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ISOTHERM OF DISSOCIATIVE ADSORPTION OF HYDROGEN ALLOWED FOR REPULSIVE INTERACTIONS AMONG ADSORBED ATOMS

By

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Introduction

OKAMOTO and the present authors were led previously to assume in accounting for experimental results of hydrogen electrode reaction that the seats of reaction and adsorption were the lattice planes of the crystal surface of the electrode, each lattice point providing a physically identical adsorption site of a hydrogen atom in distinction from the model of ununiform sites of different adsorption energies. The geometry of the former model has obliged them to take into account the quantum-mechanical repulsive interactions among adsorbed hydrogen atoms as well as between the latters and the constituent hydrogen atoms of the critical complex of the rate-determining step of the catalytic mechanism, *i.e.* the recombination of adsorbed hydrogen atoms. They have thus deduced the TAFEL's law from the catalytic mechanism on the basis of the above model of physically identical sites of adsorption on the lattice plane1)2), which could not be effected before by means of classical kinetics**). We will call the latter model the crystal surface model and that of physically ununiform sites without the interaction being taken into account the ununiform surface model.

The potential of an adsorbed hydrogen atom or of the critical complex due to the repulsion was approximated in the above treatments, on the basis of the crystal surface model, by that proportional to the coverage θ of sites by adsorbed hydrogen atoms. This approximation will be called the "proportional" approximation in what follows. The adsorption isotherm based on the same assumption

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**) KEII [Ref. 6] has recently deduced the TAFEL's law from the catalytic mechanism alternatively on the basis of the ununiform surface model under a particular assumptions on the distributions of the adsorption energies and of the energies of the critical complex of the recombination.

was proposed later by FOWLER[3] in accordance with BRAGG and WILLIAMS' approximation applied to alloys[4]. It may be noted that the isotherm and the kinetic equation derived with the "proportional" approximation on the basis of the crystal surface model are mathematically identical respectively with those advanced on the basis of the ununiform surface model with the assumption of a particular distribution function of sites as shown by DOLIN and ERSHLER[5] and KEII[6], *i.e.* the adsorption isotherm of SLYGIN and FRUMKIN[7] and TEMKIN and PYZHEV[8] and the kinetic equation advanced by ROGINSKY and ZELDOVICH[9] and ELOVICH and KHARAKHORIN[10].

One of the present authors outlined in a previous paper[11] a method to advance the approximation as far as required on the basis of the crystal surface model in extension of the BETHE and PEIERLS' method[12]. The present paper is concerned with the actual calculation of the isotherm of dissociative adsorption of hydrogen on nickel along this line, proceeding with the order of approximation until the resulting adsorption isotherm practically converges to an ultimate one and with the discussion of the validity of the underlying crystal surface model based on the comparison of the theoretical result with experimental data.

§ 1. Specification of the Model of Adsorbent and the Repulsive Potential

The lattice plane in question was taken particularly to be the (110) of f.c.c. nickel crystal on the ground of the conclusion in a previous paper[1] that hydrogen atoms were predominantly adsorbed on this lattice plane.

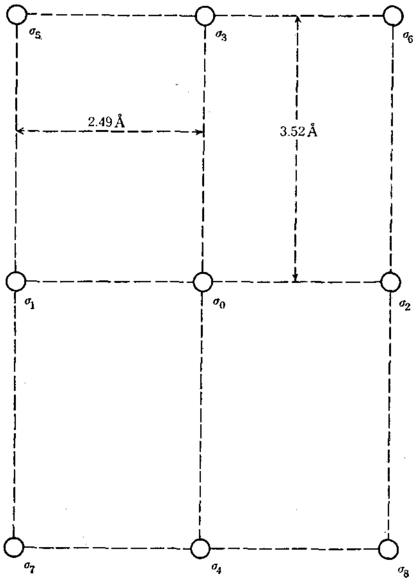

Fig. 1. (110)-lattice plane of nickel.

Fig. 1 shows the (110)-lattice plane. Two first nearest nickel atoms to that σ_0 of interest are denoted by σ_1 and σ_2, two second nearest ones by σ_3 and σ_4, and four third nearest ones by σ_5, σ_6, σ_7 and σ_8. Every nickel atom gives a site of adsorption of a hydrogen atom right above it on a definite plane parallel to the lattice plane, so that the sites themselves form a (110)-lattice congruent to the basic one. The basic lattice plane is taken extensive enough, that the sites provided by it are physically identical with each other. Each adsorption site will be signified by the same notation with that of the corresponding nickel atom on the basic lattice in what follows.

The calculation of isotherm was conducted in the zeroth, first, second, third and "proportional" approximations, which were different in the allowance for repulsion exerted upon an adsorbed hydrogen atom by surrounding ones. No repulsion was taken into account in the zeroth approximation, repulsions exerted by the two first nearest ones in the first approximation, those by the first and the second nearest ones in the second approximation and those by the first, second and the third nearest ones in the third approximation. The "proportional" approximation was that referred to in the introduction.

The repulsive potential between two adsorbed hydrogen atoms was calculated semiempirically according to EYRING[13] as -35% of the MORSE function $D_0[\exp\{-2a(r-r_0)\}-2\exp\{-a(r-r_0)\}]$ with constants $D_0=4.73$ *e*-volt, $a=1.98$ Å^{-1} and $r_0=0.7395$ Å*). Repulsive potentials R_{I}, R_{II} and R_{III} between the first, second and third nearest neighbourers were thus calculated as

$$R_{\text{I}}=0.1019\,,\quad R_{\text{II}}=0.0134\,,\quad R_{\text{III}}=0.0028\ e\text{-volt} \tag{1. III}$$

on the base of the spacing given in Fig. 1. To make the comparison of the resulting adsorption isotherms close, the total repulsive potential of an adsorbed hydrogen atom at full occupation of surrounding ones was taken equal throughout all approximations but the zeroth one, by rationing the neglected interaction potentials *pro rata* to those retained as follows. The repulsive potentials R'_{I} and R'_{II} respectively due to the first and the second nearest neighbourers in the second approximation were thus taken as

$$\begin{aligned} R'_{\text{I}}&=R_{\text{I}}+2R_{\text{III}}R_{\text{I}}/(R_{\text{I}}+R_{\text{II}})=0.1068\,,\\ R'_{\text{II}}&=R_{\text{II}}+2R_{\text{III}}R_{\text{II}}/(R_{\text{I}}+R_{\text{II}})=0.01405\ e\text{-volt}. \end{aligned} \tag{1. II}$$

Similarly

$$R''_{\text{I}}=R_{\text{I}}+R_{\text{II}}+2R_{\text{III}}=0.1209\ e\text{-volt} \tag{1. I}$$

was used for the interaction potential due to the first nearest neighbourers in the first approximation and finally

$$R_p=2(R_{\text{I}}+R_{\text{II}}+2R_{\text{III}})\theta=0.2418\theta\ e\text{-volt} \tag{1.p}$$

was taken the repulsive potential of individual adsorbed hydrogen atoms in the "proportional" approximation. Taking the above repulsive potentials into account, the isotherm of the dissociative adsorption of hydrogen on the (110)-lattice plane of nickel was formulated as in the next section.

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*) G. HERZBERG, *Molecular Spectra and Molecular Structure, I*, New York (1950).

§ 2. Statistical Mechanical Formulation of Adsorption Isotherm

Our system C in question is a macroscopic one enclosed in a definite volume at a definite temperature, consisting of adsorbent nickel with active surface of the (110)-lattice plane and hydrogen gas in the dissociative adsorption equilibrium on it. Site σ_i on the lattice plane is either occupied or unoccupied by a hydrogen atom in the equilibrium. Let $C_{\sigma_i(0)}$ or $C_{\sigma_i(\mathrm{H})}$ be the system C at the particular state specified by $\sigma_i(0)$ or $\sigma_i(\mathrm{H})$, that σ_i is respectively unoccupied or occupied by a hydrogen atom with certainty and the $\mathfrak{Q}C_{\sigma_i(0)}$ or $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}$ be the partition function respectively of $C_{\sigma_i(0)}$ or $C_{\sigma_i(\mathrm{H})}$. The partition function $\mathfrak{Q}C$ of the system C without such specification is hence the sum of $\mathfrak{Q}C_{\sigma_i(0)}$ and $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}$ *i.e.*

$$\mathfrak{Q}C = \mathfrak{Q}C_{\sigma_i(\mathrm{H})} + \mathfrak{Q}C_{\sigma_i(0)} , \tag{2}$$

while the probability of site σ_i being occupied is $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}/\mathfrak{Q}C$, which is common to all sites because of the premised physical identity of sites, hence equals the coverage θ, *i.e.*

$$\theta = \mathfrak{Q}C_{\sigma_i(\mathrm{H})}/\mathfrak{Q}C . \tag{3.a}$$

We have from (2) and (3.a) immediately

$$\frac{\theta}{1-\theta} = \frac{\mathfrak{Q}C_{\sigma_i(\mathrm{H})}}{\mathfrak{Q}C_{\sigma_i(0)}} . \tag{3.b}$$

Let now $\sum$ be a group of sites consisting of a particular site σ_0 of interest and those around it within the range of the repulsion from σ_0 specified by the degree of approximation. The $\sum$ covers thus $\sigma_0, \cdots, \sigma_8$ shown in Fig. 1 in the third approximation, $\sigma_0, \cdots, \sigma_4$ in the second, σ_0, σ_1, σ_2 in the first and σ_0 alone in zeroth approximation. The first, second and third nearest neighbouring sites to σ_0 will be called the sites of the first, second and third classes respectively. The θ is given by (3) by properly constructing $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}$ and $\mathfrak{Q}C_{\sigma_i(0)}$ or $\mathfrak{Q}C$.

Let $\mathfrak{Q}C_{\Sigma(0)}$ be the partition function of C at the particular state, where sites of $\sum$ are altogether unoccupied as specified by $\sum(0)$. By transferring a hydrogen atom within the system from outside $\sum$ onto a definite site σ_i inside, the partition function of the whole system increases by a factor $f_{i,\Sigma(0)}$, *i.e.*

$$f_{i,\Sigma(0)} = q^{\mathrm{H}}_{i,\Sigma(0)}/p^{\mathrm{H}} ,$$

where $q^{\mathrm{H}}_{i,\Sigma(0)}$ is the factor by which $\mathfrak{Q}C_{\Sigma(0)}$ is multiplied by adding an adsorbed hydrogen atom to a vacant site σ_i inside $\sum$ from outside the system $C_{\Sigma(0)}$ and p^{H} is that by which $\mathfrak{Q}C_{\Sigma(0)}$ is multiplied by adding an adsorbed hydrogen atom from outside the system $C_{\Sigma(0)}$ without any specification apart from that $\sum(0)$ of $\sum$ being kept throughout empty. It is admitted in equating $f_{i,\Sigma(0)}$ to $q^{\mathrm{H}}_{i,\Sigma(0)}/p^{\mathrm{H}}$ as above that the factor $f_{i,\Sigma(0)}$ or $q^{\mathrm{H}}_{i,\Sigma(0)}/p^{\mathrm{H}}$ is practically unchanged by increasing or decreasing constituent hydrogen atoms of the macroscopic system by one. Noting that the partition function of a system at constant volume and temperature behaves as the BOLTZMANN factor of its HELMHOLTZ free energy, we see that $q^{\mathrm{H}}_{i,\Sigma(0)}$ thus defined is the BOLTZMANN factor of the work required to bring up a hydrogen atom from a proper standard state to the state of an adsorbed hydrogen atom on σ_i keeping the whole system involved at statistical-mechanical equilibrium throughout and p^{H} is the BOLTZMANN factor of the similar work except that the added state of the hydrogen atom is subjected to no specification but that of $\sum(0)$ kept throughout. The latter sort of work done at statistical-mechanical equilibrium of the whole system involved has been called the reversible work[11]. The p^{H} thus defined is the BOLTZMANN factor of the chemical potential[11], admitted that such specification as $\sum(0)$ kept constant throughout does not virtually affect its magnitude at all, in the present case of the macroscopic system in question. The reversible work $-kT\ln q^{\mathrm{H}}_{i,\Sigma(0)}$ includes that ε'_i due to the repulsion from outside $\sum$, which is zero when $\theta=0$ or $i=0$ but positive otherwise, inasmuch as $\sum$ includes just all sites within the range of repulsion from σ_0.

We consider now a particular state $C_{\Sigma(a)}$ of C, where a certain definite set of sites inside $\sum$ are preoccupied by adsorbed hydrogen atoms of the population and the arrangement signified by $\sum(a)$ and the factor $f_{i,\Sigma(a)}$ of multiplication of the partition function $\mathfrak{Q}C_{\Sigma(a)}$ of $C_{\Sigma(a)}$ by tranferring a hydrogen atom within the same system from outside $\sum$ onto an unoccupied site σ_i inside, left vacant by the previous occupants of the specification $\sum(a)$, which includes $\sum(0)$ as its special case. The factor $f_{,\Sigma(a)}$ is given similarly as above by the equation

$$f_{i,\Sigma(a)} = q^{\mathrm{H}}_{i,\Sigma(a)}/p^{\mathrm{H}}\ , \tag{4}$$

where the relevant reversible work $-kT\ln q^{\mathrm{H}}_{i,\Sigma(a)}$ comprises, besides ε'_i, the reversible work $\varepsilon_{i,\Sigma(a)}$ due to the repulsion by the previous occupants inside $\sum$, which depends on i and $\sum(a)$. The p^{H} is the factor of multiplication of the partition function $\mathfrak{Q}C_{\Sigma(a)}$ by addition of a hydrogen atom without any specification, apart from that of $\sum(a)$ being kept constant throughout, and is identified similarly as above with the BOLTZMANN factor of the chemical potential in the present case of the macroscopic system.

The partition function $\mathfrak{Q}C_{\Sigma(A)}$ of the system $C_{\Sigma(A)}$ of a particular population and arrangement $\sum(A)$ of adsorbed hydrogen atoms inside $\sum$ is now given by $\mathfrak{Q}C_{\Sigma(0)}$ multiplied by $f_{i,\Sigma(a)}$'s respectively relevant to the successive additions to make up $\sum(A)$. There correspond to the state of $C_{\sigma_i(0)}$ or $C_{\sigma_i(\mathrm{H})}$ different $\sum(A)$'s compatible with the specification $\sigma_i(0)$ or $\sigma_i(\mathrm{H})$. The $\mathfrak{Q}C_{\sigma_i(0)}$ or $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}$ is hence the sum of partition functions $\mathfrak{Q}C_{\Sigma(A)}$'s appropriate to all such $\sum(A)$'s. Since $\mathfrak{Q}C_{\Sigma(0)}$ is the common factor of the terms $\mathfrak{Q}C_{\Sigma(A)}$'s of the summation, $\mathfrak{Q}C_{\sigma_i(0)}$ or $\mathfrak{Q}C_{\sigma_i(\mathrm{H})}$ is the product of $\mathfrak{Q}C_{\Sigma(0)}$ and the appropriate polynomial $\varphi_{\sigma_i(0)}$ or $\varphi_{\sigma_i(\mathrm{H})}$ of $f_{i,\Sigma(a)}$'s, *i.e.*

$$\varphi_{\sigma_i(0)} = \mathfrak{Q}C_{\sigma_i(0)}/\mathfrak{Q}C_{\Sigma(0)}\,, \quad \varphi_{\sigma_i(\mathrm{H})} = \mathfrak{Q}C_{\sigma_i(\mathrm{H})}/\mathfrak{Q}C_{\Sigma(0)}\,. \qquad (5.\ \mathrm{a}),\ (5.\ \mathrm{b})$$

Signifying the polynomial without any such specification as $\sigma_i(0)$ or $\sigma_i(\mathrm{H})$ by φ, we have

$$\varphi = \varphi_{\sigma_i(0)} + \varphi_{\sigma_i(\mathrm{H})} \qquad (5.\ \mathrm{c})$$

or according to (2) and (5)

$$\varphi = \mathfrak{Q}C/\mathfrak{Q}C_{\Sigma(0)} \qquad (5.\ \mathrm{d})$$

and from (3) and (5)

$$\theta = \varphi_{\sigma_i(\mathrm{H})}/\varphi\,, \quad \theta/(1-\theta) = \varphi_{\sigma_i(\mathrm{H})}/\varphi_{\sigma_i(0)}\,. \qquad (6.\ \mathrm{a}),\ (6.\ \mathrm{b})$$

The polynomials are determined statistical-mechanically in the next section on the base of the repulsive potential given in § 1.

§ 3. Polynomials

The reversible work $-kT\ln q^{\mathrm{H}}_{i,\Sigma(a)}$ relevant to the factor $f_{i,\Sigma(a)}$ by (4) is given according to the foregoing section as

$$-kT\ln q^{\mathrm{H}}_{i,\Sigma(a)} = w + \varepsilon_{i,\Sigma(a)} + \varepsilon'_i\,, \qquad (7)$$

where w is the reversible work in the absence of interaction with other adsorbed hydrogen atoms, hence of common magnitude to all sites on the basis of the crystal surface model. The reversible work ε'_i due to repulsion from outside $\sum$ is assumed to be a function of θ characteristic of each class to which σ_i belongs, irrespective of $\sum(a)$*). The part $\varepsilon_{i,\Sigma(a)}$ of the reversible work due to the interaction between a hydrogen atom brought up onto σ_i and previous occupants inside $\sum$ is equated to the sum of the corresponding interaction potentials between them each fixed at its equilibrium position.

The factor $f_{i,\Sigma(a)}$ is now given by (4) and (7) as

$$f_{i,\Sigma(a)} = \gamma\eta_i \exp(-\varepsilon_{i,\Sigma(a)}/kT)\,, \qquad (8)$$

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*) Exactly, ε'_i of each class depends on $\sum(a)$ besides on θ, since the population and the arrangement outside in the vicinity of $\sum$ depend on $\sum(a)$ through the interaction, which reciprocally affect ε'_i.

where

$$\gamma = \exp(-w/kT)/p^{\mathrm{H}}, \quad \eta_i = \exp(-\varepsilon_i'/kT) . \qquad (9.\gamma),\ (9.\eta)$$

The polynomials are deduced below first with special reference to the third approximation, which is reduced to those of lower approximations as its special cases.

Let $t_i (i=0,\cdots,8)$ be 1 or 0 according as σ_i is occupied or unoccupied respectively. The $\sum(A)$ is now defined by a set of values of t_i's. The polynomial φ is given in terms of $f_{i,\Sigma(a)}$ according to the foregoing section as

$$\varphi = \sum_{t_0,\cdots,t_8} \prod_{i=0}^{8} f_{i,\Sigma(a)}^{t_i} . \qquad (10)$$

The $\varphi_{\sigma_i(\mathrm{H})}$ or $\varphi_{\sigma_i(0)}$ is the particular part of φ, for which $t_i=1$ or $t_i=0$. The term $\prod_{i=0}^{8} f_{i,\Sigma(a)}^{t_i}$ of the summation for a particular $\sum(A)$ or for the appropriate set of values of t_i's is given by (8) as

$$\prod_{i=0}^{8} f_{i,\Sigma(a)}^{t_i} = \gamma^{\Sigma t_i} \cdot \prod_{i=0}^{i=8} \eta_i^{t_i} \cdot \exp\left(-\sum_{i=0}^{8} t_i \varepsilon_{i,\Sigma(a)}/kT\right) . \qquad (11)$$

The second factor of the above equation is expressed as

$$\prod_{i=0}^{8} \eta_i^{t_i} = \eta_{\mathrm{I}}^{t_1+t_2} \eta_{\mathrm{II}}^{t_3+t_4} \eta_{\mathrm{III}}^{t_5+t_6+t_7+t_8} , \qquad (12.\eta)$$

where η_{I}, η_{II} and η_{III} are according to $(9.\eta)$ the η_i's respectively of the first, second and third classes, each assumed as a characteristic function of θ; η_0 is unity in particular by $(9.\eta)$, since $\varepsilon_0'=0$ as referred to in the foregoing section. The $\sum_{i=0}^{8} t_i \varepsilon_{i,\Sigma(a)}$ in the last factor is the total repulsive potential among adsorbed hydrogen atoms inside $\sum$, which is developed, referring to Fig. 1, as

$$\begin{aligned}\sum_{i=0}^{8} t_i \varepsilon_{i,\Sigma(a)} = & \left\{t_0(t_1+t_2)+t_3(t_5+t_6)+t_4(t_7+t_8)\right\} R_{\mathrm{I}} \\ & + \left\{t_0(t_3+t_4)+t_1(t_5+t_7)+t_2(t_6+t_8)\right\} R_{\mathrm{II}} \\ & + \left\{t_0(t_5+t_6+t_7+t_8)+(t_1+t_2)(t_3+t_4)\right\} R_{\mathrm{III}} ,\end{aligned}$$

hence we have

$$\begin{aligned}\exp\left(-\sum_{i=0}^{8} t_i \varepsilon_{i,\Sigma(0)}/kT\right) = & \ \xi_{\mathrm{I}}^{t_0(t_1+t_2)+t_3(t_5+t_6)+t_4(t_7+t_8)} \xi_{\mathrm{II}}^{t_0(t_3+t_4)+t_1(t_5+t_7)+t_2(t_6+t_8)} \\ & \times \xi_{\mathrm{III}}^{t_0(t_5+t_6+t_7+t_8)+(t_1+t_2)(t_3+t_4)} ,\end{aligned} \qquad (12.\xi)$$

where

$$\xi_{\mathrm{I}} = \exp(-R_{\mathrm{I}}/kT) , \quad \xi_{\mathrm{II}} = \exp(-R_{\mathrm{II}}/kT) , \quad \xi_{\mathrm{III}} = \exp(-R_{\mathrm{III}}/kT) . \qquad (13)$$

TABLE 1. Polynomials $\varphi_{\sigma_0(\mathrm{H})}$, $\varphi_{\sigma_0(0)}$, $\varphi_{\sigma_1(0)}$, $\varphi_{\sigma_3(0)}$, $\varphi_{\sigma_5(0)}$

Exponents				Factors including $\xi_1 .\ \xi_2 .\ \xi_3$				
γ	η_1	η_2	η_3	$\varphi_{\sigma_0(\mathrm{H})}$	$\varphi_{\sigma_0(0)}$	$\varphi_{\sigma_1(0)}$	$\varphi_{\sigma_3(0)}$	$\varphi_{\sigma_5(0)}$
8	2	2	4	$\xi_1^6\xi_2^6\xi_3^8\gamma$	$\xi_1^4\xi_2^4\xi_3^4$	0	0	0
7	1	2	4	$2\xi_1^5\xi_2^4\xi_3^6\gamma$	$2\xi_1^4\xi_2^2\xi_3^2$	$\xi_1^4\xi_2^2\xi_3^2+\xi_1^5\xi_2^4\xi_3^6\gamma$	0	0
7	2	1	4	$2\xi_1^4\xi_2^5\xi_3^6\gamma$	$2\xi_1^2\xi_2^4\xi_3^2$	0	$\xi_1^2\xi_2^4\xi_3^2+\xi_1^4\xi_2^5\xi_3^6\gamma$	0
7	2	2	3	$4\xi_1^5\xi_2^5\xi_3^7\gamma$	$4\xi_1^3\xi_2^3\xi_3^4$	0	0	$\xi_1^3\xi_2^3\xi_3^4+\xi_1^5\xi_2^5\xi_3^7\gamma$
6	0	2	4	$\xi_1^4\xi_2^2\xi_3^4\gamma$	ξ_1^4	$\xi_1^4+\xi_1^4\xi_2^2\xi_3^4\gamma$	0	0
6	1	1	4	$4\xi_1^3\xi_2^3\xi_3^5\gamma$	$4\xi_1^2\xi_2^2\xi_3$	$2\xi_1^2\xi_2^2\xi_3+2\xi_1^3\xi_2^3\xi_3^5\gamma$	$2\xi_1^2\xi_2^2\xi_3+2\xi_1^3\xi_2^3\xi_3^5\gamma$	0
6	2	0	4	$\xi_1^2\xi_2^4\xi_3^4\gamma$	ξ_2^4	0	$\xi_2^4+\xi_1^2\xi_2^4\xi_3^4\gamma$	0
6	1	2	3	$4(\xi_1^4\xi_2^4\xi_3^5+\xi_1^4\xi_2^3\xi_3^5)\gamma$	$4(\xi_1^3\xi_2^2\xi_3^2+\xi_1^3\xi_2\xi_3^2)$	$2\xi_1^3\xi_2\xi_3^2(\xi_2+1)(1+\xi_1\xi_2^2\xi_3^3\gamma)$	0	$\xi_1^3\xi_2\xi_3^2(\xi_2+1)(1+\xi_1\xi_2^2\xi_3^3\gamma)$
6	2	1	3	$4(\xi_1^4\xi_2^4\xi_3^5+\xi_1^3\xi_2^4\xi_3^5)\gamma$	$4(\xi_1^2\xi_2^3\xi_3^2+\xi_1\xi_2^3\xi_3^2)$	0	$2\xi_1\xi_2^3\xi_3^2(\xi_1+1)(1+\xi_1^2\xi_2\xi_3^3\gamma)$	$\xi_1\xi_2^3\xi_3^2(\xi_1+1)(1+\xi_1^2\xi_2\xi_3^3\gamma)$
6	2	2	2	$6\xi_1^4\xi_2^4\xi_3^6\gamma$	$6\xi_1^2\xi_2^2\xi_3^4$	0	0	$3\xi_1^2\xi_2^2\xi_3^4(1+\xi_1^2\xi_2^2\xi_3^2\gamma)$
5	1	0	4	$2\xi_1\xi_2^2\xi_3^4\gamma$	$2\xi_2^2$	$\xi_2^2+\xi_1\xi_2^2\xi_3^4\gamma$	$2\xi_2^2+2\xi_1\xi_2^2\xi_3^4\gamma$	0
5	0	1	4	$2\xi_1^2\xi_2\xi_3^4\gamma$	$2\xi_1^2$	$2\xi_1^2+2\xi_1^2\xi_2\xi_3^4\gamma$	$\xi_1^2+\xi_1^2\xi_2\xi_3^4\gamma$	0
5	2	0	3	$4\xi_1^2\xi_2^3\xi_3^3\gamma$	$4\xi_2^3$	0	$4\xi_2^3+4\xi_1^2\xi_2^3\xi_3^3\gamma$	$\xi_2^3+\xi_1^2\xi_2^3\xi_3^3\gamma$
5	1	1	3	$4\xi_1^2\xi_2^2\xi_3^4(1+\xi_1)(1+\xi_2)\gamma$	$4\xi_1\xi_2\xi_3(1+\xi_1)(1+\xi_2)$	$2\xi_1\xi_2\xi_3(1+\xi_1)(1+\xi_2)$ $\times(1+\xi_1\xi_2\xi_3^3)\gamma$	$2\xi_1\xi_2\xi_3(1+\xi_1)(1+\xi_2)$ $\times(1+\xi_1\xi_2\xi_3^3\gamma)$	$\xi_1\xi_2\xi_3(1+\xi_1)(1+\xi_2)$ $\times(1+\xi_1\xi_2\xi_3^3\gamma)$
5	0	2	3	$4\xi_1^3\xi_2^2\xi_3^3\gamma$	$4\xi_1^3$	$4(\xi_1^3+\xi_1^3\xi_2^2\xi_3^3\gamma)$	0	$\xi_1^3+\xi_1^3\xi_2^2\xi_3^3\gamma$
5	2	1	2	$2\xi_1^2\xi_2^3\xi_3^4(\xi_1^2+4\xi_1+1)\gamma$	$2\xi_2^2\xi_3^2(\xi_1^2+4\xi_1+1)$	0	$\xi_2^2\xi_3^2(\xi_1^2+4\xi_1+1)(1+\xi_1^2\xi_2\xi_3^2\gamma)$	$\xi_2^2\xi_3^2(\xi_1^2+4\xi_1+1)(1+\xi_1^2\xi_2\xi_3^2\gamma)$
5	1	2	2	$2\xi_1^3\xi_2^2\xi_3^4(\xi_2^2+4\xi_2+1)\gamma$	$2\xi_1^2\xi_3^2(\xi_2^2+4\xi_2+1)$	$\xi_1^2\xi_3^2(\xi_2^2+4\xi_2+1)(1\xi_1\xi_2^2\xi_3^2\gamma)$	0	$\xi_1^2\xi_3^2(\xi_2^2+4\xi_2+1)(1+\xi_1\xi_2^2\xi_3^2\gamma)$
5	2	2	1	$4\xi_1^3\xi_2^3\xi_3^5\gamma$	$4\xi_1\xi_2\xi_3^4$	0	0	$3\xi_1\xi_2\xi_3^4(1+\xi_1^2\xi_2^2\xi_3\gamma)$
4	0	0	4	$\xi_3^4\gamma$	1	$1+\xi_3^4\gamma$	$1+\xi_3^4\gamma$	0
4	1	0	3	$4\xi_2(\xi_2+1)\xi_1\xi_3^3\gamma$	$4\xi_2(\xi_2+1)$	$2\xi_2(\xi_2+1)(1+\xi_1\xi_3^3\gamma)$	$4\xi_2(\xi_2+1)(1+\xi_1\xi_3^3\gamma)$	$\xi_2(\xi_2+1)(1+\xi_1\xi_3^3\gamma)$
4	0	1	3	$4\xi_1(\xi_1+1)\xi_2\xi_3^3\gamma$	$4\xi_1(\xi_1+1)$	$4\xi_1(\xi_1+1)(1+\xi_2\xi_3^3\gamma)$	$2\xi_1(\xi_1+1)(1+\xi_2\xi_3^3\gamma)$	$\xi_1(\xi_1+1)(1+\xi_2\xi_3^3\gamma)$
4	2	0	2	$6\xi_1^2\xi_2^2\xi_3^2\gamma$	$6\xi_2^2$	0	$6\xi_2^2(1+\xi_1^2\xi_3^2\gamma)$	$3\xi_2^2(1+\xi_1^2\xi_3^2\gamma)$

4	1	1	2	$4\xi_3(\xi_1^2\xi_2+\xi_2^2\xi_1+2\xi_1\xi_2+\xi_1+\xi_2)\xi_1\xi_2\xi_3^2\gamma$	$4\xi_3(\xi_1^2\xi_2+\xi_1\xi_2^2+2\xi_1\xi_2+\xi_1+\xi_2)$	$2\xi_3(\xi_1^2\xi_2+\xi_1\xi_2^2+2\xi_1\xi_2+\xi_1+\xi_2)\times(1+\xi_1\xi_2+\xi_3^2\gamma)$	$2\xi_3(\xi_1^2\xi_2+\xi_1\xi_2^2+2\xi_1\xi_2+\xi_1+\xi_2)\times(1+\xi_1\xi_2\xi_3^2\gamma)$	$2\xi_3(\xi_1^2\xi_2+\xi_1\xi_2^2+2\xi_1\xi_2+\xi_1+\xi_2)\times(1+\xi_1\xi_2\xi_3^2\gamma)$
4	0	2	2	$6\xi_1^2\xi_2^2\xi_3^2\gamma$	$6\xi_1^2$	$6\xi_1^2(1+\xi_2^2\xi_3^2\gamma)$	0	$3\xi_1^2(1+\xi_2^2\xi_3^2\gamma)$
4	2	1	1	$4\xi_1^2\xi_2^2\xi_3^3(\xi_1+1)\gamma$	$4\xi_2\xi_3^2(\xi_1+1)$	0	$2\xi_2\xi_2^2(\xi_1+1)(1+\xi_1^2\xi_2\xi_3\gamma)$	$3\xi_2\xi_3^2(\xi_1+1)(1+\xi_1^2\xi_2\xi_3\gamma)$
4	1	2	1	$4\xi_1^2\xi_2^2\xi_3^3(\xi_2+1)\gamma$	$4\xi_1\xi_3^2(\xi_2+1)$	$2\xi_1\xi_3^2(\xi_2+1)(1+\xi_1\xi_2^2\xi_3\gamma)$	0	$3\xi_1\xi_3^2(\xi_2+1)(1+\xi_1\xi_2^2\xi_3\gamma)$
4	2	2	0	$\xi_1^2\xi_2^2\xi_3^4\gamma$	ξ_3^4	0	0	$\xi_3^4+\xi_1^2\xi_2^2\xi_3^4\gamma$
3	0	0	3	$4\xi_3^3\gamma$	4	$4+4\xi_3^3\gamma$	$4+4\xi_3^3\gamma$	$1+\xi_3^3\gamma$
3	1	0	2	$2\xi_1\xi_3^2(\xi_2^2+4\xi_2+1)\gamma$	$2(\xi_2^2+4\xi_2+1)$	$(\xi_2^2+4\xi_2+1)(1+\xi_1\xi_3^2\gamma)$	$2(\xi_2^2+4\xi_2+1)(1+\xi_1\xi_3^2\gamma)$	$(\xi_2^2+4\xi_2+1)(1+\xi_1\xi_3^2\gamma)$
3	0	1	2	$2\xi_2\xi_3^2(\xi_1^2+4\xi_1+1)\gamma$	$2(\xi_1^2+4\xi_1+1)$	$2((\xi_1^2+4\xi_1+1)(1+\xi_2\xi_3^2\gamma)$	$(\xi_1^2+4\xi_1+1)(1+\xi_2\xi_3^2\gamma)$	$(\xi_1^2+4\xi_1+1)(1+\xi_2\xi_3^2\gamma)$
3	2	0	1	$4\xi_1^2\xi_2\xi_3\gamma$	$4\xi_2$	0	$4\xi_2(1+\xi_1^2\xi_3\gamma)$	$3\xi_2(1+\xi_1^2\xi_3\gamma)$
3	1	1	1	$4\xi_1\xi_2\xi_3^2(\xi_1\xi_2+\xi_1+\xi_2+1)\gamma$	$4\xi_3(\xi_1\xi_2+\xi_1+\xi_2+1)$	$2\xi_3(\xi_1\xi_2+\xi_1+\xi_2+1)\times(1+\xi_1\xi_2\xi_3\gamma)$	$2\xi_3(\xi_1\xi_2+\xi_1+\xi_2+1)\times(1+\xi_1\xi_2\xi_3\gamma)$	$3\xi_3(\xi_1\xi_2+\xi_1+\xi_2+1)\times(1+\xi_1\xi_2\xi_3\gamma)$
3	0	2	1	$4\xi_1\xi_2^2\xi_3\gamma$	$4\xi_1$	$4\xi_1(1+\xi_2^2\xi_3\gamma)$	0	$3\xi_1(1+\xi_2^2\xi_3\gamma)$
3	2	1	0	$2\xi_1^2\xi_2\xi_3^2\gamma$	$2\xi_3^2$	0	$\xi_3^2(1+\xi_1^2\xi_2\gamma)$	$2\xi_3^2(1+\xi_1^2\xi_2\gamma)$
3	1	2	0	$2\xi_1\xi_2^2\xi_3^2\gamma$	$2\xi_3^2$	$\xi_3^2(1+\xi_1\xi_2^2\gamma)$	0	$2\xi_3^2(1+\xi_1\xi_2^2\gamma)$
2	0	0	2	$6\xi_3^2\gamma$	6	$6(1+\xi_3^2\gamma)$	$6(1+\xi_3^2\gamma)$	$3(1+\xi_3^2\gamma)$
2	1	0	1	$4\xi_1\xi_3(\xi_2+1)\gamma$	$4(\xi_2+1)$	$2(1+\xi_2)(1+\xi_1\xi_3\gamma)$	$4(1+\xi_2)(1+\xi_1\xi_3\gamma)$	$3(1+\xi_2)(1+\xi_1\xi_3\gamma)$
2	0	1	1	$4\xi_2\xi_3(\xi_1+1)\gamma$	$4(\xi_1+1)$	$4(1+\xi_1)(1+\xi_2\xi_3\gamma)$	$2(1+\xi_1)(1+\xi_2\xi_3\gamma)$	$3(1+\xi_1)(1+\xi_2\xi_3\gamma)$
2	2	0	0	$\xi_1^2\gamma$	1	0	$1+\xi_1^2\gamma$	$1+\xi_1^2\gamma$
2	1	1	0	$4\xi_1\xi_2\xi_3\gamma$	$4\xi_3$	$2\xi_3(1+\xi_1\xi_2\gamma)$	$2\xi_3(1+\xi_1\xi_2\gamma)$	$4\xi_3(1+\xi_1\xi_2\gamma)$
2	0	2	0	$\xi_2^2\gamma$	1	$1+\xi_2^2\gamma$	0	$1+\xi_2^2\gamma$
1	0	0	1	$4\xi_3\gamma$	4	$4(1+\xi_3\gamma)$	$4(1+\xi_3\gamma)$	$3(1+\xi_3\gamma)$
1	1	0	0	$2\xi_1\gamma$	2	$1+\xi_1\gamma$	$2(1+\xi_1\gamma)$	$2(1+\xi_1\gamma)$
1	0	1	0	$2\xi_2\gamma$	2	$2(1+\xi_2\gamma)$	$1+\xi_2\gamma$	$2(1+\xi_2\gamma)$
0	0	0	0	γ	1	$1+\gamma$	$1+\gamma$	$1+\gamma$

The polynomial φ is now given by (10), (11) and (12) as

$$\varphi=\sum_{t_0,\cdots,t_8}\gamma^{\sum_{i=0}^{8}t_i}\eta_{\mathrm{I}}^{t_1+t_2}\eta_{\mathrm{II}}^{t_3+t_4}\eta_{\mathrm{III}}^{t_5+t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_0(t_1+t_2)+t_3(t_5+t_6)+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_0(t_3+t_4)+t_1(t_5+t_7)+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{t_0(t_5+t_6+t_7+t_8)+(t_1+t_2)(t_3+t_4)}. \tag{14}$$

The polynomial $\varphi_{\sigma_0(\mathrm{H})}$ or $\varphi_{\sigma_0(0)}$ is the particular part of the summation (14), for which $t_0=1$ or 0 respectively *i.e.*,

$$\varphi_{\sigma_0(\mathrm{H})}=\gamma\sum_{t_1,\cdots,t_8}\gamma^{\sum_{i=1}^{8}t_i}(\eta_{\mathrm{I}}\xi_{\mathrm{I}})^{t_1+t_2}(\eta_{\mathrm{II}}\xi_{\mathrm{II}})^{t_3+t_4}(\eta_{\mathrm{III}}\xi_{\mathrm{III}})^{t_5+t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_3(t_5+t_6)+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_1(t_5+t_7)+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{(t_1+t_2)(t_3+t_4)}, \tag{15. H}$$

$$\varphi_{\sigma_0(0)}=\sum_{t_1,\cdots,t_8}\gamma^{\sum_{i=1}^{8}t_i}\eta_{\mathrm{I}}^{t_1+t_2}\eta_{\mathrm{II}}^{t_3+t_4}\eta_{\mathrm{III}}^{t_5+t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_3(t_5+t_6)+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_1(t_5+t_7)+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{(t_1+t_2)(t_3+t_4)}. \tag{15. 0}$$

We have similarly the expressions of $\varphi_{\sigma_1(0)}$, $\varphi_{\sigma_3(0)}$ and $\varphi_{\sigma_5(0)}$ of sites of the first, second and third classes by fixing t_1, t_3 and t_5 respectively to zero in the summation of (14) as

$$\varphi_{\sigma_1(0)}=\sum_{t_0,t_2,\cdots,t_8}\gamma^{t_0+t_2+\cdots+t_8}\eta_{\mathrm{I}}^{t_2}\eta_{\mathrm{II}}^{t_3+t_4}\eta_{\mathrm{III}}^{t_5+t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_0t_2+t_3(t_5+t_6)+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_0(t_3+t_4)+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{t_0(t_5+t_6+t_7+t_8)+t_2(t_3+t_4)}, \tag{16. I}$$

$$\varphi_{\sigma_3(0)}=\sum_{t_0,t_1,t_2,t_4,\cdots,t_8}\gamma^{t_0+t_1+t_2+t_4+\cdots+t_8}\eta_{\mathrm{I}}^{t_1+t_2}\eta_{\mathrm{II}}^{t_4}\eta_{\mathrm{III}}^{t_5+t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_0(t_1+t_2)+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_0t_4+t_1(t_5+t_7)+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{t_0(t_5+t_6+t_7+t_8)+(t_1+t_2)t_4}, \tag{16. II}$$

$$\varphi_{\sigma_5(0)}=\sum_{t_0,\cdots,t_4,t_6,t_7,t_8}\gamma^{t_0+\cdots+t_4+t_6+t_7+t_8}\eta_{\mathrm{I}}^{t_1+t_2}\eta_{\mathrm{II}}^{t_3+t_4}\eta_{\mathrm{III}}^{t_6+t_7+t_8}\xi_{\mathrm{I}}^{t_0(t_1+t_2)+t_3t_6+t_4(t_7+t_8)}$$
$$\times\xi_{\mathrm{II}}^{t_0(t_3+t_4)+t_1t_7+t_2(t_6+t_8)}\xi_{\mathrm{III}}^{t_0(t_6+t_7+t_8)+(t_1+t_2)(t_3+t_4)}. \tag{16. III}$$

Terms of the polyniomials, $\varphi_{\sigma_0(\mathrm{H})}$, $\varphi_{\sigma_0(0)}$, $\varphi_{\sigma_1(0)}$, $\varphi_{\sigma_3(0)}$ and $\varphi_{\sigma_5(0)}$ are shown in Table 1. Every term, for instance, of $\varphi_{\sigma_0(\mathrm{H})}$ is given by the corresponding row of the Table as the product of γ, η_{I}, η_{II} and η_{III} each raised to the power of the appropriate exponent indicated on the row and multiplied by the factor given there under the head of $\varphi_{\sigma_0(\mathrm{H})}$. The polynomial of $\varphi_{\sigma_0(\mathrm{H})}$ is the total sum of such terms each given as above by a row. Other polynomials are similarly reproduced from the Table.

In the second approximation $\sum$ includes according to §2 the sites of the first and the second classes only, in the first approximation those of the first class only and in the zeroth approximation none respectively besides σ_0. The polynomials of each approximation are obtained by following the above procedure similarly in the individual cases with due regards to the constituents of $\sum$ or formally by reducing the above expressions of the third approximation putting t_i's of the classes excluded from $\sum$ for the approximation in question to zero and $\xi_K (K=\mathrm{I, II, III})$, relevant by (13) to the neglected R_K, to unity. By doing so, the polynomials retain, η_{I}, η_{II}, ξ_{I} and ξ_{II} only in the second approximation, η_{I} and ξ_{I} only in the first approximation and none in the zeroth approximation respectively besides γ.

The ξ_{I}, ξ_{II} and ξ_{III} of the third approximation are given by (1.III) and (13), particularly for 50°C, as

$$\xi_{\mathrm{I}} = 0.02555\,, \quad \xi_{\mathrm{II}} = 0.6171\,, \quad \xi_{\mathrm{III}} = 0.9040\,. \tag{17. III}$$

The ξ_{I} and ξ_{II} of the second approximation are similarly given for 50°C as the BOLTZMANN factors of R_1' and R_2' of (1.II), *i.e.*

$$\xi_{\mathrm{I}} = 0.02159\,, \quad \xi_{\mathrm{II}} = 0.6038\,, \tag{17.II}$$

and ξ_{I} of the first approximation as that of R_{I}'' of (1.I) at 50°C, *i.e.*

$$\xi_{\mathrm{I}} = 0.01301\,. \tag{17. I}$$

§ 4. Adsorption Isotherms

The η_{I}, η_{II} and η_{III} of the third approximation are determined as functions of γ on the base of ξ_{I} *etc.* given by (17.III) by equating $\varphi_{\sigma_i(0)}$ of different classes included in $\sum$ to $\varphi_{\sigma_0(0)}$ because of the physical identity of sites in extension of the BETHE and PEIERLS' method[12], as

$$\varphi_{\sigma_0(0)} = \varphi_{\sigma_1(0)} = \varphi_{\sigma_3(0)} = \varphi_{\sigma_5(0)}\,. \tag{18. III}$$

The similar relation

$$\varphi_{\sigma_0(0)} = \varphi_{\sigma_1(0)} = \varphi_{\sigma_3(0)} \tag{18. II}$$

determines two unknowns η_{I} and η_{II} in the second approximation and the single unknown η_{I} in the first approximation is fixed by the relation

$$\varphi_{\sigma_0(0)} = \varphi_{\sigma_1(0)}\,. \tag{18. I}$$

Polynomials of each approximation are now evaluated, hence θ determined by (6.b) respectively as a function of γ.

The right-hand side of (3.b) gives on the other hand the factor of multiplication of the partition function by transferring a hydrogen atom within the system in question from outside σ_i onto a preliminarily evacuated site σ_i, which factor is expressed as $q_{\sigma_i}^{\mathrm{H}}/p^{\mathrm{H}}$ similar to $f_{i,\Sigma(a)}$ of (4)[11], so that

$$\frac{\theta}{1-\theta}=\frac{q^{\mathrm{H}}_{\sigma_i}}{p^{\mathrm{H}}}\,, \tag{19}$$

where $q^{\mathrm{H}}_{\sigma_i}$ is the BOLTZMANN factor of the reversible work[11] required to bring up a hydrogen atom from its standard state onto the preliminarily evacuated site σ_i*). The latter reversible work $-kT\ln q^{\mathrm{H}}_{\sigma_i}$ is given in accordance with the "proportional" approximation as

$$-kT\ln q^{\mathrm{H}}_{\sigma_i}=w+R_p\,,$$

hence we have by (1.p), (9.γ) and (19)

$$\frac{\theta}{1-\theta}=\gamma\exp\left(-u\theta/kT\right), \tag{20. θ}$$

where

$$u=0.2418\ e\text{-volt}. \tag{20. u}$$

The θ is thus given as a function of γ at a constant temperature in every case of approximation.

The γ is now related with the pressure P of hydrogen by equating p^{H} in (9.γ) to the square root of the BOLTZMANN factor p^{H_2} of the chemical potential of hydrogen molecule in gas because of the adsorption equilibrium[11], as

$$p^{\mathrm{H}}=(p^{\mathrm{H}_2})^{1/2}\,. \tag{21. a}$$

The p^{H_2} is expressed as[11]

$$p^{\mathrm{H}_2}=Q^{\mathrm{H}_2}/N^{\mathrm{H}_2}\,, \tag{21. b}$$

where N^{H_2} is the concentration of hydrogen molecule in gas and Q^{H_2} the partition function of a single hydrogen molecule in unit volume. The Q^{H_2} is expressed with good approximation as

$$Q^{\mathrm{H}_2}=\frac{(2\pi mkT)^{3/2}}{h^3}\,\frac{4\pi^2IkT}{h^2}\exp\left(-\frac{\varepsilon(\mathrm{H}_2)_0}{kT}\right), \tag{21. c}$$

where m is the mass, I the moment of inertia, $\varepsilon(\mathrm{H}_2)_0$ the energy of the ground state respectively of the hydrogen molecule and h the PLANCK constant. The N^{H_2} in (21. b) is expressed in terms of hydrogen pressure P mmHg as

$$N^{\mathrm{H}_2}=1.360\times 980.5\,P/kT\,. \tag{21. d}$$

The BOLTZMANN factor q^{H}_0 of the reversible work w in the absence of the

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*) The $q^{\mathrm{H}}_{\sigma_i}$ is associated with no specification but that of preliminarily evacuated σ_i, whereas the $q^{\mathrm{H}}_{i,\Sigma(a)}$ is subjected besides to that of $\Sigma(a)$, *i.e.* the population and the arrangement of previous occupants inside Σ.

interactions is given according to the previous work1)*) as

$$q_0^{\mathrm{H}} = \exp(-w/kT) = \prod_{j=1}^{3}\left\{1-\exp(-h\nu_j/kT)\right\}^{-1}\exp(-\varepsilon_0/kT)\,, \quad (22)$$

where ν_j is the frequency of the j-th normal vibration of the adsorbed hydrogen atom and ε_0 its energy at the ground state.

We have now from (9.γ), (21) and (22)

$$\gamma = \frac{\exp\left(\frac{\Delta\varepsilon}{kT}\right)\sqrt{\frac{1.360\times 980.5}{kT}}}{\prod_{j=1}^{3}\left\{1-\exp\left(-\frac{h\nu_j}{kT}\right)\right\}\sqrt{\frac{(2\pi mkT)^{3/2}}{h^3}\,\frac{4\pi^2 IkT}{h^2}}}\sqrt{P}\,, \quad (23.\gamma)$$

where

$$\Delta\varepsilon = \varepsilon(\mathrm{H_2})_0/2-\varepsilon_0\,, \quad \text{or} \quad (23.\varepsilon)$$

$$\gamma = 9.603\times 10^{-5}\times\exp(\Delta\varepsilon/kT)\times\sqrt{P} \quad (24)$$

at 50°C on the base of the values

$$k = 1.380\times 10^{-16}\ \text{erg deg}^{-1}\ {}^{**)},\quad h = 6.623\times 10^{-27}\ \text{erg sec}\ {}^{**)},$$
$$N_A = 6.024\times 10^{23}\ {}^{**)},\quad mN_A = 2\times 1.008\ \text{gr},\quad I = 4.664\times 10^{-41}\ \text{gr cm}^2\ {}^{***)},$$
$$\tilde{\nu}_j = 417,\ 479,\ 1900\ \text{cm}^{-1}\ {}^{1)}, \quad (25)$$

where N_A is the AVOGADRO's number and $\tilde{\nu}_j$ the wave number of the j-th normal vibration of the adsorbed hydrogen atom.

§ 5. Adsorption Isotherms of the Third and the Second Approximations

The η_{I}, η_{II} and η_{III} of the third approximation are determined by solving (18.III) graphically with reference to (15.0), (16), (17.III) and Table 1, hence

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*) The q_0^{H} in the absence of the interaction among adsorbed hydrogen atoms is given as

$$q_0^{\mathrm{H}} = \mathfrak{Q}C_{\sigma(\mathrm{H}),0}/\mathfrak{Q}C_{\sigma(0),0}\ ,$$

where $\mathfrak{Q}C_{\sigma(\mathrm{H}),0}$ or $\mathfrak{Q}C_{\sigma(0),0}$ is the partition function of the system $C_{\sigma(\mathrm{H}),0}$ or $C_{\sigma(0),0}$, which has only one hydrogen atom adsorbed on a definite site σ or none at all respectively. Assuming that the kinetic energy of $C_{\sigma(\mathrm{H}),0}$ is separable into those of the adsorbent proper and of the hydrogen atom adsorbed, $\mathfrak{Q}C_{\sigma(\mathrm{H}),0}$ is written in the form,

$$\mathfrak{Q}C_{D(\mathrm{H}),0} = \mathfrak{Q}C_{\sigma(0),0}\exp(-\varepsilon_0/kT)\prod_{j=1}^{3}\{1-\exp(-h\nu_j/kT)\}^{-1},$$

where $\mathfrak{Q}C_{\sigma(0),0}\exp(-\varepsilon_0/kT)$ is the partition function of the system with the adsorbed hydrogen atom at the ground state. The above two equations give (22) in the text immediately.

) LANDOLT, "Tabellen" **6, I$_1$, p. 33–38 (1950).

***) LANDOLT, "Tabellen" **5**, III c, p. 2349 (1936).

θ is worked out by (15) and (6.b) as shown in Table 2 and by the curve III of $\log_{10}\theta$ plotted against $\log_{10}\gamma$ in Fig. 2.

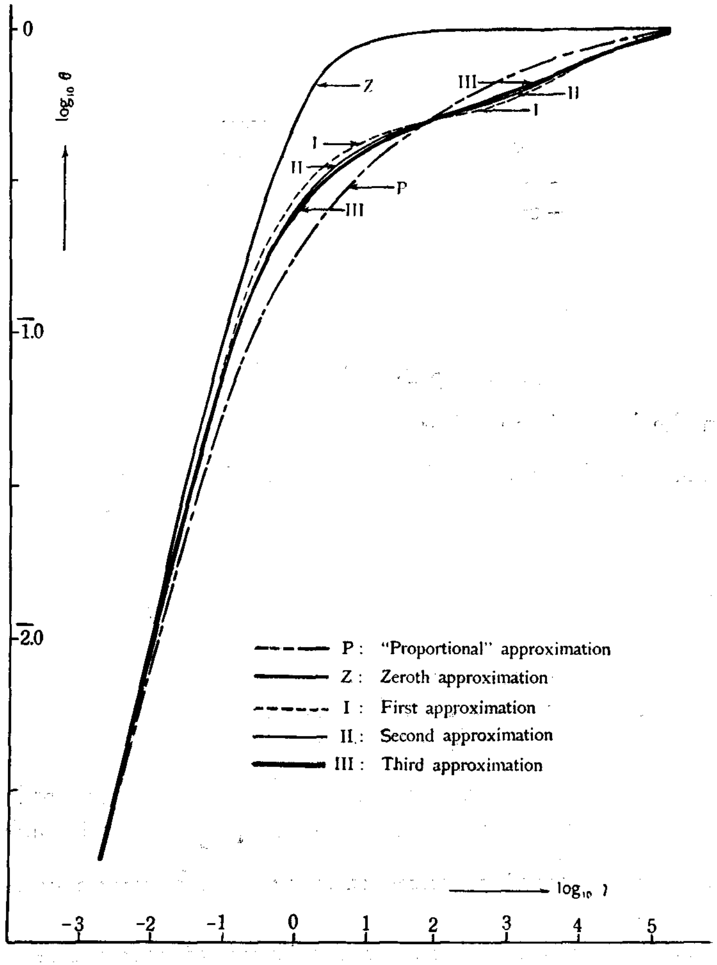

Fig. 2. $\theta(\gamma)$ of different approximations.

For the second approximation, we have by putting $t_5=t_6=t_7=t_8=0$ and $\xi_{\mathrm{III}}=1$ in (15) and (16) in accordance with §3

$$\varphi_{\sigma_0(\mathrm{H})}=\gamma\sum_{t_1,\cdots,t_4}\gamma^{\sum_{i=1}^{4}t_i}(\eta_{\mathrm{I}}\xi_{\mathrm{I}})^{t_1+t_2}(\eta_{\mathrm{II}}\xi_{\mathrm{II}})^{t_3+t_4}=\gamma(1+\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}})^2(1+\gamma\eta_{\mathrm{II}}\xi_{\mathrm{II}})^2\,, \quad (26.\,\mathrm{a})$$

$$\varphi_{\sigma_0(0)}=\sum_{t_1,\cdots,t_4}\gamma^{\sum_{i=1}^{4}t_i}\eta_{\mathrm{I}}^{t_1+t_2}\eta_{\mathrm{II}}^{t_3+t_4}=(1+\gamma\eta_{\mathrm{I}})^2(1+\gamma\eta_{\mathrm{II}})^2\,, \quad (26.\,\mathrm{b})$$

TABLE 2. $\theta(\gamma)$ of the third approximation, 50°C

$\gamma/1.887$*	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5
η_{I}	0.9978	0.9799	0.8569	0.5514	0.2620	0.1011	0.04402	0.02533	0.02163
η_{II}	0.9989	0.9899	0.9314	0.8220	0.7500	0.6878	0.6404	0.5489	0.5130
η_{III}	0.9969	0.9711	0.8084	0.4635	0.1998	0.0736	0.0302	0.0156	0.0122
$\varphi_{\sigma_0}(\mathrm{H})$	1.904×10^{-3}	2.062×10^{-2}	0.3746	34.58	1.924×10^{4}	3.095×10^{7}	3.274×10^{11}	1.193×10^{17}	7.199×10^{24}
$\varphi_{\sigma_0}(0)$	1.015	1.155	2.966	80.11	2.503×10^{4}	2.703×10^{7}	1.712×10^{11}	2.118×10^{16}	2.100×10^{23}
θ	0.001872	0.01753	0.1121	0.3015	0.4346	0.5337	0.6567	0.8493	0.9717

TABLE 3. $\theta(\gamma)$ of the second approximation, 50°C

$\gamma/1.887$	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5
η_{I}	0.9967	0.9687	0.7916	0.4226	0.1658	0.06265	0.02246	0.01097	0.008284
η_{II}	0.9960	0.9585	0.7256	0.2768	0.05355	0.007919	0.001390	0.0004466	0.0003015
$\varphi_{\sigma_0}(\mathrm{H})$	0.001891	0.01929	0.2226	3.377	55.73	1.052×10^{3}	4.616×10^{4}	2.090×10^{7}	2.845×10^{11}
$\varphi_{\sigma_0}(0)$	1.0075	1.0747	1.7074	7.484	68.88	9.230×10^{2}	2.468×10^{4}	3.841×10^{6}	8.192×10^{9}
θ	0.001873	0.01764	0.1153	0.3109	0.4472	0.5326	0.6516	0.8448	0.9720

* The present calculation was conducted earlier assuming a particular value of $\Delta\varepsilon$, which led to the relation $\gamma/1.887=\sqrt{P}$ mmHg by (24). The $\gamma/1.887$ in the above equation was used as the parameter here in order to utilize the results of the earlier calculations.

$$\varphi_{\sigma_1(0)} = \sum_{t_0,t_2,t_3,t_4} \gamma^{t_0+t_2+t_3+t_4} \eta_{\mathrm{I}}^{t_2} \eta_{\mathrm{II}}^{t_3+t_4} \xi_{\mathrm{I}}^{t_0 t_2} \xi_{\mathrm{II}}^{t_0(t_3+t_4)}$$
$$= (1+\gamma\eta_{\mathrm{I}})(1+\gamma\eta_{\mathrm{II}})^2 + \gamma(1+\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}})(1+\gamma\eta_{\mathrm{II}}\xi_{\mathrm{II}})^2 , \qquad (26.\,\mathrm{c})$$

$$\varphi_{\sigma_3(0)} = \sum_{t_0,t_1,t_2,t_4} \gamma^{t_0+t_1+t_2+t_4} \eta_{\mathrm{I}}^{t_1+t_2} \eta_{\mathrm{II}}^{t_4} \xi_{\mathrm{I}}^{t_0(t_1+t_2)} \xi_{\mathrm{II}}^{t_0 t_4}$$
$$= (1+\gamma\eta_{\mathrm{I}})^2(1+\gamma\eta_{\mathrm{II}}) + \gamma(1+\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}})^2(1+\gamma\eta_{\mathrm{II}}\xi_{\mathrm{II}}) . \qquad (26.\,\mathrm{d})$$

The values of η_{I} and η_{II} were determined by substituting $\varphi_{\sigma_0(0)}$, $\varphi_{\sigma_1(0)}$ and $\varphi_{\sigma_3(0)}$ from (26) into (18. II) and solving the latter for them on the base of the values of (17. II). These values of ξ_{I}, ξ_{II}, η_{I} and η_{II} determine θ by (6.b), (26.a) and (26.b) as a function of γ. The result is shown in Table 3 and by the curve II in Fig. 2.

§ 6. First, Zeroth and "Proportional" Approximations

The polynomials of the first approximation are obtained by putting $t_3=t_4=t_5=t_6=t_7=t_8=0$ in (15) and (16) or $t_3=t_4=0$ in (26) as

$$\varphi_{\sigma_0(\mathrm{H})} = \gamma \sum_{t_1,t_2} (\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}})^{t_1+t_2} = \gamma(1+\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}})^2 , \qquad (27.\,\mathrm{a})$$

$$\varphi_{\sigma_0(0)} = \sum_{t_1,t_2} (\gamma\eta_{\mathrm{I}})^{t_1+t_2} = (1+\gamma\eta_{\mathrm{I}})^2 , \qquad (27.\,\mathrm{b})$$

$$\varphi_{\sigma_1(0)} = \sum_{t_0,t_2} \gamma^{t_0+t_2} \eta_{\mathrm{I}}^{t_2} \xi_{\mathrm{I}}^{t_0 t_2} = 1+\gamma\eta_{\mathrm{I}} + \gamma(1+\gamma\eta_{\mathrm{I}}\xi_{\mathrm{I}}) . \qquad (27.\,\mathrm{c})$$

The η_{I} is determined on the base of the values of ξ_{I} given by (17.I) for any prescribed value of γ by solving (18.I) and the latter set of values of γ, ξ_{I} and η_{I} determine θ according to (6.b) and (27). The result is shown in Table 4 and by the curve I in Fig. 2.

In zeroth approximation we have by putting $t_1=t_2=0$ in (27)

$$\varphi_{\sigma_0(\mathrm{H})} = \gamma , \quad \varphi_{\sigma_0(0)} = 1 ,$$

hence by (6. b)

$$\theta = \frac{\gamma}{1+\gamma} , \qquad (28)$$

TABLE 4. $\theta(\gamma)$ of the first, zeroth and "proportional" approximation, 50°C

$\gamma/1.887$	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5
First	0.001879	0.01787	0.1229	0.3327	0.4567	0.5264	0.6308	0.8316	0.9715
Zeroth	0.001883	0.01852	0.1587	0.6536	0.9497	0.9944	0.9995	0.99995	0.99999
Pro.p	0.001853	0.01613	0.08363	0.2193	0.3897	0.5706	0.7451	0.8913	0.9753

which is just the LANGMUIR's adsorption isotherm as seen with reference to (23.γ). In the case of the "proportional" approximation, we have θ immediately from (20) as a function of γ. The θ calculated by the zeroth and the "proportional" approximation is shown in Table 4 and by the curves Z and P respectively in Fig. 2.

§ 7. Comparison between Theoretical and Experimental Isotherms

It is seen from Fig. 2 that the shift of the $\log_{10}\theta$, $\log_{10}\gamma$-curve with the progress of approximation diminishes rapidly, so that the curves II of the second approximation lies close to that III of the third approximation. Taking on this ground the curve III practically the ultimate theoretical relation relevant to the present model, the appropriateness of the model accompanied by the repulsive potential by the EYRING's rule[13)] [*)] was investigated as below by comparing the theoretical conclusion with experiment. The θ is given theoretically as a function of γ, whereas the quantity v cc of adsorbed hydrogen in NTP volume per unit quantity of adsorbent (reduced nickel obtained from 1 gm NiO) is determined experimentally as a function of hydrogen pressure P at adsorption equilibrium. If the model is appropriate to the experimental reults, the v/θ must be constant independent of γ or P. Eq. (23.γ) shows, however, that the proportionality constant of γ to $\sqrt{P}$ varies with $\Delta\varepsilon$. The $\Delta\varepsilon$ was now adjusted as a variable parameter to secure the constant v/θ, and the adjusted value of $\Delta\varepsilon$ and the constant value of v/θ were compared with relevant experimental data. Table 5 shows the constancy of v/θ thus attained.

TABLE 5. Comparison between theoretical[**)] and experimental isotherms[14)]
Adsorbent: reduced nickel from 1 gm NiO, 50°C

P mmHg	4.34×10^{-3}	0.153	0.544	1.79	1.92	6.30
v cc NTP	1.59	1.99	2.08	2.29	2.26	2.47
γ	1.32×10^{3}	7.82×10^{3}	1.48×10^{4}	2.68×10^{4}	2.78×10^{4}	5.02×10^{4}
θ	0.636	0.769	0.829	0.872	0.874	0.907
v/θ	2.50	2.59	2.51	2.62	2.59	2.72

Average of $v/\theta = 2.59$ cc NTP, $N_A\Delta\varepsilon = 12.3$ Kcal.

The average of v/θ and the adjusted value of $\Delta\varepsilon$ are shown beneath the Table, where N_A is the AVOGADRO's number.

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*) Cf. p. 53.

**) Theoretical isotherm of the third approximation.

The ratio v/θ gives now the number N of sites per unit area of the reduced nickel on the base of its surface area $1.7\times10^5\,\mathrm{cm}^2/\mathrm{gm}$ NiO[15] as

$$N=\frac{2N_A\times2.59}{22400\times1.7\times10^4}=0.8\times10^{15}\,\mathrm{cm}^2\,,$$

which is in a satisfactory agreement with the crystallographic value $1.1\times10^{15}\,\mathrm{cm}^{-2}$ of the (110)-lattice plane of nickel.

The adjusted value $N_A\Delta\varepsilon=12.3$ Kcal leads, on the other hand, as shown below, to the limiting value 26.0 Kcal/mol of the differential heat of adsorption at $\theta=0$ and 290°C in perfect agreement with the observed value 26 Kcal[15].

In the limiting case of θ tending to zero, t_i's $(i=1\cdots,8)$ are respectively zero, so that $\varphi_{\sigma_0(\mathrm{H})}/\varphi_{\sigma_0(0)}=\gamma$ according to (15) or by (6.b)

$$\frac{\theta}{1-\theta}=\gamma\,, \tag{29}$$

in coincidence with the isotherm (28) of the zeroth approximation. It follows now from (29) and the proportionality of θ to v that

$$\left(\frac{\partial\ln\gamma}{\partial T}\right)_v=0$$

or substituting γ from (23.γ) into the above equation that

$$RT^2\left(\frac{\partial\ln P}{\partial T}\right)_v=2N_A\Delta\varepsilon+7/2\cdot RT+2RT^2\partial\ln\prod_{j=1}^{3}\{1-\exp(-h\nu_j/kT)\}/\partial T\,, \tag{30}$$

where $RT^2(\partial\ln P/\partial T)_v$ is the differential heat of adsorption. The first term in the above equation is given by the above adjusted value $N_A\Delta\varepsilon=12.3$ Kcal. The last term is evaluated on the base of the vibrational frequencies given by (25). We have thus $RT^2(\partial\ln P/\partial T)_t=26.0$ Kcal at the temperature 290°C of the measurement[15].

These results sufficiently verify the crystal surface model of the (110)-lattice plane associated with the repulsive potential by the EYRING's rule.

§ 8. Adsorption Isotherm at Low Temperature

Present model might further be verified by the observation of adsorption isotherms at lower temperatures as follows.

The reversible work $-kT\ln q^{\mathrm{H}}_{\sigma_i}$ is expressed in general as

$$-kT\ln q^{\mathrm{H}}_{\sigma_i}=w+W/N_A\,,$$

where W/N_A is the part of the reversible work due to the interactions between the hydrogen atom brought to σ_i and those on the surrounding sites. We have from (9.γ), (19) and the above equation,

$$W=RT\ln(1-\theta)\gamma/\theta\,, \tag{31}$$

which might be called the free energy of repulsion.

W is constantly zero independent of θ in the absence of interaction as directly follows from (28).

In the presence of interactions, adsorbed hydrogen atoms assume an arrangement of the lowest potential energy at sufficiently low temperature, so that W must be zero at low θ until θ attains a point, where a further increase of θ inevitably accompanies interaction. Let the interaction range from the first to the third nearest neighbourers in accordance with our model of the third approximation. W is then zero, until θ attains to $1/4$, when sites on the (110)-lattice plane, denoted by dots in Fig. 3, are so far occupied as signified by surrounding circles. The latticework of the occupied sites being thus completed, a further addition of adsorbed hydrogen atom, indicated by a square around a dot, costs the work of $4R_{\text{III}}$ due to the repulsive interaction. Any shift of preliminarily adsorbed hydrogen atom to an unoccupied site in company with the addition is inhibited at the low temperature by an associated rise of potential as seen from Fig. 3.

It follows that W jumps up to $4R_{\text{III}}$ from zero at $\theta=1/4$ and keeps constant

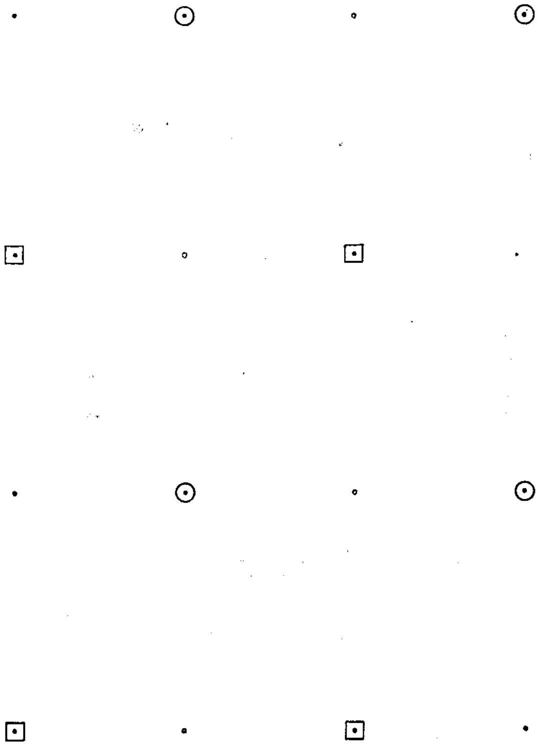

Fig. 3. Adsorption on (110)-lattice plane.

until the latticework of circles and squares in Fig. 3 is completed, when θ equals 1/2. A further addition of adsorbed hydrogen atom requires an additional work $2R_{\mathrm{I}}+2R_{\mathrm{II}}$ as seen from Fig. 3, so that W leaps again to a higher value $2R_{\mathrm{I}}+2R_{\mathrm{II}}+4R_{\mathrm{III}}$, which keeps constant until θ attains to unity.

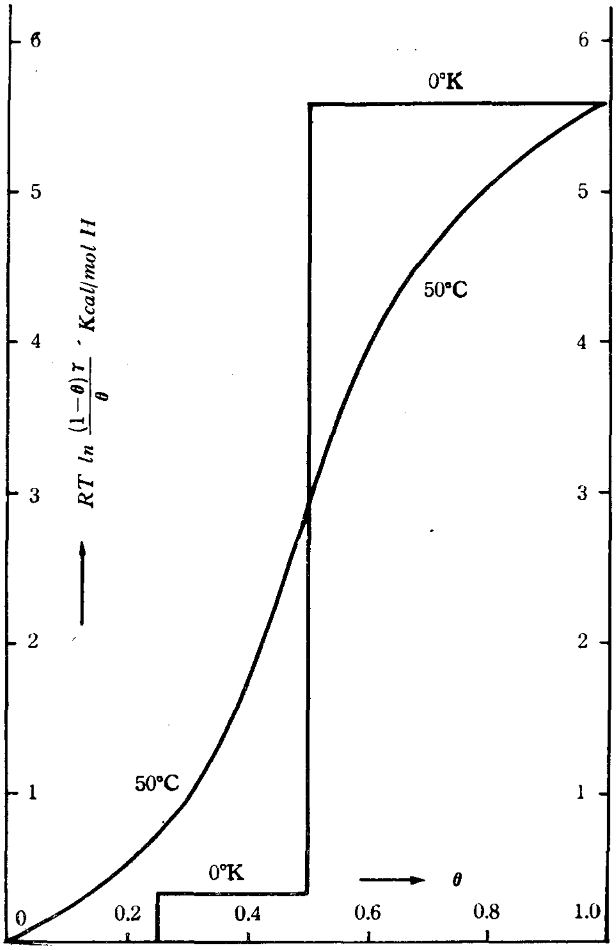

Fig. 4. Free energy of repulsion $W = RT\ln(1-\theta)\gamma/\theta$.

The above change of the free energy W of repulsion at low temperature is illustrated in Fig. 4 in comparison with that derived by (31) from the theoretical result of the third approximation at 50°C. We see from the comparison that the angular change of W at low temperatures is more or less smoothed at higher temperatures by thermal agitation. It is expected that the crystal surface model would be crucially evidenced by revealing experimentally to some extent an angular behavior of W at low temperature in accordance with the conclusion from the model.

Summary

The isotherm of dissociative adsorption of hydrogen on nickel was statistical-mechanically deduced on the basis of the crystal surface model taking the repulsive interaction among adsorbed hydrogen atoms into account in extension of BETHE and PEIERLS' method[12] as outlined in a previous work[11] in different degrees of approximation. The crystal surface model was such that the adsorption sites of hydrogen atoms were physically identical with each other, being located each on a point of the (110)-plane of f.c.c. lattice, which was congruent to that of the crystal surface of the adsorbent. The potential of interaction between hydrogen atoms was calculated according to EYRING[13] as -35% of the MORSE function of hydrogen molecule.

Repulsive interaction was taken into account in the first, second and third approximation as far as those between the first, second and third nearest neighbourers respectively and none at all in the zeroth approximation. In the "proportional" approximation the repulsive potential of an adsorbed hydrogen atom was approximated by that proportional to the covered fraction θ of adsorption sites as in the previous works[1][2][3].

The θ at the dissociative adsorption equilibrium was thus worked out as a function of a statistical-mechanical function γ, which is proportional to the square root of hydrogen pressure P, the appropriate proportionality constant implying the adsorption energy $\Delta\varepsilon$ (the excess of the half the energy of the ground state of hydrogen molecule over the energy of the ground state of adsorbed hydrogen atom), the vibrational frequencies of adsorbed hydrogen atom and the molecular constants of hydrogen molecule.

The result was that the calculated θ at each γ converged practically to a constant value, as we proceeded with the order of approximation, those of the second approximation lying close to that of the third.

The calculated result $\theta=\theta(\gamma)$ of the third approximation was now compared with the adsorbed quantity v observed as a function of P[14] by adjusting $\Delta\varepsilon$ implied in the proportionality constant of γ to $\sqrt{P}$, so as to keep the ratio v/θ constant independent of γ or P. It was found on the one hand from the constant value v/θ thus obtained and the observed area of the adsorbent[15], that the number of adsorption sites per unit surface area was 0.8×10^{15} in satisfactory agreement with the crystallographic value 1.1×10^{15} of the (110)-lattice

plane of nickel and on the other hand that the adjusted value of $\Delta\varepsilon$ led to the magnitude 26.0 Kcal/mol of the limiting value of the differential heat of adsorption of hydrogen at $\theta=0$ and 290°C, which agreed perfectly with the observed value 26 Kcal[15].

The reversible work W done against the repulsive interaction by a hydrogen atom when adsorbed or the free energy of repulsion was derived as a function of θ from the calculated result of the third approximation in comparison with an angular tierlike figure of $W(\theta)$ deduced for absolute zero temperature, it being pointed out that the crystal surface model would be crucially evidenced by observation of an isotherm at low temperature more or less like the latter figure.

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