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A THEORETICAL ADSORPTION ISOTHERM FOR HYDROGEN ON PLATINUM ELECTRODE

Analysis of the Potential Sweep Transient and Pseudo-Capacity

By

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Abstract

An isotherm for hydrogen on a Pt electrode was theoretically derived as a function of overvoltage η , assuming (a) the surface consisting of principal lattice planes of (110), (100) and (111), and (b) a repulsive interaction between the hydrogen adatoms, H(a)'s. The repulsive potential between the nearest H(a)'s was introduced statistical mechanically discretely, while minor contributions arising from the second or third nearest H(a)'s were introduced by much simpler way of a proportional approximation. Results show that (i) retardation of coverage increase with η occurs once on the (110) and (100) planes, whereas twice on the (111) plane, (ii) full coverage is achieved at higher value of η in the order of (110), (100) and (111), and (iii) the (110) plane is almost fully covered at the reversible potential of the hydrogen electrode.

The two main peaks in the hydrogen discharge region of the current-potential curve, observed with the potential sweep method, were accounted for theoretically from the calculated isotherm. The two peaks of the pseudo-capacity *vs.* potential curve are discussed on the same basis.

Introduction

Many studies of transient phenomena at a hydrogen electrode have provided evidence for the presence of a hydrogen intermediate on the surface of electrodes such as Pt, Ir and Rh in a certain range of potential: (1) In the anodic galvanostatic transient, the potential starts to shift to the positive side at a *very slow rate* initially and then rises steeply. The slow rate of potential increase indicates electrochemical desorption of the hydrogen intermediate from the surface while the high rate is understood due to the charging-up of the double layer.¹⁾ (2) The anodic potential sweep causes *two (or sometimes more) large peaks* in the current-potential curve in the potential range of the slow

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rise mentioned above in (1) (called the hydrogen region from now on), while at more positive potentials it yields only a small, constant, current due to the charging-up of the double layer.²⁾ (3) The superposition of alternating current, the electrode being maintained at a potential in the hydrogen region, shows *abnormally large pseudo-capacity*, exceeding the value expected from the charging-up of the double layer.³⁾ The pseudo-capacity *vs.* potential curve at Pt shows also two large peaks as observed in the anodic potential sweep.

Assuming the presence of hydrogen adatoms, H(a), on the electrode surface, the above results have been discussed by a shift of the equilibrium of the step¹⁻³⁾



Further information on the nature of H(a) is, however, required to explain the two or more peaks mentioned above.

Many possible explanations of the peaks could be suggested: *e.g.* (a) two or more adsorption states of H(a) on a given lattice plane; (b) a single adsorption state of H(a) but the presence of two or more different lattice planes with different heats of adsorption; (c) a single adsorption state and a single kind of lattice plane but lateral interactions between the H(a)'s.

The present paper proposes to explain the two main peaks mentioned above by the equilibrium shift of step (1), by taking into account (i) the mutual repulsive interaction⁴⁾ among H(a)'s of single adsorption state and (ii) the presence of three principal lattice planes, *i.e.* (110), (100) and (111).

§ 1. Model of the electrode surface and assumptions

We first wish to describe the model of an electrode surface presented by HORIUTI⁵⁾ (crystal plane model) and to state several assumptions used in the present calculations:

- 1° The electrode surface consists of the facets of three principal lattice planes, *i.e.* (110), (100) and (111).
- 2° Each metal atom in a given facet provides a physically identical adsorption site σ , forming a net plane of σ immediately above the facet.
- 3° The hydrogen adatom, H(a), is the hydrogen intermediate on the surface of a Pt electrode*).
- 4° Mutual repulsive interactions among the H(a)'s. From quantum mechan-

*) The adsorbed hydrogen-molecule ion, $\text{H}_2^+(a)$, will be another possibility for the hydrogen intermediate. HORIUTI *et al.*⁶⁾ have postulated the presence of $\text{H}_2^+(a)$ on Hg from a quantum mechanical calculation; they conclude that this holds, for example, for the Pt electrode at more positive potential than -0.3 V *vs.* the reversible hydrogen electrode⁷⁾.

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ics the repulsive potential between a pair of non-bonded atoms may be expressed as $K - \frac{1}{2} J$, where K and J are the Coulomb and exchange integrals between the atoms in question. The value for $K - \frac{1}{2} J$ was calculated by the method of HORIUTI⁴⁾ from a Morse function for the pair of atoms:

$$K - \frac{1}{2} J = \left(\frac{3}{2} \kappa - \frac{1}{2} \right) D \left[\exp \left\{ -2a(r-r_0) \right\} - 2 \exp \left\{ -a(r-r_0) \right\} \right], \quad (2)$$

where κ is the ratio of the Coulomb integral to $(K+J)$, *i.e.* to the Morse function, D their dissociation energy, r the distance between two atoms, r_0 the equilibrium value of r , and a the Morse constant. The κ is estimated according to ROSEN and IKEHARA.⁸⁾

- 5° The repulsive potential rapidly decays with increase of distance as seen from Eq. (2). Thus, the repulsive potential due to the nearest ($3.916/\sqrt{2}$ Å distance, Fig. 1) H(a)'s will be taken into account discretely using statistical mechanics, but minor ones due to the second (3.916 Å) and third ($3.916\sqrt{3/2}$ Å) nearest H(a)'s are introduced by much simpler statistical mechanical treatment of the proportional approximation⁴⁾, in that the potential is assumed to be proportional to the coverage of H(a). Such an approach has already been proposed by BETHE and PEIERLS⁹⁾. HORIUTI and the present author¹⁰⁾ recently applied the present method to the theoretical estimation of the velocity of the hydrogen electrode reaction on Ni.
- 6° Equilibrium of step (1) is assumed to be maintained throughout the varia-

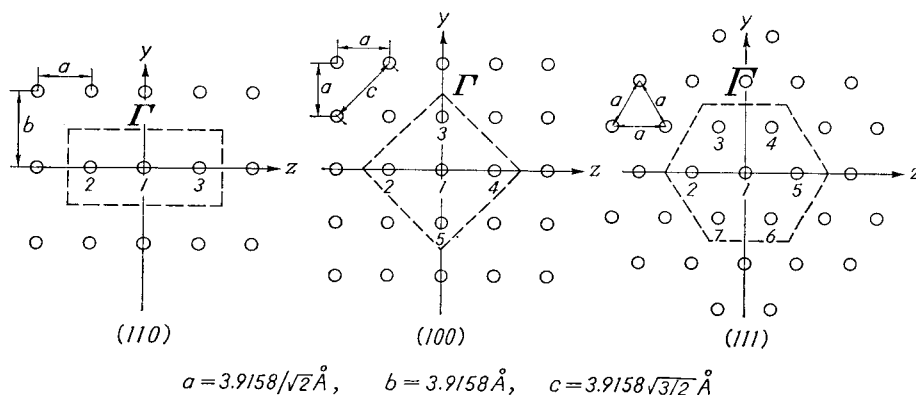


Fig. 1. Arrangement of sites and Γ on the respective lattice planes. Γ consists of σ_1 and the nearest sites to σ_1 .

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tion of the electrode potential. This assumption has been supported experimentally by many workers.^{1,2,11)} Thus, we have the following relation between the chemical potentials of the species concerned :

$$\mu(\text{H}^+) + \mu(\text{e}^-) = \mu(\text{H}) .$$

Defining the overvoltage, η , as*) $\eta \equiv \{\mu(\text{e}^-) - \mu(\text{e}^-)_{\text{rev}}\}/F$, where $\mu(\text{e}^-)_{\text{rev}}$ is the value of $\mu(\text{e}^-)$ at the reversible hydrogen electrode and F is the Faraday, the above equation is rewritten as

$$\mu(\text{H}) = F\eta + \frac{1}{2} \mu(\text{H}_2) \quad (3)$$

using the relation, $2\mu(\text{H}^+) + 2\mu(\text{e}^-)_{\text{rev}} = \mu(\text{H}_2)$, for the reversible hydrogen electrode.

§ 2. Adsorption isotherm of hydrogen

Since step (1) has been assumed to be reversible, isotherms of hydrogen on the respective lattice planes can be determined¹⁰⁾ as a function of η at constant $\mu(\text{H}_2)$.

Let \mathfrak{A} be the macroscopic assembly consisting of electrolyte solution, electrode and 1 atm hydrogen gas at a definite temperature. Let σ_1 be the site of interest which can be any one of the physically identical sites (§1.2°) on a given lattice plane. A possible state of σ_1 is either unoccupied or occupied by H(a). These states are expressed as $\sigma_1(0)$ and $\sigma_1(\text{H})$ respectively. We denote the assembly specified by the state $\sigma_1(0)$ or $\sigma_1(\text{H})$ as $\mathfrak{A}_{\sigma_1(0)}$ or $\mathfrak{A}_{\sigma_1(\text{H})}$.

The partition function of the assembly \mathfrak{A} , $\Omega\mathfrak{A}$, is expressed from its general property as the sum of the partition functions $\Omega\mathfrak{A}_{\sigma_1(0)}$ and $\Omega\mathfrak{A}_{\sigma_1(\text{H})}$ of $\mathfrak{A}_{\sigma_1(0)}$ and $\mathfrak{A}_{\sigma_1(\text{H})}$, *i. e.*

$$\Omega\mathfrak{A} = \Omega\mathfrak{A}_{\sigma_1(0)} + \Omega\mathfrak{A}_{\sigma_1(\text{H})} .$$

The probability of σ_1 being occupied is given by the ratio of $\Omega\mathfrak{A}_{\sigma_1(\text{H})}/\Omega\mathfrak{A}$. This ratio is, however, the same at all sites on a given lattice plane since all sites have been assumed to be physically identical. Thus, the above probability is equated to the coverage, θ , of a given lattice plane :

$$\theta = \Omega\mathfrak{A}_{\sigma_1(\text{H})}/\Omega\mathfrak{A}$$

or from the above two equations

$$\theta/(1-\theta) = \Omega\mathfrak{A}_{\sigma_1(\text{H})}/\Omega\mathfrak{A}_{\sigma_1(0)} . \quad (4)$$

*) A positive value of η means a negative polarization *vs.* the reversible hydrogen electrode in the same medium.

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Both partition functions, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ are now formulated by taking into account the interactions described in §1.5° as follows: We now choose a set of sites on a given lattice plane, Γ , consisting of one site σ_1 and the nearest ($3.916/\sqrt{2}$ Å distance) neighbour sites to σ_1 , see Fig. 1. With Γ thus defined, the partition function, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$ is expressed as the sum of the partition functions of assemblies, each specified with one of all possible states of Γ , keeping σ_1 occupied throughout. Any state of Γ is represented by the number of hydrogen atoms within Γ except the one in σ_1 , denoted by g , and the arrangement of these hydrogen atoms, k . We express such a state by the notation,

$$\Gamma \{ \sigma_1(\text{H}), G\sigma(g\text{H})_k \},$$

where g can have the values, $0, 1, \dots, g, \dots, G$. G is the number of the sites nearest to σ_1 , *i. e.* 2, 4 and 6 respectively for the (110), (100) and (111) planes, as seen from Fig. 1. The number of possible ways of arranging g hydrogen atoms is given by $K = G!/g!(G-g)!$. Summation of all partition functions of assemblies specified by $\Gamma \{ \sigma_1(\text{H}), G\sigma(g\text{H})_k \}$ gives

$$\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})} = \sum_{g=0}^G \sum_{k=1}^K \mathfrak{Q}\mathfrak{A}_{\Gamma \{ \sigma_1(\text{H}), G\sigma(g\text{H})_k \}}. \quad (5)$$

The partition function, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ of the assembly $\mathfrak{A}_{\sigma_1(0)}$ is expressed by an equation similar to Eq. (5) except that $\sigma_1(\text{H})$ is replaced with $\sigma_1(0)$.

We shall next formulate, generally, $\mathfrak{Q}\mathfrak{A}_{\Gamma \{ \sigma_1(\text{H}), G\sigma(g\text{H})_k \}}$ or $\mathfrak{Q}\mathfrak{A}_{\Gamma \{ \sigma_1(0), G\sigma(g\text{H})_k \}}$. Let $\mathfrak{Q}\mathfrak{A}_{\Gamma(0)}$ be the partition function of the assembly where all sites within Γ , including σ_1 , are unoccupied. $\mathfrak{Q}\mathfrak{A}_{\Gamma(0)}$ must be multiplied by the factor f_1 when one of H(a)'s outside Γ is transferred onto one of vacant sites within Γ , where f_1 is the Boltzmann factor of the reversible work required for the transfer process. Further successive transfers of H(a)'s from outside Γ onto the vacant sites within Γ introduce the respective multiplying factors, f_2, f_3, \dots . Hence, the partition function of the assembly at the final stage of successive transfers, specified in general by $\Gamma(A\text{H})$, is given by multiplying $\mathfrak{Q}\mathfrak{A}_{\Gamma(0)}$ with the product of the factors, f 's *i. e.*

$$\mathfrak{Q}\mathfrak{A}_{\Gamma(A\text{H})} = \mathfrak{Q}\mathfrak{A}_{\Gamma(0)} \prod_{j=1}^A f_j. \quad (6)$$

$\Gamma(A\text{H})$ can be any one of $\Gamma \{ \sigma_1(\text{H}), G\sigma(g\text{H})_k \}$'s or $\Gamma \{ \sigma_1(0), G\sigma(g\text{H})_k \}$'s. Here, A equals to $g+1$ for $\sigma_1(\text{H})$ and g for $\sigma_1(0)$ respectively depending on whether we are concerned with $\sigma_1(\text{H})$ or $\sigma_1(0)$.

Let us divide the reversible work required for each transfer process into two parts: One is the reversible work required to transfer H(a) from some-

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where outside Γ to the standard state, *i. e.* the negative of the chemical potential of H(a), $-\mu(\text{H})$, which is common to all processes. The other is the work required for the transfer from the standard state to the unoccupied site within Γ , $\varepsilon_j(\text{H})$, which is different for each process depending on the interaction. The general form of $\varepsilon_j(\text{H})$ is expressed as

$$\varepsilon_j(\text{H}) = \varepsilon_0(\text{H}) + \{u_j R_1 + v_j R_2 + w_j R_3\} + \{x_j X + s_j R_2 \theta + t_j R_3 \theta\}, \quad (7)$$

where

- $\varepsilon_0(\text{H})$; the value of $\varepsilon_j(\text{H})$ in the absence of repulsive interaction, (This quantity is common to all transfer processes.)
- R_1, R_2 or R_3 ; the repulsive potential between a pair of the nearest ($3.916/\sqrt{2}$ Å), the second nearest (3.916 Å), or the third nearest ($3.916\sqrt{3/2}$ Å) H(a)'s within Γ ,
- u_j, v_j or w_j ; the number of nearest, second or third nearest pairs produced within Γ by the addition of j -th H(a) into Γ ,
- X ; the repulsive potential between the j -th H(a) within Γ and the nearest H(a) outside Γ ,
- x_j, s_j or t_j ; the number of nearest, second or third nearest H(a)'s outside Γ to j -th H(a) within Γ .

It should be noted here in accordance with § 1.5° that Eq. (7) yields the nearest neighbour repulsive potential *only* if a nearest neighbour site is occupied and that the repulsive potentials due to neighbours further removed (exactly speaking, the second and third nearest H(a)'s outside Γ) are obtained assuming the presence of H(a) with the probability of θ on the respective sites as insisted by the proportional approximation. The potential X , due to the nearest H(a) outside Γ is treated here as unknown and was determined from the condition of physical identity of the σ 's, *i. e.* by the relation

$$\Omega \mathfrak{A}_{\sigma_1(0)} = \Omega \mathfrak{A}_{\sigma_2(0)}, \quad (8)$$

where $\Omega \mathfrak{A}_{\sigma_2(0)}$ is the partition function of the assembly specified by the state $\sigma_2(0)$. The latter partition function is developed in the same way as $\Omega \mathfrak{A}_{\sigma_1(0)}$. Equation (5) holds in this case by replacing $\sigma_1(\text{H})$ with $\sigma_2(0)$.

Thus, the factor, f_j , is expressed from its definition and Eqs. (3) and (7) as

$$f_j = \exp \left[\left\{ -\varepsilon_0(\text{H}) + \frac{1}{2} \mu(\text{H}_2) + F\eta - (u_j R_1 + v_j R_2 + w_j R_3) - (x_j X + s_j R_2 \theta + t_j R_3 \theta) \right\} / RT \right]. \quad (9)$$

Defining the following quantities ;

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$$\gamma \equiv \exp \left[\left\{ -\varepsilon_0(\text{H}) + \frac{1}{2} \mu(\text{H}_2) + F\eta \right\} / RT \right], \quad (10. \gamma)$$

$$I \equiv \exp(-R_1/RT), \quad II \equiv \exp(-R_2/RT), \quad III \equiv \exp(-R_3/RT), \quad (10. \text{I}), (10. \text{II}), (10. \text{III}),$$

$$II_\theta \equiv \exp(-R_2\theta/RT), \quad III_\theta \equiv \exp(-R_3\theta/RT), \quad \rho \equiv \exp(-X/RT). \quad (10. \text{II}_\theta), (10. \text{III}_\theta), (10. \rho)$$

Eq. (6) is rewritten from Eqs. (9) and (10) as

$$\mathfrak{Q}\mathfrak{A}_{\Gamma(A\text{H})} = \mathfrak{Q}\mathfrak{A}_{\Gamma(0)} \cdot \gamma^A \prod_{j=0}^A \rho^{v_j} I^{w_j} II^{v_j} III^{w_j} II_\theta^{v_j} III_\theta^{w_j}, \quad (11)$$

where $\Gamma(A\text{H})$ can be $\Gamma\{\sigma_1(\text{H}), G\sigma(g\text{H})_k\}$, $\Gamma\{\sigma_1(0), G\sigma(g\text{H})_k\}$ or $\Gamma\{\sigma_2(0), G\sigma(g\text{H})_k\}$ according to the assembly concerned being specified by $\sigma_1(\text{H})$, $\sigma_1(0)$ or by $\sigma_2(0)$.

In the next section, the partition functions, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_2(0)}$ are formulated with respect to the (110), (100) and (111) planes.

§ 3. $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_2(0)}$

$\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$: The formulation of $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$ is shown below on the respective lattice planes.

The (110) plane: As seen from Fig. 1, the number of the sites nearest to σ_1 , G , is 2 and there are no second and third nearest neighbours of σ 's within Γ . Hence, v_j and w_j in Eq. (7) or (11) are all zero. The partition functions specified by g and k , $\mathfrak{Q}\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 2\sigma(g\text{H})_k\}}$, are summed up over k as follows:

$$g=0, K=1,$$

$$\mathfrak{Q}\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 2\sigma(0)_1\}} = \mathfrak{Q}\mathfrak{A}_{\Gamma(0)} \cdot \gamma II_\theta^2 III_\theta^4$$

$$g=1, K=2,$$

$$\sum_{k=1}^2 \mathfrak{Q}\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 2\sigma(\text{H})_k\}} = \mathfrak{Q}\mathfrak{A}_{\Gamma(0)} \cdot \gamma^2 II_\theta^2 III_\theta^4 \cdot 2\rho I II_\theta^2 III_\theta^4$$

$$g=2, K=1,$$

$$\mathfrak{Q}\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 2\sigma(2\text{H})_1\}} = \mathfrak{Q}\mathfrak{A}_{\Gamma(0)} \cdot \gamma^3 II_\theta^2 III_\theta^4 \cdot \rho^2 I^2 II_\theta^4 III_\theta^8$$

The values of the exponents for each term of the right hand sides of these equations are determined by counting the pairs of H(a) responsible for ρ , I , II_θ and III_θ according to the arrangement indicated under the term.

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Thus, summing the above three equations according to Eq. (5), we obtain

$$\left. \begin{aligned} \mathfrak{A}_{\sigma_1(\text{H})} &= \mathfrak{A}_{\Gamma(0)} \cdot \zeta \{1 + 2Ix + I^2 x^2\} \\ \text{where} \end{aligned} \right\} \quad (12. \text{I})$$

$$\zeta \equiv rII_\theta^2 III_\theta^4, \quad x = r\rho II_\theta^2 III_\theta^4.$$

The (100) plane: As illustrated in Fig. 1, G is 4 and there is no third nearest ($3.916\sqrt{3/2}$ Å) neighbour. Hence, in Eq. (7) or (11) $w_j = t_j = 0$. Thus,

$$g=0, K=1,$$

$$\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 4\sigma(0)\}_1} = \mathfrak{A}_{\Gamma(0)} \cdot rII_\theta^4$$

$$\quad \quad \quad \dagger$$

$$g=1, K=4,$$

$$\sum_{k=1}^4 \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 4\sigma(\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot r^2 II_\theta^4 \cdot 4I\rho II_\theta^2$$

$$\quad \quad \quad \dagger, \dagger, \dagger, \dagger$$

$$g=2, K=6,$$

$$\sum_{k=1}^6 \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 4\sigma(2\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot r^3 II_\theta^4 \cdot [4I^2 II \rho^2 II_\theta^4 + 2I^2 \rho^2 II_\theta^4]$$

$$\quad \quad \quad \dagger, \dagger, \dagger, \dagger, \dagger, \dagger$$

$$g=3, K=4,$$

$$\sum_{k=1}^4 \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 4\sigma(3\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot r^4 II_\theta^4 \cdot 4I^3 II^2 \rho^3 II_\theta^6$$

$$\quad \quad \quad \dagger, \dagger, \dagger, \dagger$$

$$g=4, K=1,$$

$$\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}), 4\sigma(4\text{H})\}_1} = \mathfrak{A}_{\Gamma(0)} \cdot r^5 II_\theta^4 \cdot I^4 II^4 \rho^4 II_\theta^8$$

$$\quad \quad \quad \dagger$$

Summation of the above five equations yields

$$\left. \begin{aligned} \mathfrak{A}_{\sigma_1(\text{H})} &= \\ \mathfrak{A}_{\Gamma(0)} \cdot \zeta \{1 + 4Ix + (2I^2 + 4I^2 II) x^2 + 4I^3 II^2 x^3 + I^4 II^4 x^4\} \end{aligned} \right\} \quad (12. \text{II})$$

where

$$\zeta \equiv rII_\theta^4, \quad x \equiv r\rho II_\theta^2.$$

The (111) plane: Here, G is 6 and there is no possibility of second nearest (3.916 Å) neighbours of σ 's (Fig. 1). Hence, we have $v_j = s_j = 0$ in Eq. (7) or (11). The diagrams under each term of the following equations show one of several equivalent arrangements of H(a)'s within Γ , all of which yields the same exponent in Eq. (11). The number of such equivalent arrangements is

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shown beside the diagram.

$$g=0, K=1,$$

$$\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(0)_1\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma III_\theta^6$$

✱

$$g=1, K=6,$$

$$\sum_{k=1}^6 \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^2 III_\theta^6 \cdot 6I\rho III_\theta^4$$

✱^{×6}

$$g=2, K=15,$$

$$\sum_{k=1}^{15} \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(2\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^3 III_\theta^6 \cdot [6I^3\rho^2 III_\theta^8 + 6I^2 III\rho^2 III_\theta^8 + 3I^2\rho^2 III_\theta^8]$$

✱^{×6} ✱^{×6} ✱^{×3}

$$g=3, K=20,$$

$$\sum_{k=1}^{20} \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(3\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^4 III_\theta^6 \cdot [6I^5 III\rho^3 III_\theta^{12} + 12I^4 III\rho^3 III_\theta^{12} + 2I^3 III^3\rho^3 III_\theta^{12}]$$

✱^{×6} ✱^{×12} ✱^{×2}

$$g=4, K=15,$$

$$\sum_{k=1}^{15} \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(4\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^5 III_\theta^6 \cdot [6I^7 III^2\rho^4 III_\theta^{16} + 6I^6 III^3\rho^4 III_\theta^{16} + 3I^6 III^2\rho^4 III_\theta^{16}]$$

✱^{×6} ✱^{×6} ✱^{×3}

$$g=5, K=6,$$

$$\sum_{k=1}^6 \mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(5\text{H})_k\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^6 III_\theta^6 \cdot 6I^9 III^4\rho^5 III_\theta^{20}$$

✱

$$g=6, K=1,$$

$$\mathfrak{A}_{\Gamma\{\sigma_1(\text{H}),6\sigma(6\text{H})_1\}} = \mathfrak{A}_{\Gamma(0)} \cdot \gamma^7 III_\theta^6 \cdot I^{12} III^6\rho^6 III_\theta^{24}$$

✱

Summing the above seven equations :

$$\left. \begin{aligned} \mathfrak{A}_{\sigma_1(\text{H})} = \mathfrak{A}_{\Gamma(0)} \cdot \zeta [1 + 6Ix + (3I^2 + 6I^2III + 6I^3)x^2 \\ + (2I^3III^3 + 12I^4III + 6I^5III)x^3 \\ + (3I^6III^2 + 6I^6III^3 + 6I^7III^2)x^4 + 6I^9III^4x^5 + I^{12}III^6x^6], \end{aligned} \right\} (12. \text{ III})$$

where

$$\zeta \equiv \gamma III_\theta^6, \quad x \equiv \gamma\rho III_\theta^4.$$

TABLE 1 Constants, c 's, in Eqs. (13), (14), (15) and (16)

	plane g	0	1	2	3	4	5	6
$c_{1,g}$	(110)	1	2	1				
	(100)	1	4	$2+4II$	$4II^2$	II^4		
	(111)	1	6	$3+6III+6I$	$2III^3+12I III+6I^2 III$	$3I^2 III^2+6I^2 III^3+6I^3 III^2$	$6I^4 III^4$	$I^6 III^6$
$c_{2,g}$	(110)	1	1					
	(100)	1	3	$1+2II$	II^2			
	(111)	1	5	$2+4III+4I$	$III^3+6I III+3I^2 III$	$I^2 III^2+2I^2 III^3+2I^3 III^2$	$I^4 III^4$	
$c_{3,g}$	(110)	1	I					
	(100)	1	$3I$	$2I^2 II+I^2$	$I^3 II^2$			
	(111)	1	$5I$	$2I^2+4I^2 III+4I^3$	$6I^4 III+I^3 III^3+3I^5 III$	$I^6 III^2+2I^6 III^3+2I^7 III^2$	$I^9 III^4$	
$c_{4,g}$	(110)	1	$2I$	I^2				
	(100)	1	$4I$	$2I^2+4I^2 II$	$4I^3 II^2$	$I^4 II^4$		
	(111)	1	$6I$	$3I^2+6I^2 III+6I^3$	$2I^3 III^3+12I^4 III+6I^5 III$	$3I^6 III^2+6I^6 III^3+6I^7 III^2$	$6I^9 III^4$	$I^{12} III^6$
$c_{5,g}$	(110)	1	2	1				
	(100)	1	4	$2+4II$	$4II^2$	II^4		
	(111)	1	6	$3+6III+6I$	$2III^3+12I III+6I^2 III$	$3I^2 III^2+6I^2 III^3+6I^3 III^2$	$6I^4 III^4$	$I^6 III^6$
$c_{6,g}$	(110)	1	I					
	(100)	1	$3I$	$I^2+2I^2 II$	$I^3 II^2$			
	(111)	1	$5I$	$2I^2+4I^2 III+4I^3$	$6I^4 III+I^3 III^3+3I^5 III$	$I^6 III^2+2I^6 III^3+2I^7 III^2$	$I^9 III^4$	
$c_{7,g}$	(110)	1	1					
	(100)	1	$1+2II$	$3II^2$	II^4			
	(111)	1	$1+2III+2I$	$III^3+6I III+3I^2 III$	$2I^2 III^2+4I^2 III^3+4I^3 III^2$	$5I^4 III^4$	$I^6 III^6$	

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$\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_2(0)}$: Expressions for $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_2(0)}$ are obtained for the respective lattice planes by a consideration similar to $\mathfrak{Q}\mathfrak{A}_{\sigma_1(\text{H})}$ as

$$\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)} = \mathfrak{Q}\mathfrak{A}_{r(0)} \cdot \sum_{g=0}^g c_{1,g} x^g \quad (13)$$

$$\mathfrak{Q}\mathfrak{A}_{\sigma_2(0)} = \mathfrak{Q}\mathfrak{A}_{r(0)} \cdot \sum_{g=0}^{g-1} (c_{2,g} + c_{3,g} \zeta) x^g, \quad (14)$$

where $c_{1,g}$, $c_{2,g}$ and $c_{3,g}$ are the constants shown in Table 1 and x or ζ is the quantity defined on the respective lattice planes in Eqs. (12).

Isotherm: The isotherm of hydrogen is thus obtained from Eqs. (4), (12) and (13) as

$$\theta/(1-\theta) = \sum_{g=0}^g c_{4,g} \zeta x^g / \sum_{g=0}^g c_{5,g} x^g, \quad (15)$$

where $c_{4,g}$ and $c_{5,g}$ are the constants shown in Table 1. The condition of Eq. (8) on the other hand leads to the relation

$$x/\zeta = \sum_{g=0}^{g-1} c_{6,g} x^g / \sum_{g=0}^{g-1} c_{7,g} x^g \quad (16)$$

from Eqs. (13) and (14); the constants, $c_{6,g}$ and $c_{7,g}$, are also shown in Table 1. We can now determine θ from the above two equations as a function of η as seen from Eqs. (10) and the definitions of ζ and x in Eqs. (12), if we know the numerical values of $\mu(\text{H}_2)$, $\varepsilon_0(\text{H})$, R_1 , R_2 and R_3 .

§ 4. Calculation of the isotherm

Numerical values for $\mu(\text{H}_2)$, $\varepsilon_0(\text{H})$, R_1 , R_2 and R_3 are estimated as follows:

$\mu(\text{H}_2)$: The chemical potential of the gaseous hydrogen molecule is expressed in good approximation, taking the vibrational partition function as unity, by

$$\mu(\text{H}_2) = -RT \ln \left[(2\pi m k T)^{3/2} \cdot 4\pi^2 I k T \cdot h^{-5} (N^{\text{H}_2})^{-1} \cdot \exp(-\varepsilon_{g,0}^{\text{H}_2}/RT) \right], \quad (17. \mu)$$

where m is the mass, I the moment of inertia, N^{H_2} the concentration of hydrogen gas molecules and $\varepsilon_{g,0}^{\text{H}_2}$ the energy of the ground state of the molecule.

$\varepsilon_0(\text{H})$: The reversible work, $\varepsilon_0(\text{H})$, is given from statistical mechanics by

$$\varepsilon_0(\text{H}) = -RT \ln \left[\prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \cdot \exp\left(-\frac{\varepsilon_{g,0}^{\text{H}}}{kT}\right) \right], \quad (17. \varepsilon)$$

where ν_j is the frequency of j -th mode of vibration and $\varepsilon_{g,0}^{\text{H}}$ is the energy of the ground state of H(a) in its equilibrium position. The vibrational frequency,

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ν_j , is calculated from the relation,

$$\begin{aligned}\nu_x &= \left[\left(\frac{\partial^2 \varepsilon_g^H}{\partial x^2} \right)_{x=x_0} \right]^{1/2} / 2\pi m^{1/2}, & \nu_y &= \left[\left(\frac{\partial^2 \varepsilon_g^H}{\partial y^2} \right)_{y=y_0} \right]^{1/2} / 2\pi m^{1/2}, \\ \nu_z &= \left[\left(\frac{\partial^2 \varepsilon_g^H}{\partial z^2} \right)_{z=z_0} \right]^{1/2} / 2\pi m^{1/2},\end{aligned}$$

where ε_g^H is the energy of the ground state of H(a), x the normal to the surface, and y or z an axis parallel to the surface as shown in Fig. 1. The second derivatives are determined from the equation,¹⁰⁾

$$\varepsilon_g^H = D \{ e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \} + \sum_j \left(K_j - \frac{1}{2} J_j \right),$$

where the first term is the Morse function for the Pt-H bond and the second term is the repulsive potential due to the unbonded surrounding surface metal atoms, j , that is surface metal atoms of second or third nearest neighbours to the metal atom underlying σ_1 . This second term was estimated by Eq. (2), where the constants are taken as $\kappa=0.26^{11)}$, $D=63.5$ kcal mole⁻¹*) $a=1.69 \text{ \AA}^{-1}$ *) and $r_0=1.65 \text{ \AA}^{11)}$. Results are shown in Table 2. The last column of Table 2 shows the values of $\frac{1}{2} \varepsilon_{g,0}^{H_2} - \varepsilon_{g,0}^H$ which appears in the expression of γ as seen from Eqs. (10.7), (17.μ) and (17.ε). This value on the (110) plane is equated to the half of the initial heat of adsorption of H₂ on a Pt electrode, *viz.* 18 kcal mole⁻¹ 12) and the other values for the (100) and (111) planes are obtained by taking into account the difference in $\sum_j \left(K_j - \frac{1}{2} J_j \right)$ on the re-

TABLE 2 Frequencies, ν 's (cm⁻¹), of H(a) on Pt and the value of $\frac{1}{2} \varepsilon_{g,0}^{H_2} - \varepsilon_{g,0}^H$ on the respective lattice planes

	ν_x	ν_y	ν_z	$\sum_j \left(K_j - \frac{1}{2} J_j \right)$ (kcal)	$\frac{1}{2} \varepsilon_{g,0}^{H_2} - \varepsilon_{g,0}^H$ (kcal)
(110)	2058	36.1	196.1	2.48	9.0
(100)	2056	179.7	179.7	4.61	6.9
(111)	2055	210.7	210.7	6.11	5.4

*) The dissociation energy D of Pt-H is calculated from that of H₂, 109 kcal mole⁻¹, and from the initial heat of adsorption of H₂ on Pt electrode in sulfuric acid solution, 18 kcal mole⁻¹,¹³⁾ as $(109+18)/2=63.5$ kcal mole⁻¹. The parameter a was calculated from the equation $a=1.2177 \times 10^7 \omega_e \sqrt{\mu_A/D}$,¹⁴⁾ where ω_e is the frequency of Pt-H and μ_A is the reduced mass in gram mole⁻¹. The ω_e was calculated from the wave length of the adsorbed hydrogen atom on Pt observed by PLISKIN and EISCHENS.¹⁵⁾

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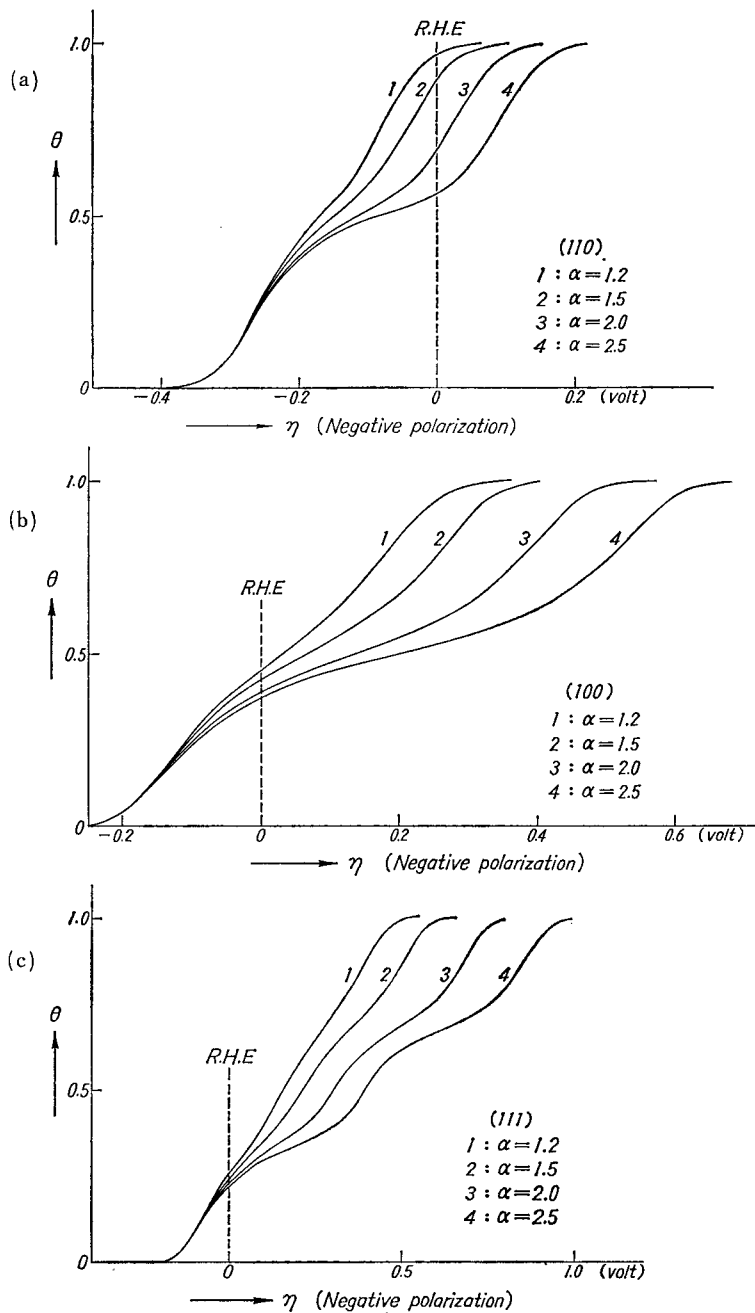


Fig. 2. Coverage of H(a) on the respective lattice planes of Pt as a function of η at 25°C and 1 atm pressure of H_2 .

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spective lattice planes. From Eqs. (10.7), (17) and Table 2, γ is calculated as $1.45 \times 10^7 \exp(F\eta/RT)$, $1.17 \times 10^5 \exp(F\eta/RT)$ and $7.63 \times 10^4 \exp(F\eta/RT)$ on the (110), (100) and (111) planes at 25°C and 1 atm pressure of hydrogen.

R_1 , R_2 , R_3 : The repulsive potentials are given by multiplying Eq. (2) by the factor α which was taken as 1.2, 1.5, 2.0 or 2.5 respectively. The α has been introduced in the previous calculations of hydrogen isotherms and the rate of hydrogen evolution reaction on Ni,^{4b,10)} in order to get the best fit of the calculated results with the experimental data. The constants in Eq. (2) are taken as $\kappa=0.1^{4a)}$ by ROSEN and IKEHARA's method,⁸⁾ $D=109$ kcal mole⁻¹, $r_0=0.7395 \text{ \AA}^5$ and $a=1.98 \text{ \AA}^{-1.5}$ respectively. Thus, we have

$$R_1 = 1.36 \alpha, \quad R_2 = 0.1415 \alpha, \quad R_3 = 0.02479 \alpha \quad \text{in kcal mole}^{-1} \quad (18)$$

Isotherms on the respective lattice planes are then calculated by Eqs. (15), (16) and values of γ , R_1 , R_2 and R_3 given in this section. Calculations were carried out by an electronic computer (NEAC 2203 G, Nippon Electric Co.). Figure 2 shows results on the respective lattice planes which are quite similar to those¹⁰⁾ obtained for Ni, having the same crystal habit as Pt (f.c.c.).

Discussion: (1) The isotherms of the respective lattice planes exhibit one or two retardations in coverage increase with η . With increase of η , the sites signified by the solid circles in Fig. 3 are first covered on account of the lowest repulsion. Once these sites are covered completely, θ is $\frac{1}{2}$ on the (110) and (100) planes, although these values are only realized approximately, except at 0°K. Further occupation of the other open circle in Fig. 3

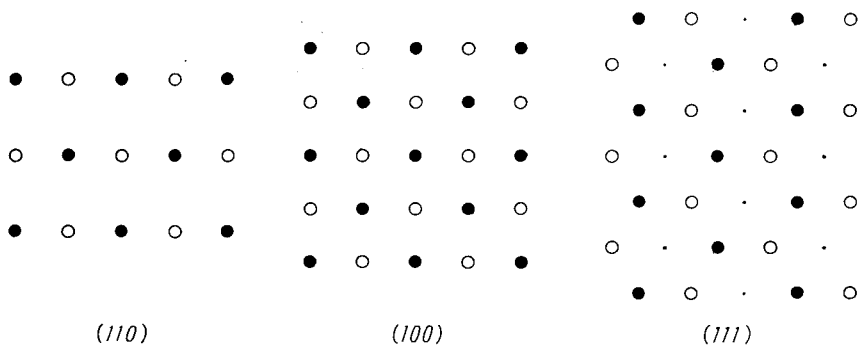


Fig. 3. Occupation sequence of sites by H(a) on the respective lattice planes. Adsorption occurs first on the sites of ● and then on ○. The sites of · on the (111) plane are occupied in the last stage of adsorption on account of the strongest repulsion.

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encounters much stronger repulsion, thus delaying further θ increase. The extent of the retardation depends on the extent of the repulsion; stronger repulsion, *i.e.* larger value of α in Eq. (18) results in a stronger retardation. As η becomes large enough to overcome this repulsion, θ starts again to increase. The occupation of the sites marked by points on the (111) plane (Fig. 3) suffers from the extremely strong repulsion, since the new occupant has six nearest neighbours as seen from the figure. In consequence, the second retardation arises in isotherm. (2) One can see from Fig. 2 that the isotherm covers wider region of η in the order of (110), (100) and (111). In other words, the reversible work to produce full surface coverage is largest on the most dense plane (111) and smallest on the least dense plane (110). This is due to the repulsive potential which is largest on (111), while smallest on (110). (3) It is seen from the comparison of the present results with previously calculated isotherms on Ni electrode,¹⁰ that the full coverage on each lattice plane of Pt is achieved at a smaller value of η than in the case of Ni. This difference is again attributed to the lower repulsive potential on Pt compared to that of Ni, because the lattice spacing of Pt is larger than that of Ni. The values of R_1 , R_2 and R_3 on Ni have been calculated at 2.346α , 0.3087α and 0.0645α , in kcal mole⁻¹, respectively.¹⁰

§ 5. Application of the isotherm to analysis of transient phenomena

In the hydrogen discharge region of the current-potential (time) curve, the current density, i , being in excess of that required for the charging-up of the double layer, is given, on the basis of the assumption § 1.6°, as

$$i = \frac{NF}{N_A} \left(\frac{d\theta}{d\eta} \right) \left(\frac{d\eta}{dt} \right), \quad (19)$$

where N is the total number of adsorption sites per cm², F and N_A are the Faraday and Avogadro's number respectively. NF/N_A is calculated as

$$NF/N_A = 1.477 \times 10^{-4}, \quad 2.089 \times 10^{-4} \text{ and } 2.412 \times 10^{-4} \text{ Coulomb cm}^{-2} \text{ for the (110), (100) and (111) planes.} \quad (20)$$

The factor, $(d\theta/d\eta)$, in Eq. (19) is obtained graphically from Fig. 2. The factor, $(d\eta/dt)$, stands for the sweep rate. Figure 4 illustrates the current-potential curve calculated by Eqs. (19) and (20) on the respective lattice planes at $\alpha = 1.2$, where the sweep rate of the potential was taken as 0.28 V/sec to allow comparison with the experimental data. It is seen from Fig. 4 that the (110) and (100) planes show two peaks, while the (111) plane exhibits

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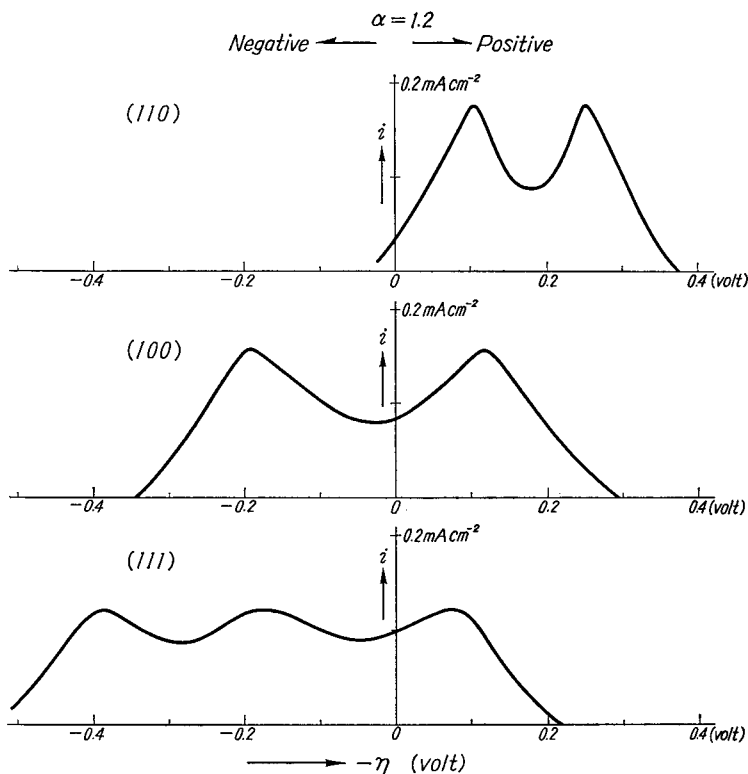


Fig. 4. Theoretical current-potential curves on the respective lattice planes of Pt at $\alpha=1.2$ (sweep rate, 0.28 V/sec).

three peaks. The peak positions shift to higher value of η in the order of (110), (100) and (111), while the repulsive potential increase in the same order. Since the experiments by the potential sweep method cover the potential range of $\eta < 0$ (positive potential), we compare the present results in the range of $\eta < 0$ with the experimental results¹⁶⁾ in Fig. 5. Curve "total" is obtained from Fig. 4 assuming that all lattice planes have equal surface areas. Curve "(110)" represents the calculated results for unit area of the (110) plane. Curve "obs" shows the observed data for Pt in acidic solution obtained by BÖLD and BREITER.¹⁶⁾ From this comparison, it is seen that the theoretical curves obtained by using the experimental value of the initial heat of adsorption, 18 kcal mole,^{-1 13)} reproduce the experimental peak values of overvoltage. The voltage difference between the two peaks is important as a measure of the repulsive potential among H(a)'s, as introduced in the present paper. The theoretical curves calculated with $\alpha=1.5$, 2.0 and 2.5 appear at much higher

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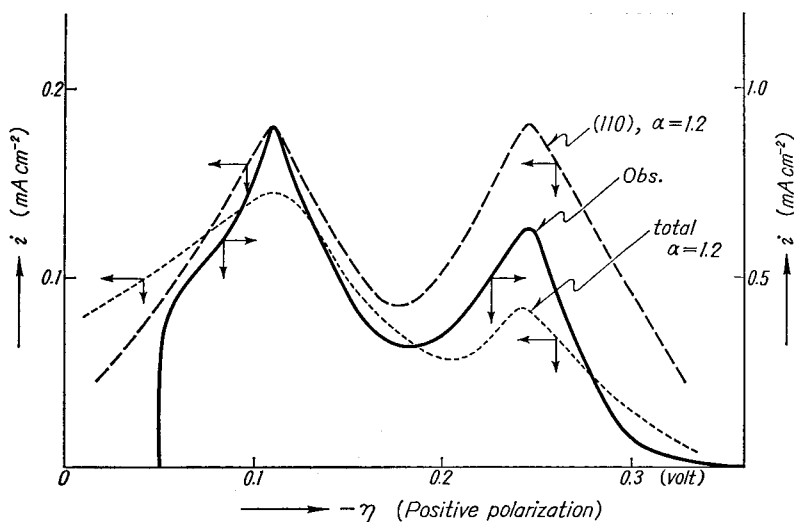


Fig. 5. Comparison of the theoretical current-potential curves with the experimental ones observed on Pt in 20% sulfuric acid solution at a sweep rate of 0.28 V/sec.¹⁶⁾ Curve "(110)" or "total" is obtained at $\alpha = 1.2$ assuming the (110) plane or equal fractions of the (110), (100) and (111) planes for the electrode surface.

values of overvoltage than either the curve calculated with $\alpha = 1.2$ or as the observed curve. Furthermore, the separation between the two peaks increases. Best agreement is thus obtained at $\alpha = 1.2$. This is somewhat smaller than the value of $\alpha = 1.5$ which was derived for a Ni electrode.¹⁰⁾

The peak values of current, on the other hand, are 3 to 5 times smaller than the experimental values. Such a difference might be attributed to the roughness of the electrode surface. The peak area calculated from the curve "obs" of Fig. 5 and the sweep rate of 0.28 V/sec, is about 4.3×10^{-4} Coulomb, approximately three times larger than the charge corresponding to the full coverage of H(a) on the (110) plane as seen from Eq. (20). The peak area of the curve "(110)" was 1.5×10^{-4} Coulomb.

The pseudo-capacity due to the shift of the equilibrium of step (1), C_{ads} , is defined as

$$C_{\text{ads}} \equiv \frac{NF}{N_A} \frac{d\theta}{d\eta}$$

or using Eq. (19) as

$$C_{\text{ads}} = i/(d\eta/dt).$$

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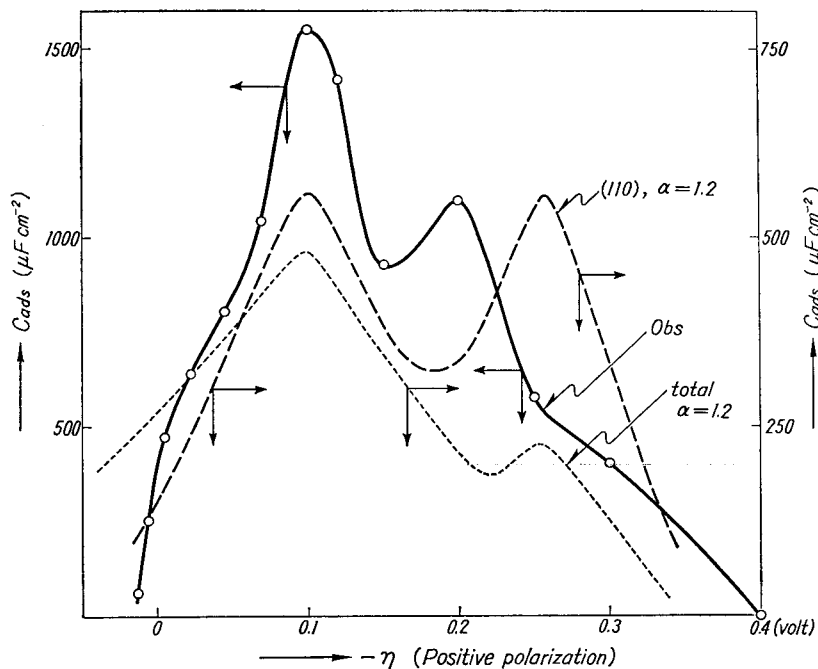


Fig. 6. Comparison of the theoretical C_{ads} -potential curves with the experimental ones observed on Pt in 8N H_2SO_4 solution.¹⁷⁾ Curve "(110)" or "total" is obtained at $\alpha = 1.2$ assuming the (110) plane or equal fractions of the (110), (100) and (111) planes for the electrode surface.

Since the term $(d\eta/dt)$ is constant, *i.e.* 0.28 V/sec in the present case, the previous discussion of current-potential curves applies also to the potential dependent behaviour of C_{ads} . Figure 6 shows the comparison of the experimental results for Pt in 8N H_2SO_4 solution¹⁷⁾ with the values calculated from the above equation and Eq. (19). Curve "(110)" or "total" represents the theoretical curve obtained under the assumption that only the (110) plane or equal fractions of the (110), (100) and (111) planes are exposed to the surface. The peak current values are again approximately three times smaller than those experimentally obtained, which might be attributed to the roughness of the surface as mentioned before.

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