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A SIMPLE METHOD OF STATISTICAL MECHANICAL CALCULATION OF ADSORPTION ISOTHERM

By

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Abstract

A simple but accurate method of statistical mechanical calculation of adsorption isotherm allowed for interactions among adsorbate has been proposed with special reference to the dissociative adsorption of hydrogen on (110)-lattice plane of adsorbent nickel, on which hydrogen atoms are predominantly adsorbed as theoretically concluded, assuming that each metal atom provides a physically identical site of a hydrogen adatom right above it at equal height.

The approximation frequently resorted to is the proportional one^{3,5,6)}, in which the repulsive potential of an adatom due to surrounding ones is assumed proportional to the covered fraction θ of sites by adatoms. In the first, second and third approximations carried out by HORIUTI and HIROTA¹⁾ the repulsive potentials due to neighbouring adatoms are taken statistical mechanically discretely into account as far as the first, second and third nearest neighbours respectively. The isotherm thus worked out appeared to converge to a definite one as we proceed with the degree of approximation in order of the proportional, first, second and third approximations¹⁾, those of the second and the third ones lying very close to each other, whereas the labour of calculation rapidly increases with the progress of the degree of approximation¹⁾.

In the simple method here proposed the repulsive potentials due to the first nearest neighbours are only treated statistical mechanically discretely, while those due to the second and the third nearest neighbours by the proportional approximation. The result is practically coincident with that of the second approximation, in which θ stays appreciably around 0.5 with increase of activity of adatoms as compared with in the proportional approximation. The present method promises an improved treatment of adsorption and hydrogen electrode kinetics, where the proportional approximation only has hitherto been practised because of extremely troublesome calculation required for higher approximations.

Introduction

OKAMOTO, HORIUTI and HIROTA¹⁾ have taken the repulsive interaction among hydrogen adatoms into consideration with regard to the derivation of the TAFEL's law from the catalytic mechanism^{1,4,5)}, assuming that the potential of an adatom or an activated state due to repulsion of surrounding adatoms was proportional to the population of the latter or the covered fraction θ of sites by adatoms. This approximation is what we call the proportional one,

which was independently applied by BRAGG and WILLIAMS⁶⁾. They^{1,2)} assumed that the sites of adsorption each of a hydrogen adatom are situated each right above a metal atom on the (110)-lattice plane and physically identical with each other, and attributed the interaction to the quantum mechanical exchange and COULOMB potential between hydrogen atoms not bonded with each other^{1,2)}. The (110)-lattice plane has been theoretically concluded^{1,7)} to adsorb hydrogen atoms predominantly among other lattice planes.

HORIUTI and HIROTA²⁾ have calculated the isotherm of dissociative adsorption of hydrogen on the base of the same model¹⁾ statistical mechanically in different degrees of approximation allowing for the repulsive interaction among hydrogen adatoms in extension of the BETHE-PEIERLS' method³⁾. They calculated the potential R_I , R_{II} or R_{III} of an adatom due to the exchange and COULOMB potential mentioned above of the first, second or third nearest neighbouring adatom for (110)-lattice plane of nickel respectively as²⁾

$$R_I = 0.1019 \text{ ev}, \quad R_{II} = 0.034 \text{ ev}, \quad R_{III} = 0.0028 \text{ ev}. \quad (1. I), (1. II), (1. III)$$

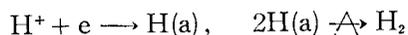
The first, second and third nearest neighbours in this case are respectively 2.49, $\sqrt{2} \times 2.49$ and $\sqrt{3} \times 2.49$ Å distant and respectively 2, 2 and 4 in number.

In the first approximation it is assumed²⁾ that there exists repulsion only between first nearest neighbours of the potential of the magnitude $R_I + R_{II} + 2R_{III}$, so that the potential of an adatom due to the repulsions of surrounding adatoms at full occupation of sites equals, for the sake of the numerical comparison of the calculated isotherms, that in the case of the third approximation, where all the three kinds of the repulsive potentials R_I , R_{II} and R_{III} are taken statistical mechanically discretely into account. In the second approximation the repulsive potential of the first and the second nearest neighbours is only discretely taken into account attributing to them the potentials of the magnitude $R_I + 2R_{III} \cdot R_I / (R_I + R_{II})$ and $R_{II} + 2R_{III} \cdot R_{II} / (R_I + R_{II})$ respectively, prorating the remaining repulsive potential $2R_{III}$ per one first or second nearest neighbour between them for the same reason²⁾. Isotherm is also calculated by the proportional approximation for comparison, assuming the potential of an adatom due to neighbouring ones to be $(2R_I + 2R_{II} + 4R_{III}) \theta$, which equals that in the first, second and third approximation at $\theta=1$, as well as by zeroth approximation, *i.e.* LANGMUIR's one, in which the interaction among adatoms is altogether ignored.

The isotherm of the second approximation thus worked out was found very close to that of the third approximation²⁾, that of the first approximation deviated somewhat from them²⁾, that of the proportional approximation wider and that of the zeroth approximation still further as seen in Fig. 1.

The degree of approximations will be termed in this paper to proceed in order of the zeroth, proportional, first, second and third ones. The calculation of these approximations became rapidly laborious with the progress of degree of approximation. The calculation of the third approximation is thus tremendously troublesome, which computes severally the partition functions of the states of different arrangements of different number of adatoms over a group of nine sites consisting of one site of interest, two first nearest ones, two second nearest ones and four third nearest ones. Less laborious second approximation appeared to be sufficient because of the isotherm obtained lying close to that of the third approximation.

The labour and the precision of this sort of calculation are important to a theoretical treatment of reaction rate allowed for the interaction. Consider for instance the catalytic mechanism



to cause the hydrogen electrode reaction $2\text{H}^+ + 2\text{e} = \text{H}_2$ to proceed, where H^+ is proton associated with BRÖNSTED base H_2O or OH^- , e the metal electron, $\text{H}(\text{a})$ the adsorbed hydrogen atom on electrode and $\xrightarrow{\Delta}$ the rate-determining step. The rate of hydrogen electrode reaction equals that of the rate-determining step and the latter depends on the activity of $\text{H}(\text{a})$, which is determined by the partial equilibrium of the preliminary step $\text{H}^+ + \text{e} \rightarrow \text{H}(\text{a})$. The activity of $\text{H}(\text{a})$ under the partial equilibrium equals now that in adsorption equilibrium with hydrogen gas under the fictitious pressure* of $P \exp(2F\eta/RT)$, where P is the actual one around the hydrogen electrode, η the overvoltage or the cathodic polarization as referred to a reversible hydrogen electrode in the same solution and the same hydrogen gas, F the Faraday and R or T of usual meaning. The rate of the hydrogen electrode reaction is thus determined by the activity of $\text{H}(\text{a})$, which equals that of $\text{H}(\text{a})$ in adsorption equilibrium with hydrogen gas under the fictitious pressure $P \exp(2F\eta/RT)$.

To take now the repulsions due to surrounding adatoms as far as the second nearest neighbours statistical mechanically discretely into account in line

*) Let μ^{H^+} etc. be the chemical potentials of H^+ etc. The partial equilibrium of the step $\text{H}^+ + \text{e} \rightarrow \text{H}(\text{a})$ is represented by $\mu^{\text{H}^+} + \mu^{\text{e}} = \mu^{\text{H}(\text{a})}$ and the equilibrium of hydrogen electrode reaction $2\text{H}^+ + 2\text{e} = \text{H}_2$ on the reversible hydrogen electrode by $2\mu^{\text{H}^+} + 2\mu_{\text{R}}^{\text{e}} = \mu^{\text{H}_2}$, where $\mu_{\text{R}}^{\text{e}}$ is the chemical potential of metal electron in the reversible hydrogen electrode. We have from the above two equations $\mu^{\text{H}(\text{a})} = 1/2 \cdot \mu^{\text{H}_2} + \mu^{\text{e}} - \mu_{\text{R}}^{\text{e}}$. The μ^{H_2} is expressed in terms of the hydrogen pressure P around the electrode and the value $\mu_{\text{R}}^{\text{H}_2}$ of μ^{H_2} at $P=1$, as $\mu^{\text{H}_2} = \mu_{\text{R}}^{\text{H}_2} + RT \ln P$, while $\mu^{\text{e}} - \mu_{\text{R}}^{\text{e}} = F\eta$ by definition of η . The last three equations yield $2\mu_{\text{H}(\text{a})} = \mu_{\text{R}}^{\text{H}_2} + RT \ln P + 2F\eta$ or $2\mu_{\text{H}(\text{a})} = \mu_{\text{R}}^{\text{H}_2} + RT \ln P \exp(2F\eta/RT)$, which states that the chemical potential or the activity of $\text{H}(\text{a})$ is that in equilibrium with hydrogen gas under the fictitious pressure $P \exp(2F\eta/RT)$.

with the second approximation, the two adjacent sites occupied by the activated complex^{1,4,5)} and six ones around it have to be taken into account with regard to different arrangements of different number of adatoms⁸⁾ on them, which would cost as much labour as the third approximation mentioned above. The proportional approximation has thus been resorted to practically exclusively as regards the reaction kinetics^{1,4,5)} but the result could not be accurate enough as judged from the considerable deviation mentioned above of the isotherm of the proportional approximation from those of higher approximations.

It is hence significant to find out a simple but enough accurate method of approximation, which is effected in the present paper by a proper combination of the first and the proportional approximations as described in what follows.

Method of Approximation

The present method consists in deriving adsorption isotherm by treating the repulsive potential of an adatom^{*)} due to the first nearest neighbours statistical mechanically discretely but that $R_{II,III}$ due to the second and the third nearest neighbours as proportional to the covered fraction θ , *i. e.* as

$$R_{II,III} = R'\theta, \quad (2. a)$$

where

$$R' = 2R_{II} + 4R_{III} \quad (2. b)$$

is the value of $R_{II,III}$ at $\theta=1$. Adsorption isotherm is determined under these premises, by the simultaneous equations

$$\theta/(1-\theta) = \gamma\zeta (1 + \gamma\zeta \xi_1\rho)^2 / (1 + \gamma\zeta\rho)^2 \quad (3. \theta)$$

and

$$\rho + \gamma\zeta\rho^2 = 1 + \gamma\zeta \xi_1\rho, \quad (3. \rho)$$

*) TOYA⁹⁾ has arrived at the conclusion that there exist two sorts of hydrogen adatom on metallic adsorbent, *i. e.* r-adatom and s-adatom as called by him, by applying the first principle of quantum mechanics to metallic adsorbent interacting with hydrogen atom. The r-adatom is an adatom of ordinary sense, *i. e.* that situated outside the electronic surface of the adsorbent forming with the latter more or less polarized covalent bond. The s-adatom is a sort of hydrogen atom dissolved in the adsorbent but situated close to the electronic surface inside it. What is termed adatom in the text is exclusively r-adatom.

TOYA has further concluded on the basis of his theory⁹⁾ that the repulsive potentials among r-adatoms are appreciably larger than the values estimated^{1,2)} as given by (1), although not precisely estimated numerically. Since the present work is concerned with the relative accuracy of different approximations but not with the absolute evaluation of isotherms, numerical values of (1) are used in the present approximation for the sake of comparison with those of other approximations, which have been conducted on the same base.

where

$$\xi_1 = \exp(-R_1/kT), \quad \zeta = \exp(-R'\theta/kT). \quad (3. \xi), (3. \zeta)$$

The θ is given as a function of γ and T by eliminating ζ , ξ_1 and ρ from the above four equations. The γ is proportional to the square root of the pressure of hydrogen gas which is in equilibrium with adatoms^{2)*}, hence to the activity of the latter. The physical meaning of ρ is accounted for in course of deriving (3) as below.

Let $\mathfrak{D}C$ be the partition function of a system C consisting of a macroscopic adsorbent and a definite amount of adatoms on it, Σ a definite group of three adjacent sites on the macroscopic adsorbent consisting of one site σ_0 of interest and its two first nearest neighbouring sites σ_1 and σ_2 , which are in line with each other according to the present model of adsorbent and $\mathfrak{D}C_{\Sigma(0)}$ the partition function of $C_{\Sigma(0)}$, *i.e.* C at the particular state, where Σ is completely unoccupied with certainty. The C at the particular state, $C_{\Sigma(0,H,0)}$, where only σ_0 is occupied by an adatom leaving σ_1 and σ_2 unoccupied, is now derived from $C_{\Sigma(0)}$ by extracting an adatom from outside Σ and putting it to σ_0 . Following this operation, the partition function $\mathfrak{D}C_{\Sigma(0,H,0)}$ of $C_{\Sigma(0,H,0)}$ is derived from $\mathfrak{D}C_{\Sigma(0)}$ as follows.

Let ρ^H be the factor of multiplication of partition function, *i.e.*

$$\rho^H = \mathfrak{D}C^H/\mathfrak{D}C \quad (4)$$

caused by addition of an adatom to C to increase the definite amount of adatoms on C by one to make C^H , where $\mathfrak{D}C^H$ or $\mathfrak{D}C$ is the partition function of C^H or C respectively both without any microscopic constraint, *e.g.* that indicated by $\Sigma(0)$ or $\Sigma(0,H,0)$. Since $-kT \ln \mathfrak{D}C^H$ or $-kT \ln \mathfrak{D}C$ has the property of the free energy of the system C^H or C respectively, $-kT \ln \rho^H$ equals, according to (4), the free energy increase caused by addition of an adatom to C to make C^H or the chemical potential of adatom per atom, *i.e.* the reversible work required to bring up a hydrogen atom from its standard state to the state of an adatom on C . The extraction of an adatom from $C_{\Sigma(0)}$ converts hence its partition function from $\mathfrak{D}C_{\Sigma(0)}$ to $\mathfrak{D}C_{\Sigma(0)}/\rho^H$, neglecting the effect on ρ^H of the microscopic constraint indicated by $\Sigma(0)$ imposed upon the macroscopic system C or C^H . Let now $q_{\Sigma(0,H,0)}^H$ be the factor of multiplication of the partition function caused by putting an adatom on σ_0 leaving σ_1 and σ_2 unoccupied. Because of the property of partition function mentioned above, $-kT \ln q_{\Sigma(0,H,0)}^H$ is the increment of free energy of the system caused by the addition of an adatom to σ_0 or the reversible work required for bringing an adatom from its standard state mentioned above onto σ_0 , which is expressed as

$$-kT \ln q_{\Sigma(0,H,0)}^H = -kT \ln q_0^H + R_{II,III},$$

where $-kT \ln q_0^H$ is the particular value of the reversible work in the absence of interaction and $R_{II,III}$ is identified with that part of the reversible work due to the interaction of the adatom to be brought to σ_0 with the second and the third nearest neighbours outside Σ . We have from the above equation

$$q_{\Sigma(0,H,0)}^H = q_0^H \zeta, \quad (5. a)$$

*) The constant of proportion is given as a known function of temperature²⁾.

where

$$\zeta = \exp(-R'\theta/kT) \quad (5. b)$$

according to (2. a). The partition function $\mathfrak{D}C_{\Sigma^{(0, H, 0)}}$ of $C_{\Sigma^{(0, H, 0)}}$ *i. e.* C at the particular state, where σ_0 is occupied by an adatom but σ_1 and σ_2 are unoccupied, is now expressed as $\mathfrak{D}C_{\Sigma^{(0)}}$ $q_{\Sigma^{(0, H, 0)}}^H/p^H$ or by (5. a) as

$$\mathfrak{D}C_{\Sigma^{(0, H, 0)}} = \mathfrak{D}C_{\Sigma^{(0)}} \tau \zeta, \quad (6. a)$$

where

$$\tau = q_0^H/p^H. \quad (6. b)$$

We now turn to the particular state of C , where either σ_1 or σ_2 as well as σ_0 is occupied. This particular state of C implies two different ones $C_{\Sigma^{(H, H, 0)}}$ and $C_{\Sigma^{(0, H, H)}}$ according as σ_1 or σ_2 is occupied besides σ_0 . The respective state $C_{\Sigma^{(H, H, 0)}}$ or $C_{\Sigma^{(0, H, H)}}$ is derived from $C_{\Sigma^{(0, H, 0)}}$ by bringing an adatom from outside Σ onto σ_1 or σ_2 respectively, similarly as in deriving $C_{\Sigma^{(0, H, 0)}}$ from $C_{\Sigma^{(0)}}$. The respective partition function $\mathfrak{D}C_{\Sigma^{(H, H, 0)}}$ of $C_{\Sigma^{(H, H, 0)}}$ or $\mathfrak{D}C_{\Sigma^{(0, H, H)}}$ of $C_{\Sigma^{(0, H, H)}}$ is thus given as

$$\mathfrak{D}C_{\Sigma^{(H, H, 0)}} = \mathfrak{D}C_{\Sigma^{(0, H, 0)}} q_{\Sigma^{(H, H, 0)}}^H/p^H, \quad (7. a)$$

$$\mathfrak{D}C_{\Sigma^{(0, H, H)}} = \mathfrak{D}C_{\Sigma^{(0, H, 0)}} q_{\Sigma^{(0, H, H)}}^H/p^H, \quad (7. b)$$

where $q_{\Sigma^{(H, H, 0)}}^H$ or $q_{\Sigma^{(0, H, H)}}^H$ is the factor of multiplication of partition function caused by bringing an adatom from its standard state onto the vacant site σ_1 or σ_2 respectively of $C_{\Sigma^{(0, H, 0)}}$. The $q_{\Sigma^{(H, H, 0)}}^H$ and $q_{\Sigma^{(0, H, H)}}^H$ are identical with each other on account of the symmetry of Σ and the relevant reversible works are expressed as

$$-kT \ln q_{\Sigma^{(H, H, 0)}}^H = -kT \ln q_{\Sigma^{(0, H, H)}}^H = -kT \ln q_0^H + R_I + R_e + R_{II, III}, \quad (8)$$

where R_I is identified with the part of the reversible work due to the repulsion exerted by the adatom preliminarily situated on σ_0 , $R_{II, III}$ with that due to the repulsion exerted by adatoms on the second and third nearest sites to σ_1 or σ_2 and R_e is the part of the reversible work due to the repulsion of an adatom, which may occupy the first nearest site to σ_1 or σ_2 outside Σ .

The above equation is written with reference to (2. a) and (5. b) as

$$q_{\Sigma^{(H, H, 0)}}^H = q_{\Sigma^{(0, H, H)}}^H = q_0^H \zeta_1^2 \rho, \quad (9. q)$$

where

$$\zeta_1 = \exp(-R_I/kT), \quad \rho = \exp(-R_e/kT). \quad (9. \xi), (9. \rho)$$

We have now according to (7), (9. q) and (6. b)

$$\mathfrak{D}C_{\Sigma^{(H, H, 0)}} = \mathfrak{D}C_{\Sigma^{(0, H, H)}} = \mathfrak{D}C_{\Sigma^{(0, H, 0)}} \tau \zeta_1^2 \rho,$$

or by (6. a)

$$\mathfrak{D}C_{\Sigma^{(H, H, 0)}} = \mathfrak{D}C_{\Sigma^{(0, H, H)}} = \mathfrak{D}C_{\Sigma^{(0)}} \tau^2 \zeta_1^2 \rho. \quad (10)$$

The remaining possible particular state of C satisfying the condition that σ_0 is occupied is that where all the three constituent sites of Σ are occupied, which is derived from $C_{\Sigma^{(H, H, 0)}}$ or $C_{\Sigma^{(0, H, H)}}$ by transferring another adatom from outside Σ to the vacant site σ_2 or σ_1 respectively. The partition function is reduced by a factor p^H by extracting an adatom from outside Σ and multiplied by a factor $q_{\Sigma^{(H, H, H)}}^H$ or $q_{\Sigma^{(H, H, H)}}^H$ by bringing the extracted adatom

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onto the vacant site of $C_{\Sigma(\text{H},\text{H},0)}$ or $C_{\Sigma(0,\text{H},\text{H})}$. The factors $q_{\Sigma(\text{H},\text{H},\text{H})}^{\text{H}}$ and $q_{\Sigma(0,\text{H},\text{H})}^{\text{H}}$ are identical with each other as well as with $q_{\Sigma(\text{H},\text{H},0)}^{\text{H}} = q_{\Sigma(0,\text{H},\text{H})}^{\text{H}}$ because of the premises on repulsion and the symmetry of Σ , hence according to (9. q)

$$q_{\Sigma(\text{H},\text{H},\text{H})}^{\text{H}} = q_{\Sigma(0,\text{H},\text{H})}^{\text{H}} = q_0^{\text{H}} \zeta \xi_1 \rho.$$

$\mathfrak{D}C_{\Sigma(\text{H},\text{H},\text{H})}$ is in consequence with reference to (6. b)

$$\begin{aligned} \mathfrak{D}C_{\Sigma(\text{H},\text{H},\text{H})} &= \mathfrak{D}C_{\Sigma(0,\text{H},\text{H})} q_{\Sigma(\text{H},\text{H},\text{H})}^{\text{H}} / p^{\text{H}} = \mathfrak{D}C_{\Sigma(\text{H},\text{H},0)} q_{\Sigma(\text{H},\text{H},\text{H})}^{\text{H}} / p^{\text{H}} \\ &= \mathfrak{D}C_{\Sigma(0,\text{H},\text{H})} \tau \zeta \xi_1 \rho = \mathfrak{D}C_{\Sigma(\text{H},\text{H},0)} \tau \zeta \xi_1 \rho \end{aligned}$$

or according to (10)

$$\mathfrak{D}C_{\Sigma(\text{H},\text{H},\text{H})} = \mathfrak{D}C_{\Sigma(0)} \tau^3 \zeta^3 \xi_1^2 \rho^2. \quad (11)$$

Let now $\mathfrak{D}C_{\sigma_0(\text{H})}$ be the partition function of $C_{\sigma_0(\text{H})}$ *i.e.* C at the particular state, where σ_0 is occupied with certainty irrespective as to whether σ_1 and σ_2 are occupied or not. $\mathfrak{D}C_{\Sigma(0,\text{H},0)}$, $\mathfrak{D}C_{\Sigma(\text{H},\text{H},0)}$, $\mathfrak{D}C_{\Sigma(0,\text{H},\text{H})}$ and $\mathfrak{D}C_{\Sigma(\text{H},\text{H},\text{H})}$ are now the partition functions of all possible particular states of $C_{\sigma_0(\text{H})}$, which are exclusive of each other, hence

$$\mathfrak{D}C_{\sigma_0(\text{H})} = \mathfrak{D}C_{\Sigma(0,\text{H},0)} + \mathfrak{D}C_{\Sigma(\text{H},\text{H},0)} + \mathfrak{D}C_{\Sigma(0,\text{H},\text{H})} + \mathfrak{D}C_{\Sigma(\text{H},\text{H},\text{H})},$$

or according to (6. a), (10) and (11)

$$\mathfrak{D}C_{\sigma_0(\text{H})} = \mathfrak{D}C_{\Sigma(0)} \tau \zeta (1 + \tau \zeta \xi_1 \rho)^2. \quad (12)$$

Similarly the partition function $\mathfrak{D}C_{\sigma_0(0)}$ of $C_{\sigma_0(0)}$, *i.e.* C at the particular state, where σ_0 is unoccupied with certainty is given as

$$\mathfrak{D}C_{\sigma_0(0)} = \mathfrak{D}C_{\Sigma(0,0,0)} + \mathfrak{D}C_{\Sigma(\text{H},0,0)} + \mathfrak{D}C_{\Sigma(0,0,\text{H})} + \mathfrak{D}C_{\Sigma(\text{H},0,\text{H})},$$

where $\mathfrak{D}C_{\Sigma(0,0,0)}$ is the partition function of the particular state $C_{\Sigma(0,0,0)}$, where all the constituent sites of Σ are unoccupied, hence $\mathfrak{D}C_{\Sigma(0)}$ itself by definition; $\mathfrak{D}C_{\Sigma(\text{H},0,0)}$, $\mathfrak{D}C_{\Sigma(0,0,\text{H})}$ or $\mathfrak{D}C_{\Sigma(\text{H},0,\text{H})}$ is the partition function of $C_{\Sigma(\text{H},0,0)}$, $C_{\Sigma(0,0,\text{H})}$ or $C_{\Sigma(\text{H},0,\text{H})}$ respectively, *i.e.* C at the particular state, where σ_1 only, σ_2 only or both σ_1 and σ_2 are respectively occupied leaving σ_0 commonly unoccupied. $\mathfrak{D}C_{\Sigma(\text{H},0,0)}$ and $\mathfrak{D}C_{\Sigma(0,0,\text{H})}$ are identical with each other because of the symmetry of Σ and expressed by the similar reasoning to the above as

$$\mathfrak{D}C_{\Sigma(\text{H},0,0)} = \mathfrak{D}C_{\Sigma(0,0,\text{H})} = \mathfrak{D}C_{\Sigma(0)} \tau \zeta \rho. \quad (13)$$

The lack of the factor $\tau \zeta \xi_1$ here as compared with $\mathfrak{D}C_{\Sigma(\text{H},\text{H},0)} = \mathfrak{D}C_{\Sigma(0,\text{H},\text{H})}$ in (10) is due to the absence of an adatom on σ_0 , which gives rise among others to the part of reversible work identified with R_{I} in (8).

$\mathfrak{D}C_{\Sigma(\text{H},0,\text{H})}$ is similarly expressed as

$$\mathfrak{D}C_{\Sigma(\text{H},0,\text{H})} = \mathfrak{D}C_{\Sigma(0)} \tau^2 \zeta^2 \rho^2$$

and we have from the above four equations

$$\mathfrak{D}C_{\sigma_0(0)} = \mathfrak{D}C_{\Sigma(0)} (1 + \tau \zeta \rho)^2. \quad (14)$$

The ratio of $\mathfrak{D}C_{\sigma_0(\text{H})}$ to $\mathfrak{D}C_{\sigma_0(0)}$ is now the ratio of the probability θ that σ_0 is occupied by an adatom to the probability $1 - \theta$ that σ_0 is unoccupied, hence (3. θ) from (12) and (14), identifying θ with the covered fraction θ on the ground of the premised physical identity of the sites.

The ζ or ξ_1 in (3. θ) is given as a known function of θ and T by (1. II), (1. III), (2) and (5. b) or that of T by (1. I) and (9. ξ) respectively. The ρ is yet to be determined in order to

find θ as a function of r and T as in the other cases of approximation to be compared with the present one.

We have for the partition function $\mathfrak{D}C_{\sigma_1(\theta)}$ of $C_{\sigma_1(\theta)}$, i.e. C in the particular state, where σ_1 is unoccupied with certainty,

$$\mathfrak{D}C_{\sigma_1(\theta)} = \mathfrak{D}C_{\Sigma(\theta, \theta, \theta)} + \mathfrak{D}C_{\Sigma(\theta, \text{H}, \theta)} + \mathfrak{D}C_{\Sigma(\theta, \theta, \text{H})} + \mathfrak{D}C_{\Sigma(\theta, \text{H}, \text{H})},$$

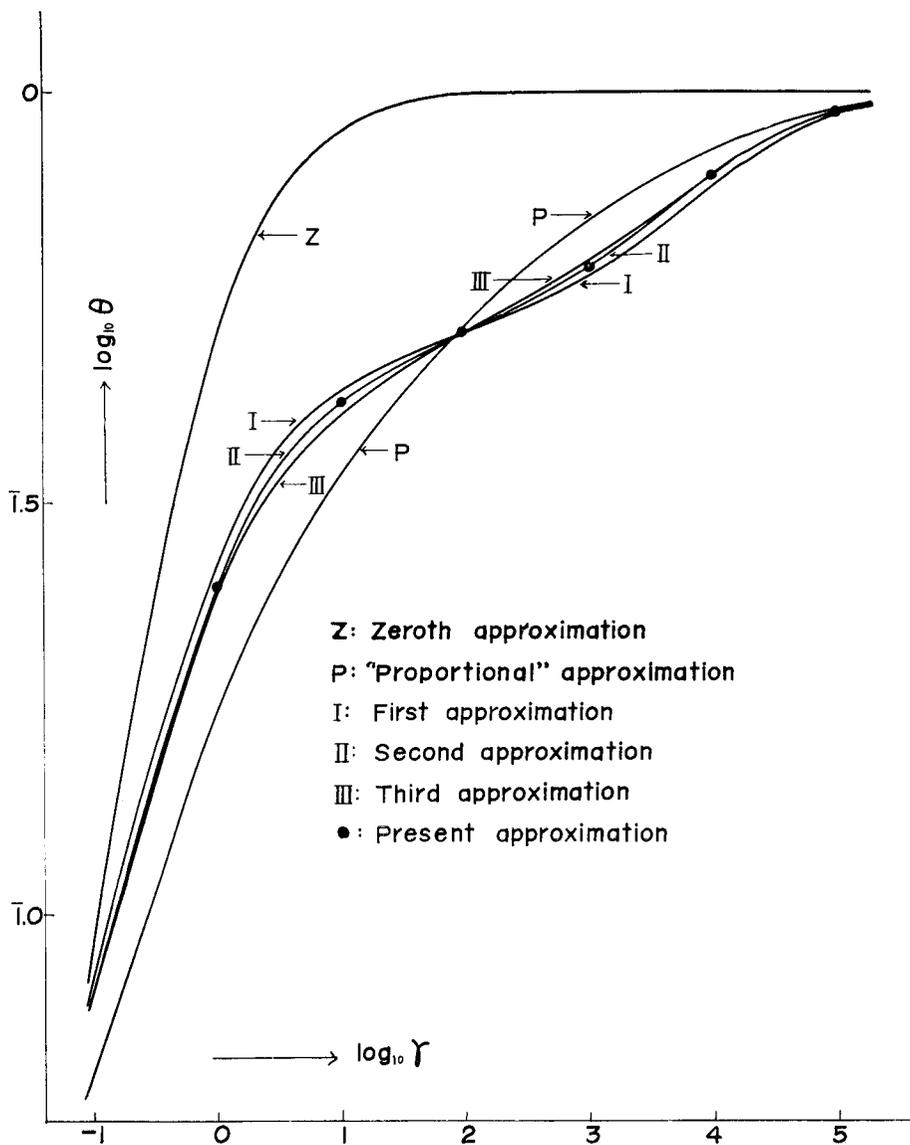


Fig. 1. Coverage θ versus Activity r of Hydrogen Adatom.

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where $\mathfrak{D}C_{\Sigma(0, H, \theta)}$ is given by (6. a), $\mathfrak{D}C_{\Sigma(0, \theta, H)}$ by (13) and $\mathfrak{D}C_{\Sigma(0, H, H)}$ by (10), hence

$$\mathfrak{D}C_{\sigma_i(0)} = \mathfrak{D}C_{\Sigma(0)}(1 + \gamma\zeta + \gamma\zeta\rho + \gamma^2\zeta^2\xi_1, \rho). \quad (15)$$

Equating $\mathfrak{D}C_{\sigma_i(0)}$ to $\mathfrak{D}C_{\sigma_i(0)}$ on the ground of the physical identity of sites according to the BETHE-PEIERLS' method³⁾, we have (3. θ) from (14) and (15).

Results

Fig. 1 shows $\log_{10} \theta$ plotted against $\log_{10} \gamma$ of other approximations²⁾ than the present one by the respective curves and that of the present one by solid dots. The curve of the zeroth approximation or the LANGMUIR'S adsorption isotherm is drawn according to the equation

$$\frac{\theta}{1-\theta} = \gamma,$$

to which (3. θ) reduces in the absence of interaction, when ζ , ξ_1 and ρ equal respectively unity according to (5. b), (9. ξ) and (3. ρ).

We see that the solid dots fall precisely on the isotherm of the second approximation or the present approximation much simpler than the second approximation practically exactly reproduce the result of the latter, which is, on the other hand, very close to that of the most laborious third approximation. The result of the present approximation or of the second approximation differs mainly from that of the proportional approximation hitherto applied to reaction kinetics in that θ stays longer around 0.5 with increase of γ than that of the proportional approximation. The present approximation will be later applied to the kinetics of hydrogen electrode reaction.

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