\theta'_A}{1-\theta'}\exp\left(\frac{w_{AB}\theta'_B}{kT}\right) = \frac{\theta''_A}{1-\theta''}\exp\left(\frac{w_{AB}\theta''_B}{kT}\right)\left(=\frac{q_0^{A(a)}}{p^{A(b)}}\right) \tag{9}$$

and
$$\frac{\theta'_B}{1-\theta'}\exp\left(\frac{w_{BB}\theta'_B+w_{AB}\theta'_A}{kT}\right)$$
$$= \frac{\theta''_B}{1-\theta''}\exp\left(\frac{w_{BB}\theta''_B+w_{AB}\theta''_A}{kT}\right)\left(=\frac{q_0^{B(a)}}{(p^{A(b)})^2 p_0^{\varepsilon}}e^{-\frac{e\eta_c}{kT}}\right), \tag{10}$$

where the single and double primes denote the quantities appropriate to higher and lower values of E at the discontinuity respectively.

The E is on the other hand the sum of the number of elementary charges in the adsorbed phase and that required for the reaction $2H^+(a)+\varepsilon \rightarrow H_2^+(a)$, i. e.,

$$E = N_S(\theta_A+2\theta_B) \tag{11}$$

where N_S is the number of σ's per unit area of the surface of the electrode determined at 8.8×10^{14} cm^{-2} on the basis of radius of Hg atom at the closest packing. It is read from Fig. 1 as,

$$\left.\begin{aligned} \frac{E'}{N_S} &= \alpha' = \theta'_A + 2\theta'_B = 0.0250 \\ \frac{E''}{N_S} &= \alpha'' = \theta''_A + 2\theta''_B = 0.0174 \end{aligned}\right\} \tag{12}$$

and $-\frac{\partial\eta}{\partial E} = 1.48\times10^{14}$ volt·cm, the latter values gives 23.8 μF/cm^2 for the capacity, a magnitude of current acceptance.

Six unknowns, i. e. w_{AB}/kT, w_{BB}/kT and the individual fractions of coverage at $\eta=\eta_c$, may now be solved from six equations (7), (8), (9), (10) and (12) as follows.

Eliminating θ'_A, θ''_A, θ' and θ'' from (6), (9) and (12) we have,

$$\frac{w_{AB}}{kT} = \frac{1}{\theta'_B - \theta''_B} \ln \frac{(1+\theta'_B-\alpha')(\alpha''-2\theta''_B)}{(1+\theta''_B-\alpha'')(\alpha'-2\theta'_B)} \tag{13}$$

on one hand and eliminating similarly $(\partial\theta_A/\partial E)$ and $(\partial\theta/\partial E)$ from (7), (8) and two relations derived from (6) and (11), i. e. $\frac{\partial\theta_A}{\partial E} + \frac{\partial\theta_B}{\partial E} = \frac{\partial\theta}{\partial E}$ and $\frac{\partial\theta_A}{\partial E} + 2\frac{\partial\theta_B}{\partial E} = \frac{1}{N_S}$,

$$\left.\begin{aligned} \frac{w_{BB}}{kT} &= \left(\frac{w_{AB}}{kT}\right)^2 u' - \left(\frac{w_{AB}}{kT}\right) v' + w' \\ &= \left(\frac{w_{AB}}{kT}\right)^2 u'' - \left(\frac{w_{AB}}{kT}\right) v'' + w'', \\ &\text{on the other hand, where,} \\ u' &= \frac{(1+\theta'_B-\alpha')(\alpha'-2\theta'_B)}{1-\theta'_B}, \\ v' &= -u' N_S \frac{e}{kT} \left(\frac{\partial\eta}{\partial E}\right)_{\eta=\eta_c} - 2\frac{\alpha'-2\theta'_B}{1-\theta'_B}, \\ w' &= \frac{1}{1-\theta'_B}\left[(\alpha'-2)\, N_S \frac{e}{kT}\left(\frac{\partial\eta}{\partial E}\right)_{\eta=\eta_c} - \frac{1}{\theta'_B}\right], \end{aligned}\right\} \tag{14}$$

u'', v'' and w'' being similarly expressed as u' etc. respectively, with α' and θ'_B replaced by α'' and θ''_B. According to (14) we have further,

$$\frac{w_{AB}}{kT} = \frac{\Delta v}{2\Delta u} \pm \sqrt{\left(\frac{\Delta v}{2\Delta u}\right)^2 - \left(\frac{\Delta w}{\Delta u}\right)}, \tag{15}$$

where $\Delta u = u' - u''$, $\Delta v = v' - v''$ and $\Delta w = w' - w''$, and from (10) and (13),

$$\frac{w_{BB}}{kT} = \frac{1}{\theta'_B-\theta''_B}\left[\ln\frac{\theta''_B(1+\theta'_B-\alpha')}{\theta'_B(1+\theta''_B-\alpha'')}\right.$$
$$\left.-\left(\frac{\alpha'-\alpha''}{\theta'_B-\theta''_B}-2\right)\ln\frac{(1+\theta'_B-\alpha')(\alpha''-2\theta''_B)}{(1+\theta''_B-\alpha'')(\alpha'-2\theta'_B)}\right]. \tag{16}$$

Eqs. (13) and (15) incorporated with above values of α', α'' and $\left(\frac{\partial\eta}{\partial E}\right)_{\eta=\eta_c}$ determines now (θ'_B, θ''_B) relation, which falls within the range,

$$0 < \theta'_B < \frac{\alpha'}{2} = 0.0125 \qquad 0 < \theta''_B < \frac{\alpha''}{2} = 0.0087$$

required by (12) for positive sign of the root of (15) but not for negative one. The expression of w_{AB}/kT with the former sign substituted in (14) gives another expression for w_{BB}/kT which provides a further (θ'_B, θ''_B) relation when combined with (16). Both the relations were now solved graphically for θ'_B and θ''_B and henceforth θ'_A, θ''_A, w_{AB}/kT and w_{BB}/kT determined as below.

$$\theta'_A = 1.62\times10^{-2},\ \theta'_B = 5\times10^{-4} \text{ for the higher value of } E \tag{18}$$

and $$\theta''_A = 5\times10^{-5},\quad \theta''_B = 1.25\times10^{-2} \text{ for the lower one,} \tag{19}$$

and $$w_{AB}/kT = 490.3 \text{ and } w_{BB}/kT = 398.6 \quad \text{at } 19°\text{C}. \tag{20}$$

(3). Conclusion.

Conclusion is that there may exist at least formally*) such discontinuity as observed by HONDA and the change of appropriate θ_A and

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*) It has been shown [K. MIYAHARA and T. TAKAISI: "Busseiron-Kenkyu", **40**, 70 (1951) (printed in Japanese), or partly FOWLER and GUGGENHEIM: "Statistical Thermodynamics" (Cambride Univ. Press, 1939) Chap. X.] that the condition required for the stable coexistence of two adsorbed phases is, besides the equality of the chemical potentials of individual components, that of spreading pressures π' and π'' i. e.

$$\pi' = \pi''$$

of the phases denoted respectively by single and double primes. The expression of π is,

$$\frac{\pi}{kT} = -\ln(1-\theta) + \frac{1}{2}(\theta_A{}^2 w_{AA} + \theta_B{}^2 w_{BB} + 2\theta_A\theta_B w_{AB}),$$

which gives $\pi'/kT = 4.4\times10^{-2}$ and $\pi''/kT = 2.1\times10^{-2}$ at 19°C for this case. These values and that of $\left(\frac{\partial\pi}{\partial\eta}\right)$ at π' and π'', i e. $\left(\frac{\partial\pi}{\partial\eta}\right)_{\pi=\pi'} = \left(\frac{\partial\alpha}{\partial\eta}\right)\times3.05$ and $\left(\frac{\partial\pi}{\partial\eta}\right)_{\pi=\pi''} = \left(\frac{\partial\alpha}{\partial\eta}\right)\times1.93$, indicate, according to the general behaviour of π in the neighbourhood of the discontinuity [cf. the paper quoted above], that the consistent value of η_c is somewhat higher than -0.35 volt of the observed one as shown in Fig. 3.

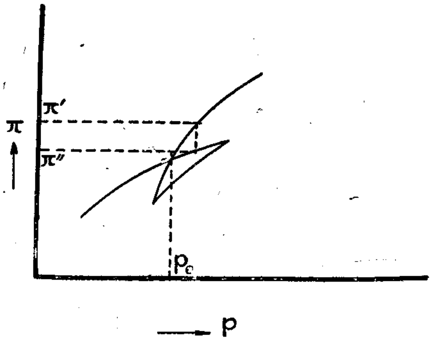

Figure 3.

The behaviour of π near the transition point p_C ; p is the equilibrium pressure of adsorptives in gas phase.

θ_B there shown above is compatible with the suggested picture; relevant magnitude of w_{AB} and w_{BB} is however extravagant for the picture reasonably to be accepted.

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