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THEORETICAL ISOTHERM OF HYDROGEN ADSORPTION ON NICKEL (I)

By

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Summary

Isotherm of hydrogen adatom on nickel was statistical mechanically calculated on the basis of the previous conclusion that there exist two kinds of hydrogen adatoms, *i. e.* r-adatoms and s-adatoms; the r-adatoms are adatoms of ordinary sense situated outside the electronic surface of adsorbent metal, while s-adatoms are a sort of dissolved atoms, almost imbedded in the electron cloud between the electronic surface and the plane through the centres of outermost metal atoms. Repulsion between r-adatoms as well as that between s-adatoms were taken into account, whereas that between r- and s-adatoms ignored. The above calculation was conducted exclusively on (110) lattice plane of nickel in accordance with the previous theoretical and experimental inferences that the adsorption occurs practically there at relatively low coverage on account of the lowest energy of adsorption. The values of energies both of r- and s-adatoms without interaction potentials and values of the latter are adjusted, so that the theoretical coverage $\theta(T, P)$ runs proportional to the experimental amount $v(T, P)$ of adsorption with proportional constant independent of temperature T and pressure P. The initial heat of adsorption was thus calculated at 27.0 kcal/mol in satisfactory agreement with observation and the (110) lattice plane was concluded to occupy one third of the BET surface area.

Introduction

It is a general conclusion from observations that the differential heat of adsorption of hydrogen on catalyst's surface decreases with increase of coverage. This decrease has been interpreted from different angles on the bases of the two contrasting models of catalyst's surface, *i.e.* the homogeneous and the heterogeneous models respectively originating from LANGMUIR[1] and H. S. TAYLOR[2]. It is assumed with the latter model that there are no interaction between adatoms and that sites provide different energies of adsorption, so that those with the lower energies are occupied initially resulting in the decrease of the differential heat of adsorption with increase of coverage.

Mathematical methods have been developed by several authors[3][4][5] to determine the distribution of sites as a function of adsorption energy from the experimental isotherm. One of the present authors (J. H.)[5] has determined the distribution function from experimental isotherms of hydrogen on nickel and tungsten at different temperatures. He found that the functions thus determined at various temperatures from 0°C to 300°C shifted remarkably with temperature concluding that the heterogeneous model implying the neglect of interaction between adatoms was not applicable to the hydrogen adsorption on nickel and tungsten. The other of the present authors (T. T.)[6] showed that the preferential desorption of the portion subsequently adsorbed, as observed by means of isotopic tracer, does not exclusively evidence the heterogeneous model, but is equally accounted for on the basis of the homogeneous model with a proper allowance for the interaction.

The homogeneous or the lattice plane model has been developed by ROBERTS[7] and OKAMOTO, HORIUTI and HIROTA[8] as follows with reference to the dissociative adsorption of hydrogen gas on metallic adsorbent. According to these authors the surface of metallic adsorbent consists of different lattice planes of metallic crystal and each lattice plane furnishes a congruent lattice plane of adsorption sites of adatoms, which are practically physically identical with each other. The lattice plane model has been elaborated in the two points as below with reference to the state of adatoms. One of the present authors (T. T.)[9-11] concluded by quantum mechanical investigation that there existed two sorts of adatoms in distinctly different states; one is that of usual sense, which is situated outside the electronic surface of adsorbent metal and the other is almost imbedded in the electron cloud between the electronic surface and the plane through the centres of outermost metal atoms, as called by him r- and s-adatoms respectively. It was thus concluded that each lattice plane provided a group of physically identical sites for r-adatoms and such for s-adatoms which were each equal in number to metal atoms on the lattice plane, that the energy of a single isolated r-adatom as well as that of single isolated s-adatom depended only on the kind of the lattice plane, which it rested upon, that r-adatoms repulsed each other even stronger than estimated previously by OKAMOTO, HORIUTI and HIROTA[8] as exchange repulsion and that the lattice imperfections, *i.e.* steps, kinks, defects and grain boundaries furnished sites of s-adatom of extraordinary low energy[10][12][13].

The sites for r-adatoms and those for s-adatoms will be called r-sites and s-sites respectively and the model thus elaborated particularly termed the lattice plane model in what follows[14].

The present paper is devoted to derive the coverage θ as a function of temperature T and pressure P of hydrogen in adsorption equilibrium on the basis of the following theoretical inferences.

I) The equilibrium position of r-adatom is situated right above a metal atom on an exposed lattice plane of metallic adsorbent, *ca.* 1 Å apart from its electronic surface, whereas that of s-adatom is in an interstitial surface site, *ca.* 0.5 Å inside the electronic surface[10)12)13)]. The r-sites or s-sites on a lattice plane are respectively physically identical with each other and there exists each one r-site and s-site per one metal atom on the lattice plane.

II) The r-adatoms repulse each other more intensively than estimated as exchange repulsion[8)] between hydrogen atoms unbonded with each other by EYRING's semi-empirical equation, while s-adatoms do weaker[10)12)].

III) Both r- and s-adatoms on the sites specified in I) vibrate normal to the electronic surface with frequencies of valence vibrations[8)3)]; parallel to the electronic surface, r-adatoms vibrate with frequencies of bending vibrations, whereas s-adatoms conduct practically two dimentional translation parallel to the surface[12)13)].

IV) The energies both of r- and s-adatoms without the repulsive interaction are respectively lower on a less dense lattice plane, *i.e.* the energies both of the adatoms are lowest on the least dense lattice plane (110) of Ni(f.c.c.) surface and highest on the most dense lattice plane (111)[8)12)15)].

V) Lattice imperfections on the surface, *i.e.* steps, kinks, defects and grain boundaries provide adsorption sites for s-adatoms with appreciably low energy, even lower than that of r-adatoms on the (110) lattice plane. However, such s-sites are only a small fraction of the whole adsorption sites, so that the adsorption on these s-sites is predominant only at the very initial stage of adsorption[10)12)13)].

The function $\theta(T, P)$ theoretically deduced ought to be proportional to the observed amount of adsorption, with a proportional constant independent of T and P. The $\theta(T, P)$ is thus adjusted to the proportionality by varying the energies of r- and s-adatoms, the repusive potential between r-adatoms and that between s-adatoms around their respective reasonable values, admitting that r- and s- adatoms are in equilibrium with each other. The interaction between r- and s-adatoms is ignored, and the adsorption on (110) lattice plane is only taken into account in the present paper, leaving the allowance for other lattice planes to a subsequent paper.

§ 1. Statistical Mechanical Equations of Adsorption*)

The chemical potential μ^{H} of hydrogen adatom H is connected with a factor p^{H} of multiplication of partition function of a macroscopic adsorbent C retaining a definite amount of adsorbate, caused by addition of one adatom H to it to

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*) As to the present formulation, see refs. (12), (13), (16) and (17).

make C^{H}, *i.e.*

$$p^{\mathrm{H}} = \mathfrak{Q}C^{\mathrm{H}}/\mathfrak{Q}C\,, \tag{1}$$

as

$$\mu^{\mathrm{H}} = -RT\ln p^{\mathrm{H}}\,, \tag{2}$$

where $\mathfrak{Q}C$ or $\mathfrak{Q}C^{\mathrm{H}}$ is the partition function of C or C^{H} respectively. Eq. (2) follows from the definition of chemical potential and a property of partition function that $-kT\ln\mathfrak{Q}C$ or $-kT\ln\mathfrak{Q}C^{\mathrm{H}}$ behaves as the free energy of C or C^{H} respectively.

We define further

$$q^{\mathrm{H}} = \mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}/\mathfrak{Q}C_{\sigma(0)}\,, \tag{3}$$

where $\mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}$ is the partition function of the particular state $C^{\mathrm{H}}_{\sigma(\mathrm{H})}$ of C^{H} that a definite r- or s-site σ is occupied by an adatom with certainty and $\mathfrak{Q}C_{\sigma(0)}$ is the partition function of the particular state $C_{\sigma(0)}$ of C that the same definite site is unoccupied with certainty. We see similar to the case of p^{H} that $-kT\ln q^{\mathrm{H}}$ is the free energy increase of the relevent macroscopic assembly caused by addition of an adatom to a definite, preliminarily evacuated site σ.

The ratio of q^{H} to p^{H} is according to (1) and (3)

$$\frac{q^{\mathrm{H}}}{p^{\mathrm{H}}} = \frac{\mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}}{\mathfrak{Q}C^{\mathrm{H}}}\bigg/\frac{\mathfrak{Q}C_{\sigma(0)}}{\mathfrak{Q}C}\,. \tag{4}$$

It follows from another property of partition function that the fraction $\mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}/\mathfrak{Q}C^{\mathrm{H}}$ or $\mathfrak{Q}C_{\sigma(0)}/\mathfrak{Q}C$ equals the probability, with which the definite site σ is occupied by H or unoccupied respectively. Hence, we have

$$\mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}/\mathfrak{Q}C^{\mathrm{H}} + \mathfrak{Q}C_{\sigma(0)}/\mathfrak{Q}C = 1\,, \tag{5}$$

ignoring the effect of the addition of a single adatom to the macroscopic assembly C on the probability. Denoting $\mathfrak{Q}C^{\mathrm{H}}_{\sigma(\mathrm{H})}/\mathfrak{Q}C^{\mathrm{H}}$ by θ^{H}, we have from Eqs. (4) and (5),

$$q^{\mathrm{H}}/p^{\mathrm{H}} = \theta^{\mathrm{H}}/(1-\theta^{\mathrm{H}})\,. \tag{6}$$

Eq. (6) is now written for r- and s-adatom individually, noting that there is no difference between p^{r} and p^{s}, *i.e.* p^{H} written severally for r- or s-adatom, as follows from the equilibrium between them; we have in consequence

$$q^{\mathrm{r}}/p^{\mathrm{H}} = \theta^{\mathrm{r}}/(1-\theta^{\mathrm{r}})\,, \tag{6. r}$$

$$q^{\mathrm{s}}/p^{\mathrm{H}} = \theta^{\mathrm{s}}/(1-\theta^{\mathrm{s}})\,, \tag{6. s}$$

where $q^{\rm r}$ or $q^{\rm s}$ is the particular value of $q^{\rm H}$ for r- or s-adatom respectively, and $\theta^{\rm r}$ or $\theta^{\rm s}$ the probability of the r- or s-site being occupied. The $\theta^{\rm r}$ or $\theta^{\rm s}$ is identical with the covered fraction of r- or s-sites respectively because of the physical identity of sites of the respective kind as mentioned in I) in the introduction. We define θ as

$$\theta \equiv \theta^{\rm r} + \theta^{\rm s} \tag{7}$$

as a measure of the adsorbed amount, which attains 2 at full coverage both of r- and s-sites.

§ 2. Formulation of $q^{\rm r}$

The $q^{\rm r}$ is the special case of $q^{\rm H}$ defined by Eq. (3), hence $-kT \ln q^{\rm r}$ is the free energy increase of C caused by addition of r-adatom to a definite, preliminarily evacuated r-site in C. The relevant free energy increase $-RT \ln q^{\rm r}$ is expressed as

$$-RT \ln q^{\rm r} = -RT \ln q_0^{\rm r} + W^{\rm r}\,, \tag{8}$$

where $-RT \ln q_0^{\rm r}$ is that in the absence of interaction with surrounding r-adatoms and $W^{\rm r}$ is the rest of the free energy increase due to the repulsion, which will be called the free energy of repulsion.

The $q_0^{\rm r}$ in (8) is identified by definition with the particular case of $q^{\rm r}$, where C is a bare adsorbent C_0, hence

$$q_0^{\rm r} = \mathfrak{Q}C^{\rm r}_{\sigma({\rm r}),0} / \mathfrak{Q}C_0\,, \tag{9}$$

where $\mathfrak{Q}C_0$ is the partition function of C_0 and $\mathfrak{Q}C^{\rm r}_{\sigma({\rm r}),0}$ is that of $C^{\rm r}_{\sigma({\rm r}),0}$ formed by adding one r-adatom to C_0 at a definite r-site. The $\mathfrak{Q}C^{\rm r}_{\sigma({\rm r}),0}$ is now calculated, assuming that the lattice vibrations of adsorbent proper and the motion of the r-adatom are not coupled with each other and that the lattice vibrations are not affected by the r-adatom, the mass of Ni atom being about 60 times as large as that of H. Actually, the frequency of H-adatom on Pt is $1.39 \approx \sqrt{2}$ times that of D-adatom as observed by PLISKIN and EISCHENS[18], which warrants the above procedure.

The free energy $-kT \ln \mathfrak{Q}C^{\rm r}_{\sigma({\rm r}),0}$ consists now of three parts, *i.e.* that $-kT \ln \mathfrak{Q}C_0$ of C_0 proper without influence of the r-adatom, that $-kT \ln \mathfrak{Q}{\rm r}$ of the r-adatom in the potential field of C_0 and the potential energy $\varepsilon_0^{\rm r}$ of H in its equilibrium position in the field, hence

$$-kT \ln \mathfrak{Q}C^{\rm r}_{\sigma({\rm r}),0} = -kT \ln \mathfrak{Q}C_0 - kT \ln \mathfrak{Q}{\rm r} + \varepsilon_0^{\rm r}\,, \tag{10}$$

or

$$\mathfrak{Q}C^{\mathrm{r}}_{\sigma(\mathrm{r}),0} = \mathfrak{Q}C_0 \cdot \mathfrak{Q}\mathrm{r} \cdot \exp(-\varepsilon^{\mathrm{r}}_0/kT)\,. \tag{11}$$

The factor $\mathfrak{Q}\mathrm{r}$ in the above equation is developed in accordance with III) in the introduction as

$$\mathfrak{Q}\mathrm{r} = \prod_{j=1}^{3}\left\{1-\exp\left(-\frac{h\nu_j}{kT}\right)\right\}^{-1}\exp\left(-\frac{h\nu_j}{2kT}\right), \tag{12}$$

where $j=1$, 2 and 3 signify the three modes of vibration, *i.e.* one normal and two parallel respectively to the surface and ν_j is the frequency of j-th mode.

Eqs. (9), (11) and (12) lead to the equation of q^{r}_0, as

$$q^{\mathrm{r}}_0 = \prod_{j=1}^{3}\left\{1-\exp\left(-\frac{h\nu_j}{kT}\right)\right\}^{-1}\exp\left(-\frac{\varepsilon^{\mathrm{r}}}{kT}\right), \tag{13}$$

where

$$\varepsilon^{\mathrm{r}} = \varepsilon^{\mathrm{r}}_0 + \sum_{j=1}^{3} h\nu_j/2 \tag{14}$$

is the energy of the ground state of r-adatom.

The free energy of repulsion W^{r} of hydrogen adatom on (110)-lattice plane of nickel has been formulated previously in extension of BETHE-PEIERLS method[13)], taking account of the repulsions of the first and the second nearest neighbouring r-adatoms. The W^{r} is thus given as a function $W^{\mathrm{r}}(T, \gamma^{\mathrm{r}})$ of T and $\gamma^{\mathrm{r}} = q^{\mathrm{r}}_0/p^{\mathrm{H}}$, by eliminating η_{I} and η_{II} from the three simultaneous equations

$$W^{\mathrm{r}} = 2RT\ln\left\{(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}})(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}})/(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}}\xi^{\mathrm{r}}_{\mathrm{I}})(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}}\xi^{\mathrm{r}}_{\mathrm{II}})\right\} \tag{15}$$

and

$$\begin{aligned}(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}})^2(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}})^2 &= (1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}})(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}})^2+\gamma^{\mathrm{r}}(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}}\xi^{\mathrm{r}}_{\mathrm{I}})(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}}\xi^{\mathrm{r}}_{\mathrm{II}})^2\\ &= (1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}})^2(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}})+\gamma^{\mathrm{r}}(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{I}}\xi^{\mathrm{r}}_{\mathrm{I}})^2(1+\gamma^{\mathrm{r}}\eta^{\mathrm{r}}_{\mathrm{II}}\xi^{\mathrm{r}}_{\mathrm{II}})\,,\end{aligned} \tag{16}$$

where

$$\xi^{\mathrm{r}}_{\mathrm{I}} = \exp(-R^{\mathrm{r}}_{\mathrm{I}}/kT) \quad \text{or} \quad \xi^{\mathrm{r}}_{\mathrm{II}} = \exp(-R^{\mathrm{r}}_{\mathrm{II}}/kT)\,, \qquad (17\,\mathrm{a}),\ (17\,\mathrm{b})$$

is the BOLTZMANN factor of the free energy increase identified with the repulsive potential $R^{\mathrm{r}}_{\mathrm{I}}$ or $R^{\mathrm{r}}_{\mathrm{II}}$ respectively, between two r-adatoms each in the equilibrium position at the first or the second nearest distance on (110) lattice plane, *i.e.* 2.49 or 3.52 Å and $\eta^{\mathrm{r}}_{\mathrm{I}}$ or $\eta^{\mathrm{r}}_{\mathrm{II}}$ is the factor which cares for the interaction respectively of the first or the second nearest adatoms to a particularly observed one with other adatoms.

§ 3. Formulation of q^{s}

The q^{s} is the special case of q^{H} defined by Eq. (3), similar to q^{r}, hence $-kT$

$\ln q^s$ is the free energy increase of C caused by addition of s-adatom to a definite, preliminarily evacuated s-site in C. The relevant free energy increase $-RT \ln q^s$ is expressed as

$$-RT \ln q^s = -RT \ln q_0^s + W^s \,, \tag{18}$$

where $-RT \ln q_0^s$ is that in the absence of interaction with surrounding adatoms and W^s is the rest of the free energy increase due to the repulsion.

The q_0^s in (18) is identified by definition with the particular case of q^s, where C is a bare adsorbent C_0, hence

$$q_0^s = \mathfrak{Q}C^s_{\sigma(s),0} / \mathfrak{Q}C_0 \,, \tag{19}$$

where $\mathfrak{Q}C^s_{\sigma(s),0}$ is the partition function of $C^s_{\sigma(s),0}$ formed by adding one s-adatom to C_0 at the definite s-site. The $\mathfrak{Q}C^s_{\sigma(s),0}$ is caluculated similar to $\mathfrak{Q}C^r_{\sigma(r),0}$ in § 2. The free energy $-kT \ln \mathfrak{Q}C^s_{\sigma(s),0}$ consists of three parts, *i.e.* that $-kT \ln \mathfrak{Q}C_0$ of C_0 proper, that $-kT \ln \mathfrak{Q}s$ of the s-adatom in the potential field of C_0 and the potential energy ε_0^s of the s-adatom in its equilibrium position in the potential field of C_0, *i.e.*

$$-kT \ln \mathfrak{Q}C^s_{\sigma(s),0} = -kT \ln \mathfrak{Q}C_0 - kT \ln \mathfrak{Q}s + \varepsilon_0^s \,, \tag{20}$$

hence

$$\mathfrak{Q}C^s_{\sigma(s),0} = \mathfrak{Q}C_0 \cdot \mathfrak{Q}s \cdot \exp(-\varepsilon_0^s / kT) \,. \tag{21}$$

The $\mathfrak{Q}s$ is developed in accordance with III) in the introduction, as

$$\mathfrak{Q}s = A \frac{2\pi mkT}{h^2} \left\{ 1 - \exp\left(-\frac{h\nu}{kT} \right) \right\}^{-1} \exp\left(-\frac{h\nu}{2kT} \right), \tag{22}$$

where $A \cdot 2\pi mkT / h^2$ is the partition function of the two dimentional translation parallel to the electronic surface of adsorbent over the area A appropriate to the s-site, m the effective mass of the translation and ν the frequency of the vibration normal to the electronic surface.

We have from Eqs. (19), (21) and (22)

$$q_0^s = A \frac{2\pi mkT}{h^2} \left\{ 1 - \exp\left(-\frac{h\nu}{kT} \right) \right\}^{-1} \exp\left(-\frac{\varepsilon^s}{kT} \right), \tag{23}$$

where

$$\varepsilon^s = \varepsilon_0^s + h\nu / 2 \tag{24}$$

is the energy of s-adatom in its ground state.

The value of A has been estimated previously as follows[13]. Let θ^s be small enough for their interaction to be practically ignorable with regard to the two dimentional translation as in the case of atenuated gas. $\mathfrak{Q}C$ of C retaining N^s-1 s-adatoms is given as[13)]

$$\mathfrak{Q}C = \mathfrak{Q}C_0(Q^s)^{N^s-1}/(N^s-1)\,! \,, \tag{25}$$

where

$$Q^s = [A]\frac{2\pi mkT}{h^2}\left\{1-\exp\left(-\frac{h\nu}{kT}\right)\right\}^{-1}\exp\left(-\frac{\varepsilon^s}{kT}\right), \tag{26}$$

and $[A]$ is the whole area of the electronic surface of the adsorbent. The partition function $\mathfrak{Q}C^s$ of C^s formed by adding another s-adatom to C is given similar to $\mathfrak{Q}C$ as

$$\mathfrak{Q}C^s = \mathfrak{Q}C_0(Q^s)^{N^s}/N^s\,! \,. \tag{27}$$

The p^{H} is now expressed with special reference to s-adatom by Eqs. (25), (27) and (1), as

$$p^{\mathrm{H}} = Q^s/N^s$$

or according to Eq. (6. s)

$$q_0^s/\theta^s = Q^s/N^s \,,$$

neglecting θ^s as compared with unity and identifying q^s with q_0^s for $\theta^s \ll 1$. Subsituting q_0^s from Eq. (23) and Q^s from Eq. (26) into the above equaton, we have

$$A = [A]/(N^s/\theta^s) \,,$$

where N^s/θ^s is equal to the total number of s-sites. Hence A is the surface area alloted to a metal atom, which amounts to *ca.* 10 Å^2 for (110) lattice plane.

The W^s is given similar to the W^r by replacing γ^r, η_{I}^r, η_{II}^r, ξ_{I}^r, ξ_{II}^r, R_{I}^r and R_{II}^r in Eqs. (15), (17 a) and (17 b) by $\gamma^s = q_0^s/p^{\mathrm{H}}$, η_{I}^s, η_{II}^s, ξ_{I}^s, ξ_{II}^s, R_{I}^s and R_{II}^s respectively, where R_{I}^s or R_{II}^s is the repulsive potential between two s-adatoms respectively on the first or the second nearest sites on (110) lattice plane,

$$\xi_{\mathrm{I}}^s = \exp(-R_{\mathrm{I}}^s/kT) \qquad \text{or} \qquad \xi_{\mathrm{II}}^s = \exp(-R_{\mathrm{II}}^s/kT)$$

and η_{I}^s or η_{II}^s is the factor similar to η_{I}^r or η_{II}^r respectively.

W^s is expressed as a function of T and γ^s by eliminating η_{I}^s and η_{II}^s from the equations obtained from Eqs. (15) and (16) by substituting η_{I}^s *etc.* for η_{I}^r *etc.*

§ 4. Parameters in q^r and q^s

The q^r is given as a function of T and $\gamma^r = q_0^r/p^{\mathrm{H}}$ according to Eqs. (8), (13), (15) and (16) with parameters ε^r, ν_1, ν_2, ν_3, R_{I} and R_{II}, as

$$q^{\mathrm{r}} = q_0^{\mathrm{r}}(T;\, \varepsilon^{\mathrm{r}},\, \nu_1,\, \nu_2,\, \nu_3) \exp\left\{ - W^{\mathrm{r}}(T, \gamma^{\mathrm{r}};\, R_{\mathrm{I}}^{\mathrm{r}},\, R_{\mathrm{II}}^{\mathrm{r}})/RT \right\} \tag{28. r}$$

and q^{s} is similarly given as a function of T and $\gamma^{\mathrm{s}} = q_0^{\mathrm{s}}/p^{\mathrm{H}}$ according to Eqs. (18), (23) and the equation for W^{s} similar to Eqs. (15) and (16) for W^{r}, as

$$q^{\mathrm{s}} = q_0^{\mathrm{s}}(T;\, \varepsilon^{\mathrm{s}},\, A,\, m,\, \nu) \exp\left\{ - W^{\mathrm{s}}(T, \gamma^{\mathrm{s}};\, R_{\mathrm{I}}^{\mathrm{s}},\, R_{\mathrm{II}}^{\mathrm{s}})/RT \right\}. \tag{28. s}$$

The p^{H} is a function of T and γ^{r} with parameters $\varepsilon^{\mathrm{r}}, \nu_1, \nu_2, \nu_3$ according to Eqs. $\gamma^{\mathrm{r}} = q_0^{\mathrm{r}}/p^{\mathrm{H}}$ and (13), or alternatively a function of T and γ^{s} with parameters $\varepsilon^{\mathrm{s}}, A, m, \nu$ according to Eqs. $\gamma^{\mathrm{s}} = q_0^{\mathrm{s}}/p^{\mathrm{H}}$ and (23), as

$$p^{\mathrm{H}} = p^{\mathrm{H}}(T, \gamma^{\mathrm{r}};\, \varepsilon^{\mathrm{r}},\, \nu_1,\, \nu_2,\, \nu_3)$$

or

$$p^{\mathrm{H}} = p^{\mathrm{H}}(T, \gamma^{\mathrm{s}};\, \varepsilon^{\mathrm{s}},\, A,\, m,\, \nu)\,. \tag{28. p}$$

We have thus θ^{r} or θ^{s} as a function of T and p^{H} by Eqs. (6) and (28).

On the other hand, we have for the adsorption equilibrium

$$\mu^{\mathrm{H}} = \mu^{\mathrm{H}_2}/2 \tag{29. a}$$

or according to Eq. (2)

$$p^{\mathrm{H}} = \sqrt{p^{\mathrm{H}_2}}\,, \tag{29. b}$$

where μ^{H_2} is the chemical potential of H_2, which relates to p^{H_2} as

$$\mu^{\mathrm{H}_2} = -RT \ln p^{\mathrm{H}_2}\,.$$

The p^{H_2} is expressed statistical mechanically as

$$p^{\mathrm{H}_2} = Q^{\mathrm{H}_2}/N^{\mathrm{H}_2}\,, \tag{30}$$

where

$$Q^{\mathrm{H}_2} = \frac{(2\pi m^{\mathrm{H}_2} kT)^{3/2}}{h^3} \cdot \frac{4\pi^2 IkT}{h^2} \tag{31}$$

is the partition function of a single hydrogen molecule in unit volume, the vibrational partition function being identified with unity with sufficient accuracy, N^{H_2} the concentration of hydrogen molecule in adsorption equilibrium and m^{H_2} or I is the mass or the moment of inertia of the molecule; energy of the ground state is taken zero, to which the values of ε^{r} and ε^{s} are referred. N^{H_2} is expressed by hydrogen pressure P in mmHg as

$$P = kTN^{\mathrm{H}_2}/980.5 \times 1.360\,. \tag{32}$$

We have

$$p^{\mathrm{H}} = \left\{ \frac{(2\pi m^{\mathrm{H}_2} kT)^{3/2}}{h^3} \frac{4\pi^2 IkT}{h^2} \frac{kT}{980.5 \times 1.360\, P} \right\}^{1/2} \tag{33}$$

from Eqs. (29. b), (30), (31) and (32), hence $\theta \equiv \theta^{r} + \theta^{s}$ as a function of T and P, with parameters ε^{r}, ε^{s}, ν_1, ν_2, ν_3, ν, R_{I}^{r}, R_{II}^{r}, R_{I}^{s}, R_{II}^{s}, A and m.

The value of A is estimated at *ca.* 10 Å^2 in § 3, while the effective mass m of s-adatom is identified with the mass of proton. The frequencies have been estimated with special reference to (110)-lattice plane of nickel as[8]

$$\nu_1 = 419\,, \quad \nu_2 = 479\,, \quad \nu_3 = 1900 \tag{34. r}$$

and

$$\nu = 1000\,^{*)\,13)} \tag{34. s}$$

in units of wave number per cm. The values of Eqs. (34) are used, as they are, inasmuch as, the frequencies being stiff enough, the inaccuracies associated, if any, would hardly affect the numerical values of q^{r} and q^{s} as seen in Eqs. (13) and (23).

The R_{I}^{r} and R_{II}^{r} were previously estimated at 0.1019 ev and 0.0134 ev respectively by EYRING's semi-empirical equation for exchanage repulsion between unbonded hydrogen atoms at first and second nearest distances, *i.e.* 2.49 Å and 3.52 Å.[16] It has been concluded by the quantum-theoretical investigation on r-adatom[9][10][12] that the repulsive potential must be fairly greater than the above estimated values. The R_{I}^{r} and R_{II}^{r} are assumed for the moment respectively proportional to the above values, *i.e.*

$$R_{\mathrm{I}}^{r} = 0.1019\,\alpha \text{ ev}, \qquad R_{\mathrm{II}}^{r} = 0.0134\,\alpha \text{ ev} \tag{35}$$

introducing a single parameter α. The R_{I}^{s} and R_{II}^{s} are also tentatively assumed as

$$R_{\mathrm{I}}^{s} = 0.1019\,\beta \text{ ev}, \qquad R_{\mathrm{II}}^{s} = 0.0134\,\beta \text{ ev} \tag{36}$$

with a single parameter β.

The theoretical investigation[9)-12] has shown further that ε^{r} should be lower than ε^{s} roughly by a few kcal/mol for Ni. These quantities as well as α and β are adjusted, as mentioned in the introduction, to the equation

$$v_1 \theta\,(T, P;\, \varepsilon^{r}, \varepsilon^{s}, \alpha, \beta) = v\,(T, P)\,,$$

where v_1 is the proportional constant.

§ 5. Determination of Parameters

The values of the function $\theta\,(T, P;\, \varepsilon^{r}, \varepsilon^{s}, \alpha, \beta)$ are numerically calculated for

---

*) Estimated from the potential curve (VII) of s-adatom given in Fig. 5 in ref. (10). See also ref. (11).

different pressure ranges lying between 0.01 and 100 mmHg at temperatures 0, 50, 100, 150, 200, 250 and 300°C for the values of parameters,

$$-\varepsilon^{r} = 10.3,\ 10.8,\ 11.3,\ 11.8,\ 12.3,\ 12.8\ \text{kcal/mol},$$

$$\varepsilon^{s}-\varepsilon^{r} = 4.5,\ 5.0,\ 5.5,\ 6.0,\ 6.5\ \text{kcal/mol},$$

$$\alpha = 1.0,\ 1.2,\ 1.5,$$

and

$$\beta = 0.0,\ 0.5\ .$$

The theoretical values of θ thus calculated are now examined for its proportionality to the experimental results of $v(T, P)$ by KINUYAMA and KWAN[19] as exemplified in Figs. 1∼18; the broken lines represent $\theta^{r}(T,P)$ *vs.* $v(T,P)$ and the fine lines or bold lines show $\theta(T,P)$ *vs.* $v(T,P)$ for $\beta=0$ or $\beta=0.5$ respectively.

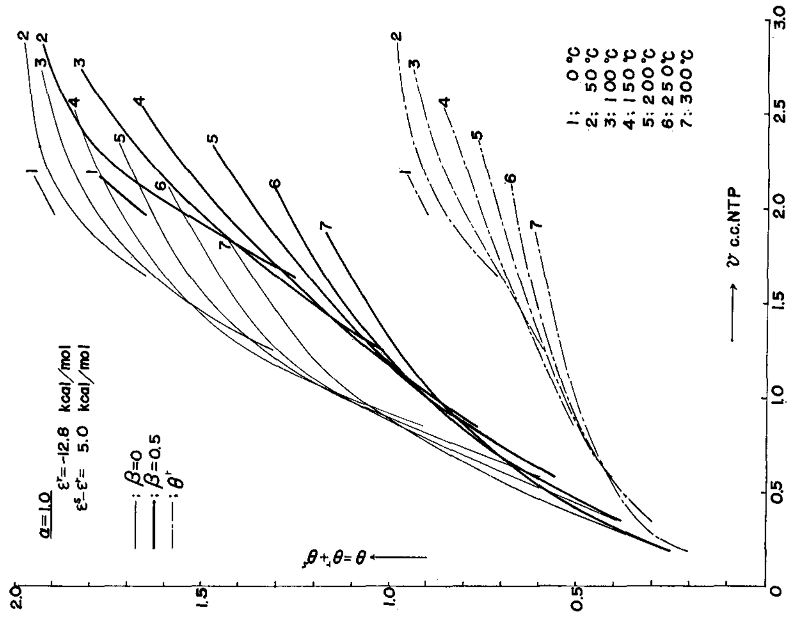
The proportionality of $\theta^{r}(T,P)$ to $v(T,P)$ was examined previously by one of the present authors (J. H.)[17] by varying the value of ε^{r} with α fixed at unity. It was hence inferred that the proportionality would be improved by allowing for s-adatoms. The best proportionality is located in the present calculation by varying the parameters, at $\varepsilon^{r}=-12.8$ kcal/mol, $\varepsilon^{s}-\varepsilon^{r}=5.0$ kcal/mol, $\alpha=1.5$ and $\beta=0.0$ (see Fig. 16). However, the observed v exceeds the value relevant to the proportionality at higher P at every temperature and the θ where the deviation begins to occur is the lower, the higher the temperature. This deviation is to some extent eliminated by increasing α (*cf.* Fig. 3, 12, 16) and presumably by allowing for other lattice planes.

The proportional constant v_1 is 1.0 cc NTP for the above parameters. From this value of v_1 we have the number $N_{(110)}$ of r-sites or the number of surface metal atoms of (110) lattice plane per cm² of BET surface area, which amounts to 1.7×10^{5} cm² per gm of NiO used for preparation of the adsorbent by reduction, as (N_A: the AVOGADORO number)

$$N_{(110)} = \frac{2N_A\times1.0}{22400\times1.7\times10^{5}} = 0.32\times10^{15}/\text{cm}^2\,,$$

admitting in accordance with IV) in the introduction that adsorption occurs only on (110) lattice plane at relatively low coverage on account of the lowest energy of adsorption on it. The number of metal atoms is 1.1×10^{15} per cm² of (110) lattice plane, hence the latter amounts to $0.32/1.1 \doteqdot 1/3$ of the BET surface in area.

The theoretical heat of adsorption at $\theta=0$ is calculated at 27.0 kcal/mol both at 0° and 300°C by the equation[16]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; β=0.5
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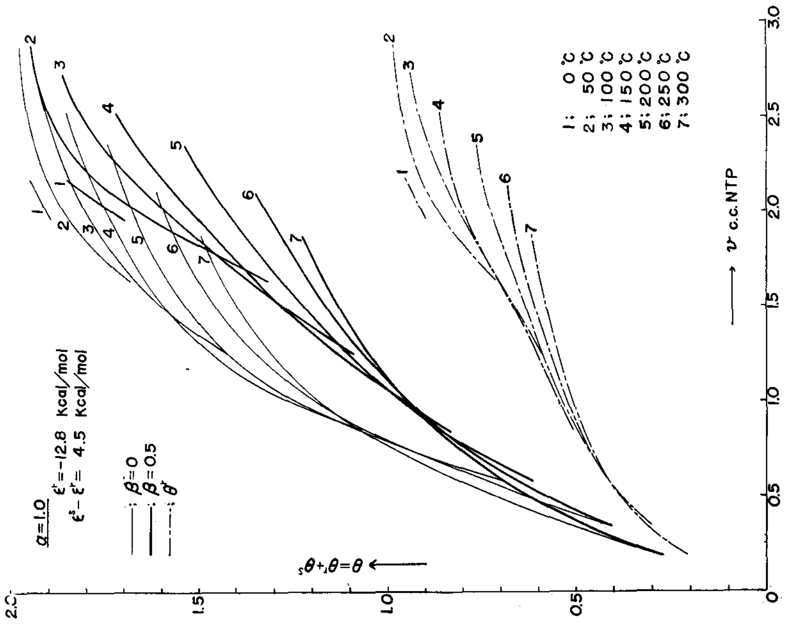
v c.c.NTP
1: 0 °C
2: 50 °C
3: 100 °C
4: 150 °C
5: 200 °C
6: 250 °C
7: 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0
1
2
3
4
5
6
7

Fig. 2.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ε^s-ε^r= 4.5 Kcal/mol
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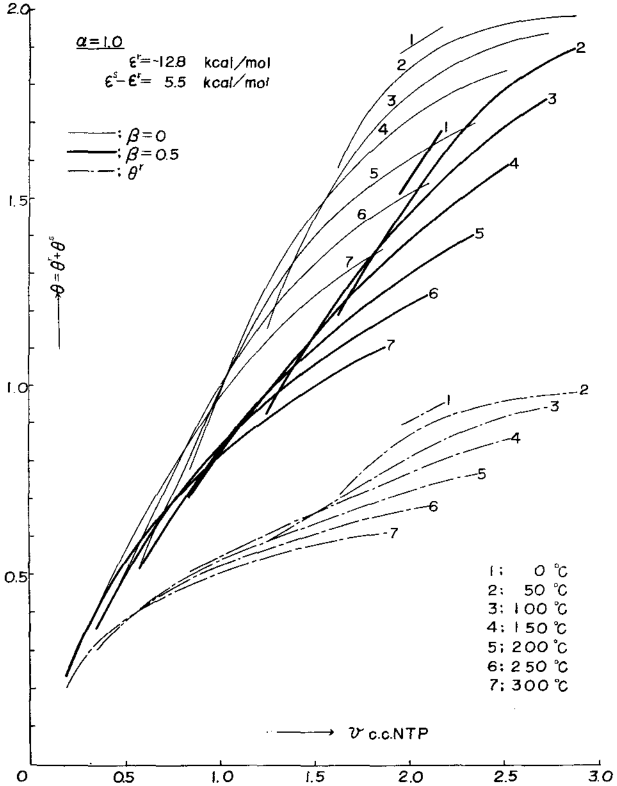
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1: 0 °C
2: 50 °C
3: 100 °C
4: 150 °C
5: 200 °C
6: 250 °C
7: 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0
1
2
3
4
5
6
7

Fig. 1.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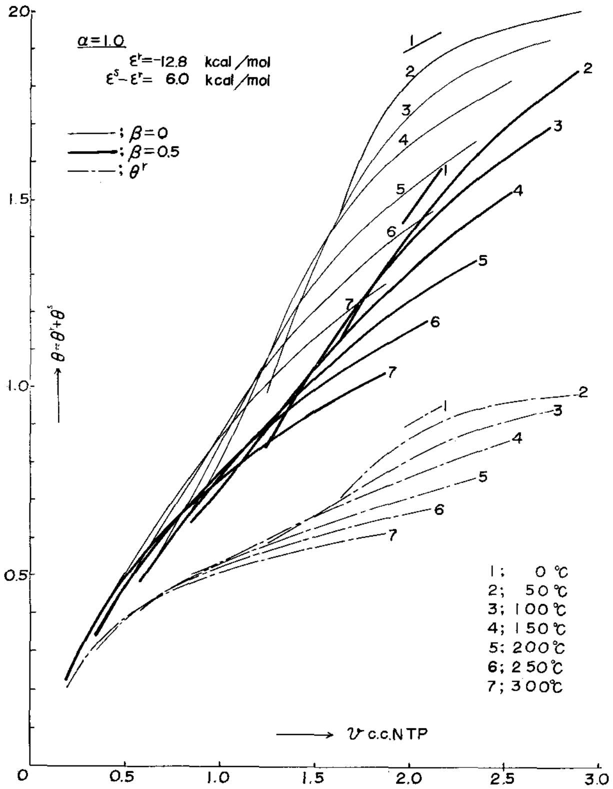
; β=0.5
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
1
2
3
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 3.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; β=0.5
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
1
2
3
4
5
6
7
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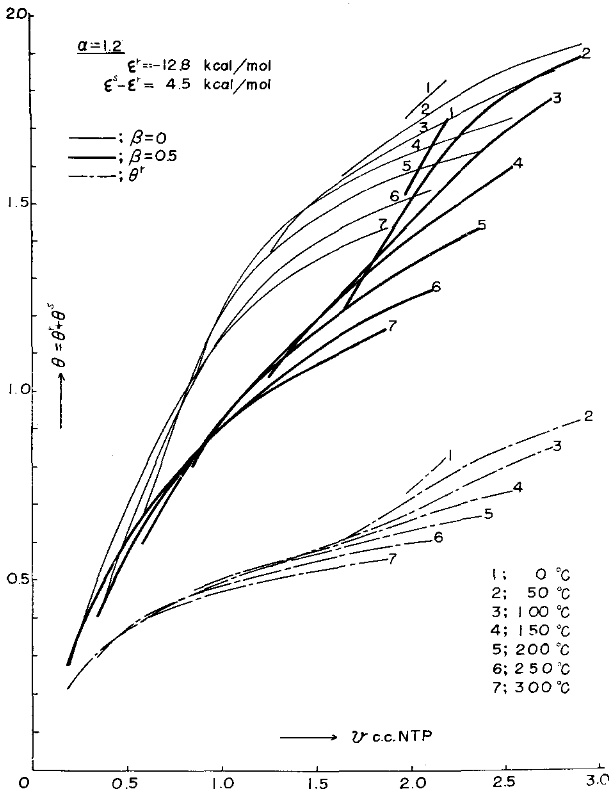
0.5
1.0
1.5
20
2.0
2.5
3.0

Fig. 4.



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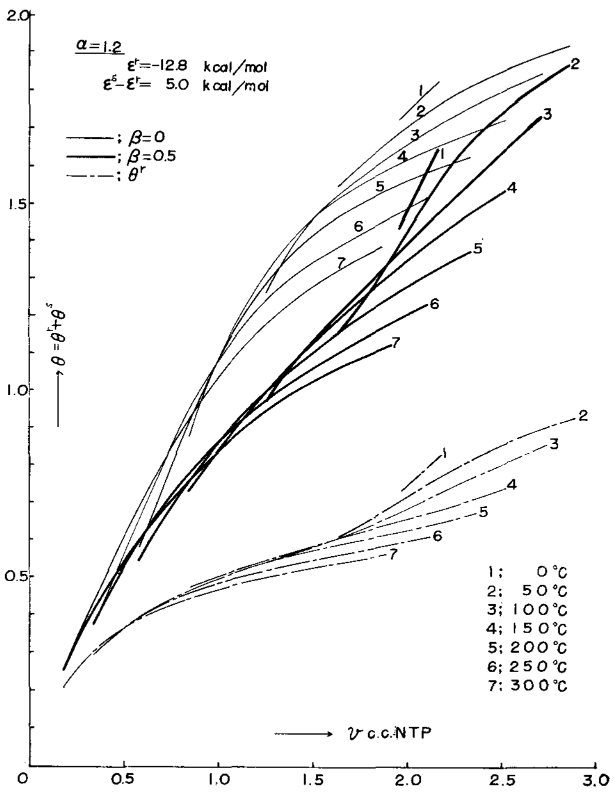
$\varepsilon^r = -12.8$ kcal/mol
$\varepsilon^s - \varepsilon^r = 4.5$ kcal/mol
; $\beta = 0$
; $\beta = 0.5$
; θ^r
$\theta = \theta^r + \theta^s$
v c.c. NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0
1
2
3
4
5
6
7

Fig. 5.



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$\varepsilon^s - \varepsilon^r = 5.0$ kcal/mol
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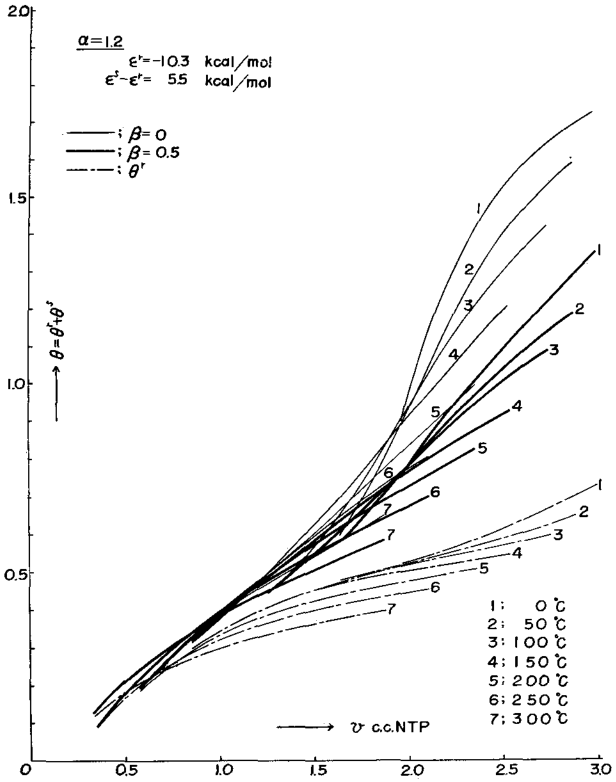
; $\beta = 0.5$
; θ^r
$\theta = \theta^r + \theta^s$
v c.c. NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0
1
2
3
4
5
6
7

Fig. 6.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ε^s-ε^r= 5.5 kcal/mol
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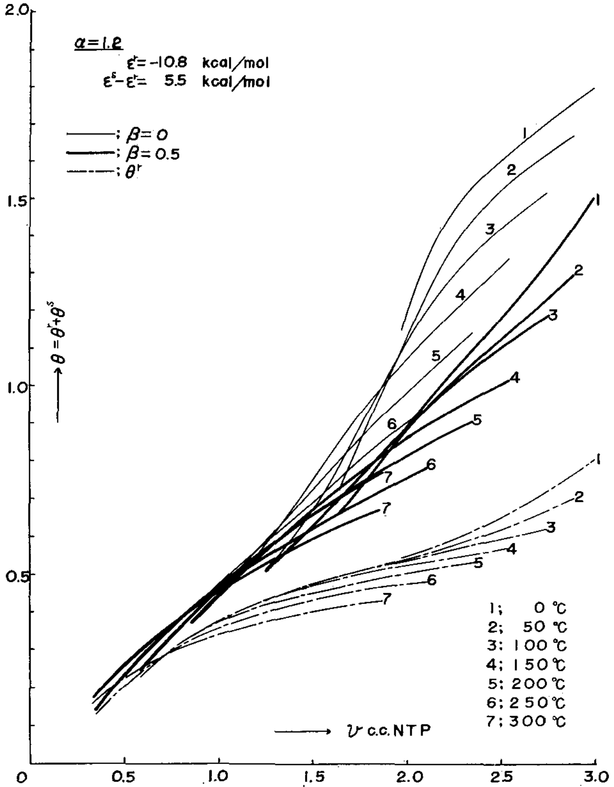
; β=0.5
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 ℃
2; 50 ℃
3; 100 ℃
4; 150 ℃
5; 200 ℃
6; 250 ℃
7; 300 ℃
1
2
3
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0

Fig. 7.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; β=0.5
; θ^r
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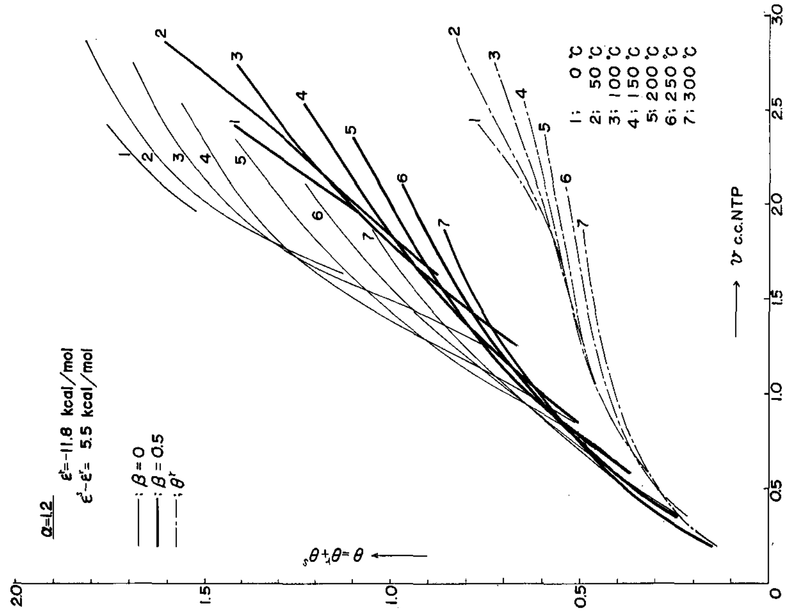
v c.c.NTP
1; 0 ℃
2; 50 ℃
3; 100 ℃
4; 150 ℃
5; 200 ℃
6; 250 ℃
7; 300 ℃
1
2
3
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0
0.5
1.0
1.5
2.0

Fig. 8.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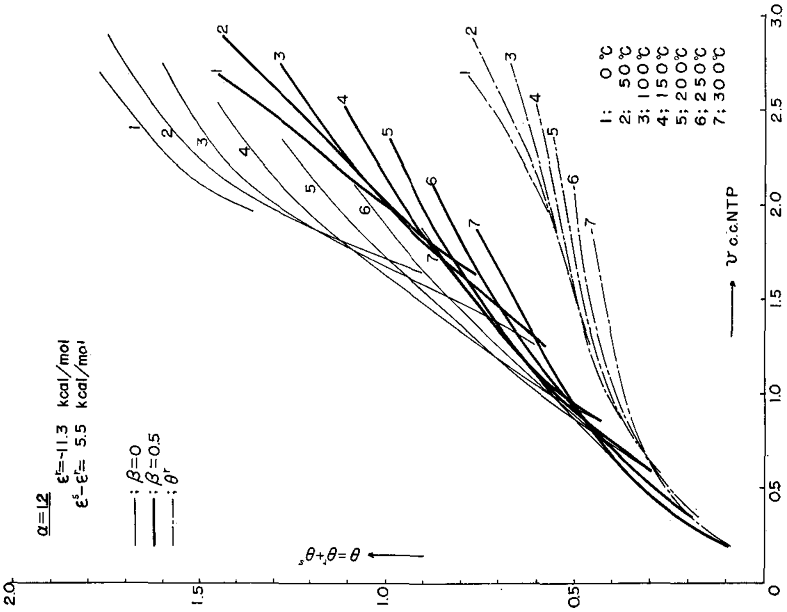
; β=0.5
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 10.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ε^s-ε^r= 5.5 kcal/mol
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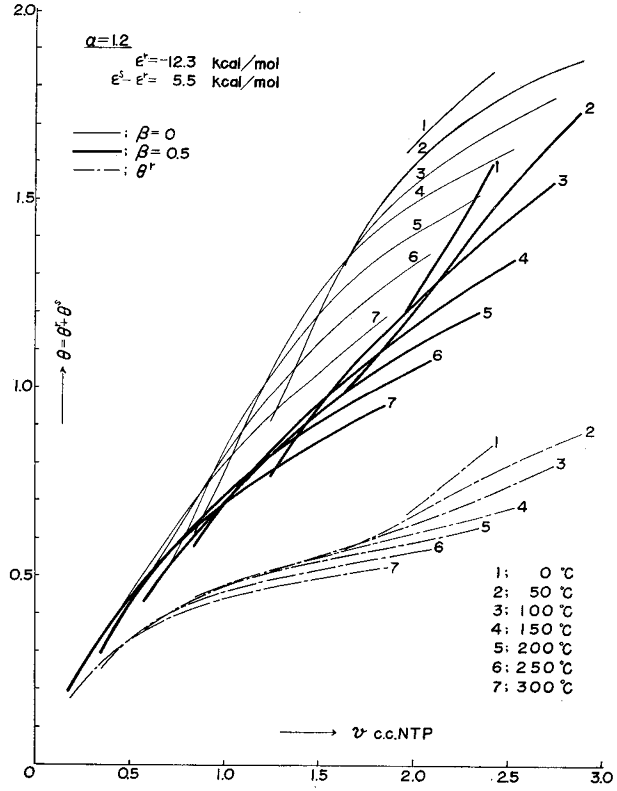
; β=0.5
; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 9.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——; β=0.5
—·—; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
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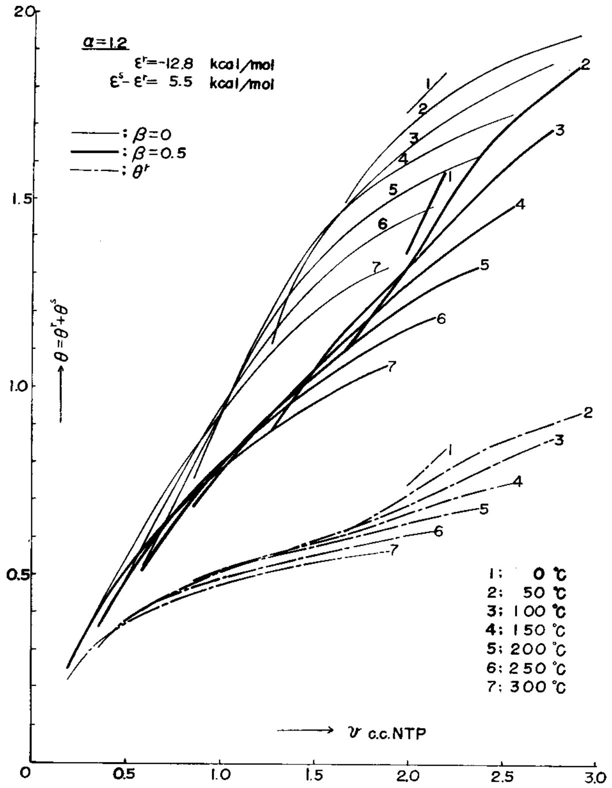
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7

Fig. 11.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ε^s-ε^r= 5.5 kcal/mol
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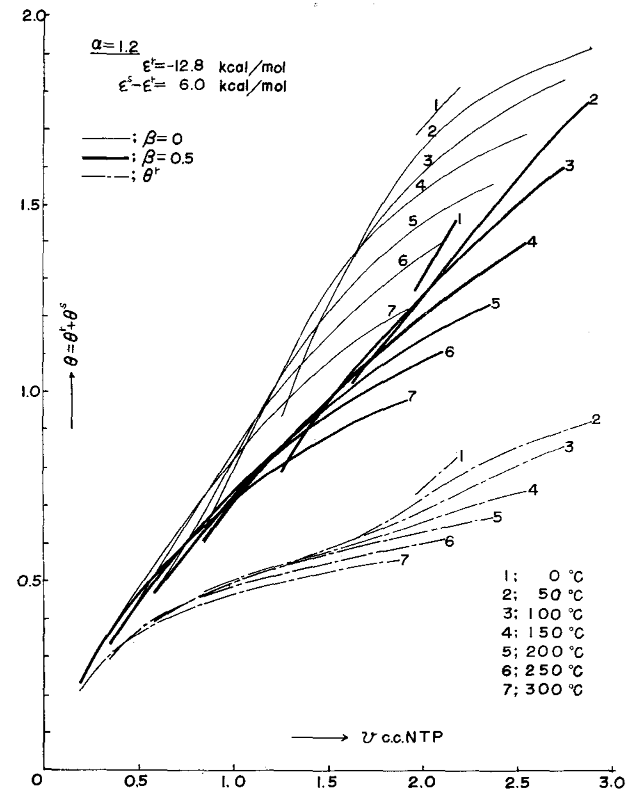
—·—; θ^r
θ=θ^r+θ^s
v c.c.NTP
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
0
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7

Fig. 12.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ε^s-ε^r= 6.0 kcal/mol
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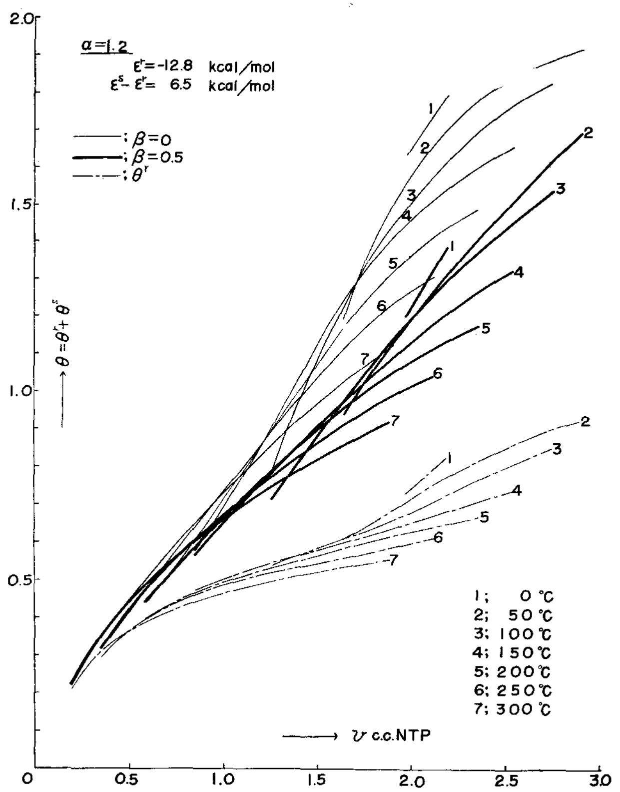
; β=0.5
; θ^r
θ=θ^r+θ^s
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
v c.c.NTP
0
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7

Fig. 13.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ε^s-ε^r= 6.5 kcal/mol
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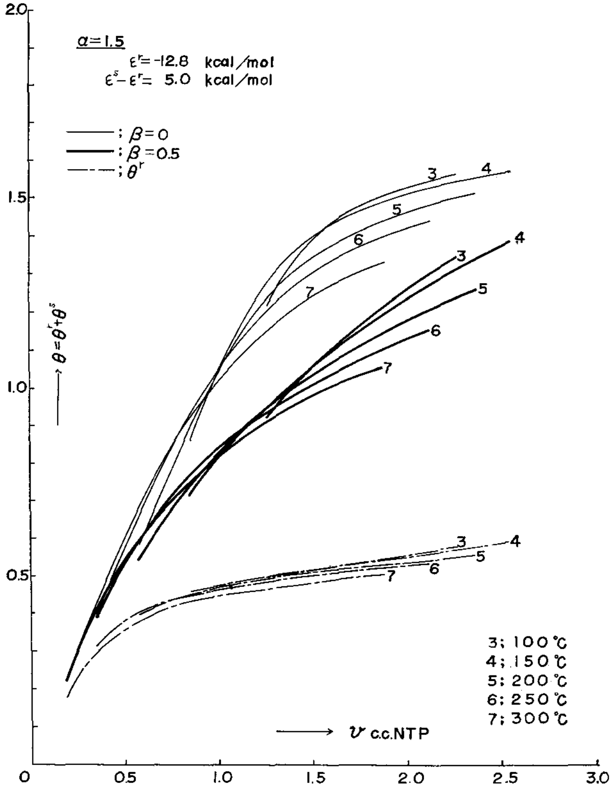
; β=0.5
; θ^r
θ=θ^r+θ^s
1; 0 °C
2; 50 °C
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
v c.c.NTP
0
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7

Fig. 14.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ε^r=−12.8 kcal/mol
ε^s−ε^r= 5.0 kcal/mol
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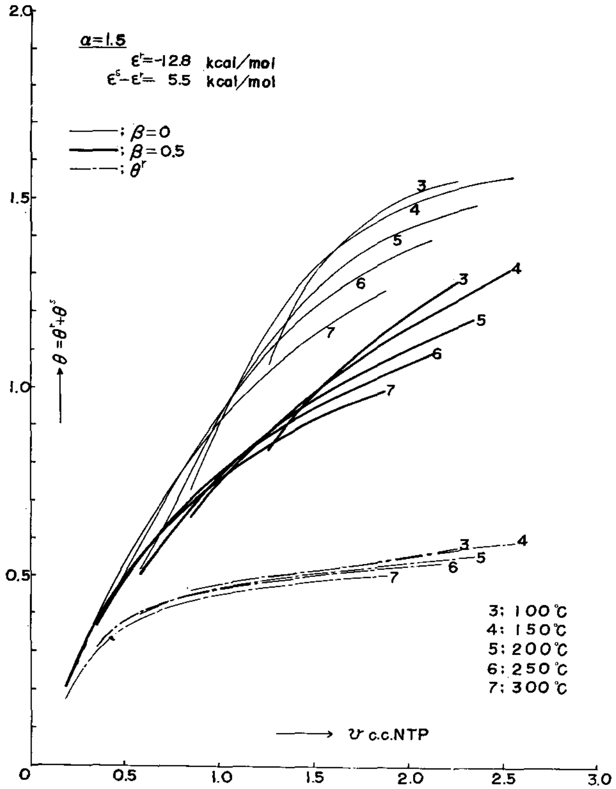
—— ; β=0.5
—·— ; θ^r
θ=θ^r+θ^s
v c.c.NTP
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
3
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 15.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ε^s−ε^r= 5.5 kcal/mol
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—— ; β=0.5
—·— ; θ^r
θ=θ^r+θ^s
v c.c.NTP
3; 100 °C
4; 150 °C
5; 200 °C
6; 250 °C
7; 300 °C
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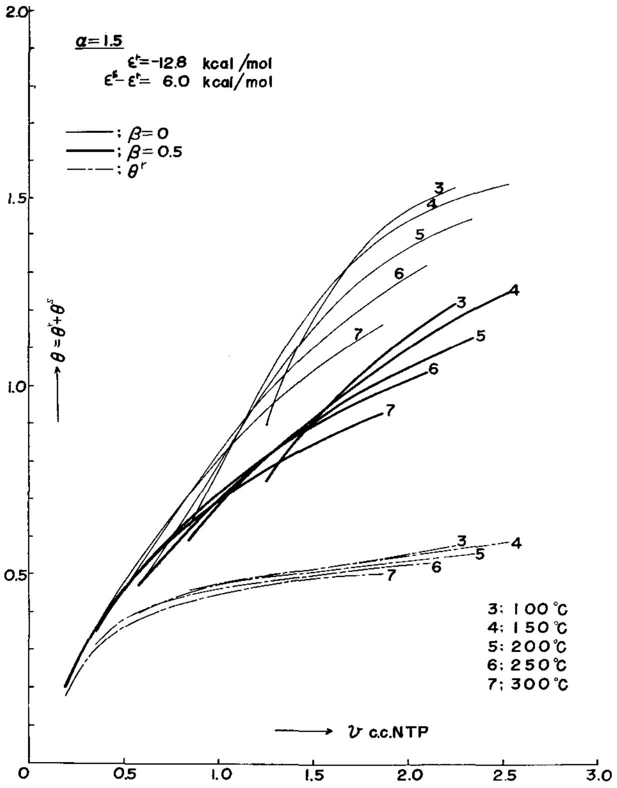
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 16.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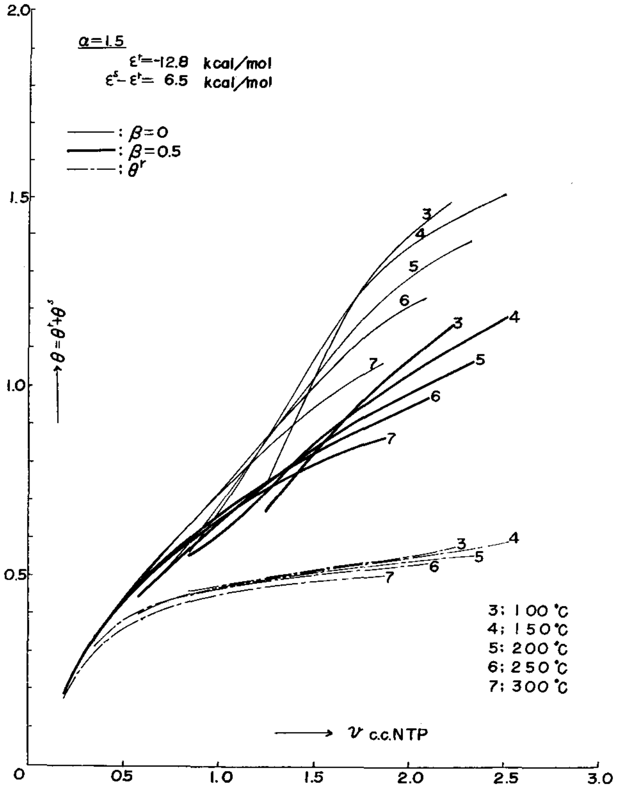
; θ^r
θ=θ^r+θ^s
3
4
5
6
7
3: 100 °C
4: 150 °C
5: 200 °C
6: 250 °C
7: 300 °C
v c.c.NTP
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 17.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3
4
5
6
7
3: 100 °C
4: 150 °C
5: 200 °C
6: 250 °C
7: 300 °C
v c.c.NTP
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 18.

$$RT^2(\partial \ln P/\partial T)_{\theta} = -2\varepsilon^{\mathrm{r}} + 7/2 \cdot RT + 2RT^2\, \partial \ln \prod_{j=1}^{3} \left\{1-\exp(-h\nu_j/kT)\right\}/\partial T,$$

ignoring s-adatoms in good agreement with the experimentally determined value 26 kcal/mol by KWAN[20]. Recently, GERMER *et al.*[15] determined the heat of adsorption on (110) lattice plane of nickel by means of low energy electron diffraction; they have estimated it at 28 kcal/mol, slightly higher than the above value.

Conclusion

The function $\theta(T, P)$ of hydrogen adatom on nickel was theoretically calculated on the basis of the lattice plane model detailed in the introduction and was adjusted to the experimental results by varying the parameters α, β, ε^{r} and ε^{s}. The congruity thus observed was found much improved as compared with the previous calculation[17], where the ratio $\gamma^{\mathrm{s}}/\gamma^{\mathrm{r}}$ was only varied with the approximation $\gamma^{\mathrm{s}}/\gamma^{\mathrm{r}} = \exp\{(\varepsilon^{\mathrm{r}}-\varepsilon^{\mathrm{s}})/kT\}$, ε^{r}, α and β being fixed at -10.3 kcal/mol, 1.0 and 0 respectively. The heat of adsorption of r-adatom is now determined at 27.0 kcal/mol for $\theta=0$ in satisfactory agreement with observation. The repulsive potential between r-adatoms is concluded appreciablly higher than that estimated as exchange repulsion between them in conformity with the prediction by one of the present authors[9],[10]. The area of the (110) lattice plane is approximately one third of the BET area. It is expected from the above result that the congruity would be further improved by varying α more finely and allowing for adsorption on other lattice planes.

The present authors wish to thank Mrs. R. WAKE, Mr. T. NAGAYAMA, Miss T. KAWAI and Miss A. HIRATUKA for their sincere assistances.

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