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# ENTROPY OF HYDROGEN ADATOM ON NICKEL

By

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## Summary

Entropy  $S^H$  of hydrogen adatom on a metallic adsorbent was statistical mechanically calculated on the basis of the previous conclusion that there exist two kinds of hydrogen adatoms, *i.e.* r-adatom and s-adatom, and compared with that derived thermodynamically from observed adsorption isotherms. 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 in the adsorbent metal but situated close to its electronic surface inside it. Repulsion between r-adatoms was taken into account, while that between s-adatoms each other and r-adatoms ignored in the present treatment idealizing the theoretical conclusion. The above calculation was conducted first with the homogeneous model, which is specified in accordance with previous theoretical and experimental inferences as follows; the adsorption occurs practically exclusively on (110)-lattice plane of f.c.c. crystal of nickel, there exists each one site for an r-adatom and an s-adatom per one metal atom on the lattice plane, the sites for r-adatoms and those for s-adatoms are respectively physically identical with each other, and r-adatom conducts a valence vibration normal to the electronic surface, and bending vibrations parallel to it, while s-adatom conducts similarly valence vibration normal to the electronic surface, but practically two dimensional translation parallel to it.

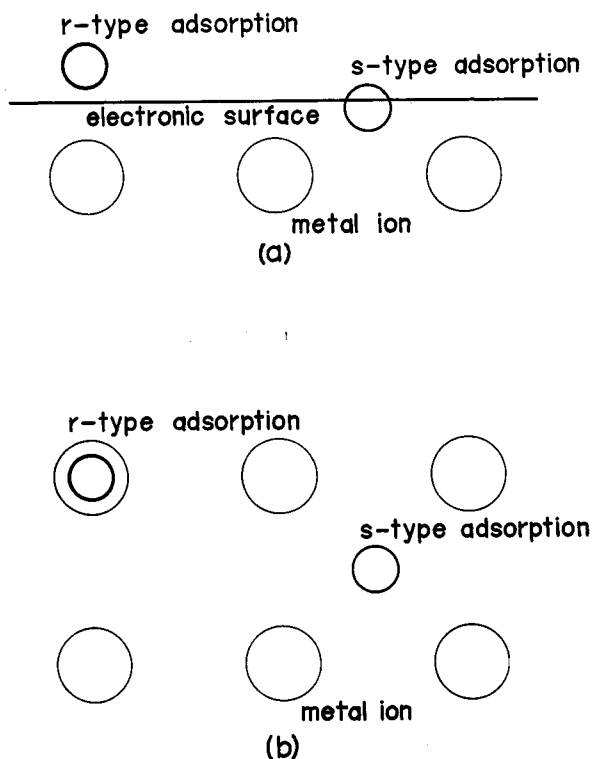
The statistical mechanical value of  $S^H$  thus calculated was found to reproduce the general features of variation of its thermodynamical value with increase of coverage except at extremely low coverage, where the latter fell appreciably below the former. The latter aspect as well as the extraordinarily high heat of adsorption observed at extremely low coverage was semiquantitatively accounted for on the basis of a revised model consisting of a vast majority of sites identical with those of the homogeneous model mentioned above and a minority of sites formed by lattice imperfections, *i.e.* steps, kinks, defects and grain boundaries, which accommodate s-adatoms alone with much lower energy than that of r- or s-adatom on the majority of sites.

## Introduction

Adsorption of hydrogen on nickel was extensively observed by KINUYAMA and KWAN<sup>1)</sup> and recently by RIDEAL and SWEET<sup>2)</sup>. The latter group of authors deduced from their experimental result the entropy of hydrogen atom, which increased steeply with increase of coverage at its higher value and hence suggested two dimensional translation as conducted by hydrogen adatoms at higher coverage.

It is generally admitted that hydrogen is dissociatively adsorbed to form statistically independent adatoms. One of the present authors has quantum mechanically deduced<sup>3,4)</sup> the existence of the two sorts of hydrogen adatoms, *i.e.* r-adatoms and s-adatoms, and demonstrated it with reference to experimental results on the electric conductivity<sup>5)</sup>, the work function of adsorbent<sup>6)</sup>, and the infrared absorption of adatoms<sup>7)</sup>. The r-adatom is an adatom of ordinary sense, *i.e.* that lying outside the electronic surface of adsorbent forming more or less polarized covalent bond with the latter. The s-adatom is a sort of dissolved atom in the adsorbent but lying close to the electronic surface inside it.

On this basis the present authors have discussed<sup>8)</sup> the adsorbed state of hydrogen on metallic adsorbent, referring preliminarily to the entropy of hydrogen adatom. This preliminary treatment of entropy of adatoms is now developed in the present paper on the basis of the following theoretical



**Fig. 1.** Two types of adsorption. The r-type adatom is slightly negatively polarized, and its equilibrium position right above a metal ion at *ca.* 1Å outside the electronic surface of the metal. The equilibrium position of s-type adsorption is interstitial and *ca.* 0.5Å inside the electronic surface.

inferences<sup>3,5)</sup>.

I) The equilibrium position of r-adatom is situated right above a metal atom on a lattice plane exposed at the surface of metallic adsorbent, *ca.* 1Å outside its electronic surface<sup>6)</sup>, whereas that of s-adatom is in an interstitial surface site, *ca.* 0.5Å inside the electronic surface<sup>6)</sup> as seen from its elevation (a) and plan (b) in Fig. 1. It follows from this inferences that the sites of r-adatoms and those of s-adatoms on a lattice plane of a sufficient magnitude without lattice imperfections, *i.e.* steps, kinds, defects and grain boundaries, are respectively practically physically identical with each other and there exists each one site for r- and s-adatom per one metal atom on the lattice plane.

II) The r-adatoms repulse each other more intensely than estimated quantum mechanically between hydrogen atoms unbonded with each other<sup>4,6)</sup>, while s-adatoms much weaker, if at all, each other and r-adatoms. This conclusion is idealized in the present paper that s-adatoms do not interact neither with each other nor with r-adatoms, so that the two sorts of adatoms occupy respectively appropriate sites independent of each other. The r-adatom specified in the above inferences is essentially the same as adatom hitherto conceived regardless of the dual state of adatom<sup>7,8)</sup>.

III) Both r- and s-adatom on the sites specified in I) vibrate normal to the electronic surface with frequencies comparable with those of valence vibrations; parallel to the electronic surface, r-adatom vibrates with frequencies comparable with those of bending vibrations, whereas s-adatom conducts practically two dimensional translational motion parallel to the surface<sup>5,6)</sup>.

IV) Adsorption both of r- and s-adatoms occurs practically exclusively on (110)-lattice plane in case of f.c.c. crystal of nickel apart from the lattice imperfections<sup>7,9,10)\*</sup>.

The entropy  $S^H$  of adatom or precisely its partial molal entropy is now statistical mechanically formulated and its course with increase of coverage is compared with that of  $S^H$  derived thermodynamically from observed adsorption isotherm.

The theoretical formulation is carried out first on the base of lattice plane without imperfections, as called the homogeneous model in what follows. The statistical mechanical value was found approximately to reproduce the thermodynamical value except at extremely low coverage, where the latter value was found to run appreciably lower than the former. The latter discrepancy was accounted for by revising the model to allow for the lattice imperfections.

\*) GERMER and MACRAE<sup>10)</sup> concluded that the adsorption process causes a reconstructive rearrangement of nickel atoms. Their conclusions disagreeing in this point with those basic to the present paper will be discussed elsewhere in detail.

It is a matter of course that r- and s-adatoms are in equilibrium with each other in case of adsorption equilibrium as dealt with exclusively in the present paper.

### § 1. Entropy of Hydrogen Adatom

The entropy  $S^H$  of hydrogen adatom H, is expressed as

$$S^H = -(\partial \mu^H / \partial T)_v, \quad (1)$$

irrespective of r- or s-state of H, where  $\mu^H$  is the chemical potential of the adatom,  $T$  the absolute temperature and suffix  $v$ , representing adsorbed quantity, indicates the isosteric differentiation.

The chemical potential  $\mu^H$  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 make  $C^H$ , *i. e.*

$$p^H = \Omega C^H / \Omega C, \quad (2)$$

as

$$\mu^H = -RT \ln p^H, \quad (3)$$

where  $\Omega C$  or  $\Omega C^H$  is the partition function of  $C$  or  $C^H$  respectively. Eq. (3) follows from the definition of the chemical potential and a property of partition function that  $-kT \ln \Omega C$  or  $-kT \ln \Omega C^H$  behaves as the free energy of  $C$  or  $C^H$  respectively.

We define further<sup>7,11)</sup>

$$q^H = \Omega C_{\sigma(H)}^H / \Omega C_{\sigma(0)}, \quad (4)$$

where  $\Omega C_{\sigma(H)}^H$  is the partition function of the particular state  $C_{\sigma(H)}^H$  of  $C^H$  that a definite site  $\sigma$  is occupied by an adatom with certainty and  $\Omega C_{\sigma(0)}$  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  $-kT \ln q^H$  is the free energy increase of the relevant macroscopic system caused by addition of an adatom to a definite, preliminarily evacuated site  $\sigma$ .

The ratio of  $q^H$  to  $p^H$  is according to (2) and (4)

$$\frac{q^H}{p^H} = \frac{\Omega C_{\sigma(H)}^H / \Omega C_{\sigma(0)}}{\Omega C^H / \Omega C}.$$

It follows from another property of partition functions that the fraction  $\Omega C_{\sigma(H)}^H / \Omega C^H$  or  $\Omega C_{\sigma(0)} / \Omega C$  equals the probability, with which the definite site  $\sigma$  is occupied by H or unoccupied respectively. Ignoring the effect of the addition of a single adatom to the macroscopic system  $C$  on the probability, we have

$$\Omega C_{\sigma(H)}^H / \Omega C^H + \Omega C_{\sigma(0)} / \Omega C = 1,$$

provided that  $\sigma$  is either occupied by one H or unoccupied exclusively. Denoting  $\Omega C_{\sigma(H)}^H / \Omega C^H$  by  $\theta^H$  we have from the above two equations<sup>11)</sup>

$$q^H / p^H = \theta^H / (1 - \theta^H). \quad (5)$$

Eq. (5) is now written for r- and s-adatom individually, noting that there is no distinction between  $p^r$  and  $p^s$ , *i. e.*  $p^H$  written for r- or s-adatom severally, as follows from the equilibrium between them mentioned in the introduction and (3), *i. e.*

$$q^r / p^H = \theta^r / (1 - \theta^r), \quad (6. r)$$

$$q^s / p^H = \theta^s / (1 - \theta^s), \quad (6. s)$$

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

$$\theta \equiv \theta^r + \theta^s \quad (7)$$

as a measure of adsorbed amount, which attains 2 at full coverage.

Eqs. (1) and (3) leads to the expression of  $S_I^H$ , *i. e.*

$$S_I^H = (\partial RT \ln p^H / \partial T)_\theta, \quad (8)$$

where suffix I signifies the quantity statistical mechanically calculated on the basis of the homogeneous model and suffix  $v$  is replaced by  $\theta$ . Eq. (8) is developed according to (6) as shown in Appendix 1, as

$$S_I^H = \frac{\theta^r (1 - \theta^r) S^r + \theta^s (1 - \theta^s) S^s}{\theta^r (1 - \theta^r) + \theta^s (1 - \theta^s)} \quad (9. S)$$

where

$$S^r = R(\partial T \ln q^r / \partial T)_\theta + R \ln \{(1 - \theta^r) / \theta^r\} \quad (9. r)$$

and

$$S^s = R(\partial T \ln q^s / \partial T)_\theta + R \ln \{(1 - \theta^s) / \theta^s\}. \quad (9. s)$$

The  $S_I^H$  is obtained as a function of  $T$  and  $\theta$  according to (9), by determining  $q^r$  and  $q^s$ , as respective functions of  $T$  and  $\theta$ .

## § 2. Formulation of $q^r$

The  $q^r$  is the special case of  $q^H$  defined by (4), hence  $-kT \ln q^r$  is the free energy increase of  $C$  caused by addition of r-adatom to a definite,

preliminarily evacuated site  $\sigma$  on  $C$ . The relevant free energy increase  $-RT \ln q^r$  is expressed as

$$-RT \ln q^r = -RT \ln q_0^r + W, \quad (10)$$

where  $-RT \ln q_0^r$  is that in the absence of interaction with the surrounding r-adatoms and  $W$  is the rest of the free energy increase due to the repulsion, which will be called the *free energy of repulsion*. The  $q_0^r$  in (10) is identified by definition with the particular case of  $q^r$ , where  $C$  is a bare adsorbent  $C_0$ , hence

$$q_0^r = \Omega C_{\sigma(r),0}^r / \Omega C_0, \quad (11)$$

where  $\Omega C_0$  is the partition function of  $C_0$  and  $\Omega C_{\sigma(r),0}^r$  is that of  $C_{\sigma(r),0}^r$  formed by adding one r-adatom to  $C_0$  at a definite site  $\sigma$ . The  $\Omega C_{\sigma(r),0}^r$  is now calculated under the assumption that the lattice vibrations of the adsorbent proper and those of the r-adatom are hardly coupled together and that the former vibrations are not practically affected by the r-adatom. These approximations appear to be close enough, since the maximum frequency  $150 \text{ cm}^{-1}$  deduced from the DEBYE temperature of the adsorbent nickel is sufficiently low as compared with the estimated lowest frequency<sup>\*)</sup>  $417 \text{ cm}^{-1}$  of the r-adatom and the approximately covalent nature of the bond of r-adatom<sup>4)</sup> would scarcely vary the number of free electrons in the adsorbent proper to affect its elastic property, hence its lattice vibrations. The free energy  $-kT \ln \Omega C_{\sigma(r),0}^r$  consists now of three parts *i.e.* the partition function  $-kT \ln \Omega C_0$  of  $C$  proper without influence of the r-adatom, that  $-kT \ln \Omega r$  of the r-adatom in the potential field of  $C_0$  and the potential  $\epsilon_0^r$  at the equilibrium position of the adatom in the field, *i.e.*

$$-kT \ln \Omega C_{\sigma(r),0}^r = -kT \ln \Omega C_0 - kT \ln \Omega r + \epsilon_0^r,$$

hence

$$\Omega C_{\sigma(r),0}^r = \Omega C_0 \cdot \Omega r \cdot \exp(-\epsilon_0^r/kT). \quad (12)$$

The factor  $\Omega r$  in the above equation is developed in accordance with III) in the introduction as<sup>7)</sup>

$$\Omega r = \prod_{j=1}^3 \exp\left(-\frac{h\nu_j}{2kT}\right) \left\{1 - \exp\left(-\frac{h\nu_j}{kT}\right)\right\}^{-1} \quad (13)$$

as previously deduced from the above mentioned potential field of r-adatom<sup>7)</sup>, where  $j$  numbers the three normal vibrations mentioned in III) in the introduction.

Eqs. (11), (12) and (13) lead to the equation of  $q_0^r$ , *i.e.*

\*) Cf. (30. r).

$$q^r = \prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \exp\left(-\frac{\varepsilon^r}{kT}\right), \quad (14. q)$$

where

$$\varepsilon^r = \varepsilon_0^r + \sum_{j=1}^3 h\nu_j/2 \quad (14. \varepsilon)$$

is the energy of ground state of r-atom.

The formulation of  $q^r$  is yet to be completed with that of  $W$  in (10).

### § 3. Free Energy of Repulsion $W$

The  $q^r$  has been formulated in previous papers<sup>11,12,13)</sup> in different degrees of approximations, which implies that of  $W$  in the appropriate approximations. The first, second and third approximations take into account the repulsions of neighbouring r-atoms as far as the first, second and third nearest ones respectively in extension of the BETHE-PEIERLS method<sup>14)</sup>. It has been found that the adsorption isotherm of the second approximation thus obtained is close enough to that of the third approximation, which is however extremely laborious. The  $W$  of the second approximation is formulated as shown in Appendix 2 as a sufficiently accurate one on the ground of the above result on the basis of the homogeneous model of (110)-lattice plane, which predominantly adsorb hydrogen according to IV) in the introduction. The  $W$  is thus given as a function  $W(T, r)$  of  $T$  and  $r$ , *i.e.*

$$r = q^r/p^H \quad (15)$$

by eliminating  $\eta_I$  and  $\eta_{II}$  between the three simultaneous equations

$$W = 2RT \ln \left\{ (1 + r\eta_I) (1 + r\eta_{II}) / (1 + r\eta_I \xi_I) (1 + r\eta_{II} \xi_{II}) \right\} \quad (16. a)$$

and

$$\begin{aligned} (1 + r\eta_I)^2 (1 + r\eta_{II})^2 &= (1 + r\eta_I) (1 + r\eta_{II})^2 + r (1 + r\eta_I \xi_I) (1 + r\eta_{II} \xi_{II})^2 \\ &= (1 + r\eta_I)^2 (1 + r\eta_{II}) + r (1 + r\eta_I \xi_I)^2 (1 + r\eta_{II} \xi_{II}), \end{aligned} \quad (16. b)$$

where

$$\xi_I = \exp(-R_I/kT) \quad \text{or} \quad \xi_{II} = \exp(-R_{II}/kT), \quad (17. I), (17. II)$$

is the BOLTZMANN factor of the free energy increase due to repulsion  $R_I$  or  $R_{II}$  respectively identified with the repulsive potential between two r-atoms each at the equilibrium position and at the first or the second nearest distance on (110)-lattice plane, *i.e.* 2.49 or 3.52 Å respectively.

### § 4. Formulation of $q^s$

Since the repulsion between s-atoms is ignored according to II) in the



introduction,  $q^s$  is identified, similar to  $q_o^r$  of (11), with that of adding an s-adatom on a bare adsorbent  $C_o$ , as

$$q^s = \Omega C_{\sigma(s),0}^s / \Omega C_o \quad (18)$$

where  $\Omega C_{\sigma(s),0}^s$  is the partition function of the adsorbent with a single s-adatom on a definite site  $\sigma$ . The  $\Omega C_{\sigma(s),0}^s$  is developed similar to  $\Omega C_{\sigma(r),0}^r$  of (12), as

$$\Omega C_{\sigma(s),0}^s = \Omega C_o \cdot \Omega s \cdot \exp(-\epsilon_o^s/kT), \quad (19)$$

where  $\Omega s$  or  $\epsilon_o^s$  is the partition function or the minimum potential energy of s-adatom in the potential field of  $C_o$ , which corresponds to  $\Omega r$  or  $\epsilon_o^r$  in (12) respectively. The above expression rests upon the assumption similar to that underlying  $\Omega C_{\sigma(r),0}^r$ , that there exists practically no coupling between the lattice vibration of the adsorbent proper and that of adsorbate, and the former is hardly affected by the s-adatom.

The  $\Omega s$  is developed in accordance with (III) in the introduction, as

$$\Omega s = A \frac{2\pi mkT}{h^2} \exp\left(-\frac{h\nu}{2kT}\right) \left\{1 - \exp\left(-\frac{h\nu}{kT}\right)\right\}^{-1}, \quad (20)$$

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

We have from (18), (19) and (20)

$$q^s = A \frac{2\pi mkT}{h^2} \exp\left(-\frac{\epsilon^s}{kT}\right) \left\{1 - \exp\left(-\frac{h\nu}{kT}\right)\right\}^{-1}, \quad (21. a)$$

where

$$\epsilon^s = \epsilon_o^s + h\nu/2 \quad (21. b)$$

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

The  $A$  in (21. a) is estimated as follows. Let  $\theta^s$  be small enough for their mutual interference to be practically ignorable with regard to the two dimensional translation as in the case of attenuated gas.  $\Omega C$  of  $C$  retaining  $N^s-1$  s-adatoms is given as

$$\Omega C = \Omega C_o (Q^s)^{N^s-1} / (N^s-1)!, \quad (22. a)$$

where

$$Q^s = [A] \frac{2\pi mkT}{h^2} \exp\left(-\frac{\epsilon^s}{kT}\right) \left\{1 - \exp\left(-\frac{h\nu}{kT}\right)\right\}^{-1}, \quad (22. b)$$

and  $[A]$  is the whole area of the electronic surface of the adsorbent; the factor  $(N^s-1)!$  removes the separate countings in the partition function of the

states, which differ solely in the interchange of identical particles. The partition function  $\Omega C^s$  of  $C^s$  formed by adding another s-adatom to  $C$  is given similar to  $\Omega C$  as

$$\Omega C^s = \Omega C_0 (Q^s)^{N^s} / N^s! \quad (23)$$

The  $p^H$  is now expressed with special reference to s-adatom by (22. a), (23) and (2) as

$$p^H = Q^s / N^s$$

or according to (6. s), neglecting  $\theta^s$  as compared with unity

$$q^s / \theta^s = Q^s / N^s.$$

Substituting  $q^s$  from (21. a) and  $Q^s$  from (22. b) into the above equation, we have

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

where  $N^s / \theta^s$  equals the total number of sites, hence the number of surface metal atoms of the homogeneous model according to I) in the introduction.  $A$  is now the surface area allotted to a metal atom, which amounts to *ca.*  $10 \text{ \AA}^2$  for (110)-lattice plane, *i. e.*

$$A = 10 \text{ \AA}^2. \quad (24)$$

It may be noted that the conclusion (24), which is applied throughout the present treatment, rests upon the assumption of the sparse coverage by s-adatoms.

### § 5. $(\partial RT \ln q^r / \partial T)_\theta$

The partial differential coefficient  $(\partial RT \ln q^r / \partial T)_\theta$  in (9. r) is developed according to (10) and (14. q) as

$$(\partial RT \ln q^r / \partial T)_\theta = dRT \ln Q_v^r / dT - (\partial W / \partial T)_\theta, \quad (25. a)$$

where

$$Q_v^r = \prod_{j=1}^3 \left\{ 1 - \exp \left( - \frac{h\nu_j}{kT} \right) \right\}^{-1} \quad (25. b)$$

is the vibrational partition function of r-adatom comprised in (14. q) and is a sole function of temperature.  $W$  in (25. a) is now a function of  $T$  and  $r$  according to (16) and (17) with parameters  $R_I$  and  $R_{II}$ , *i. e.*

$$W = W(T, r; R_I, R_{II}), \quad (26. a)$$

where  $r$  is connected with  $\theta^r$  by (6. r), (10) and (15) as

$$r \exp(-W/RT) = \theta^r / (1 - \theta^r). \quad (26. b)$$

It follows from (26. a) and (26. b) that  $W$  is given as a function of  $T$  and  $\theta^r$  with parameters  $R_I$  and  $R_{II}$ , i.e.

$$W = W(T, \theta^r; R_I, R_{II}), \quad (26. c)$$

hence we have

$$\left(\frac{\partial W}{\partial T}\right)_\theta = \left(\frac{\partial W}{\partial T}\right)_{\theta^r} + \left(\frac{\partial W}{\partial \theta^r}\right)_T \left(\frac{\partial \theta^r}{\partial T}\right)_\theta. \quad (27)$$

Fig. 2 shows  $W(T, \theta^r)$  of the second approximation as calculated in extension of the previous work<sup>12)\*</sup>.

The differential coefficients  $(\partial W/\partial T)_{\theta^r}$  and  $(\partial W/\partial \theta^r)_T$  in (27) are determined from the function  $W = W(T, \theta^r)$  on the base of parameters  $R_I$  and  $R_{II}$  in (17), whose values are given in § 6. The  $(\partial \theta^r/\partial T)_\theta$  is determined as follows. We have from (6) and (10)

$$\ln q_0^r - W/RT - \ln q^s = \ln \frac{\theta^r}{1 - \theta^r} - \ln \frac{\theta^s}{1 - \theta^s},$$

where both  $q_0^r$  and  $q^s$  are functions solely of temperature respectively according to (14. q) and (21. a). Differentiating the above equation as

$$\begin{aligned} \frac{d \ln q_0^r}{dT} dT + \frac{W}{RT^2} dT - \frac{(\partial W/\partial T)_{\theta^r}}{RT} dT - \frac{(\partial W/\partial \theta^r)_T}{RT} d\theta^r \\ - \frac{d \ln q^s}{dT} dT = \frac{d\theta^r}{\theta^r(1 - \theta^r)} - \frac{d\theta^s}{\theta^s(1 - \theta^s)}, \end{aligned}$$

and noting the condition of constant  $\theta$  in accordance with (7), i.e.

$$d\theta^r + d\theta^s = 0,$$

we have

$$\left(\frac{\partial \theta^r}{\partial T}\right)_\theta = \left\{ \frac{d \ln(q_0^r/q^s)}{dT} + \frac{W}{RT^2} - \frac{(\partial W/\partial T)_{\theta^r}}{RT} \right\} / \left\{ \frac{1}{\theta^r(1 - \theta^r)} + \frac{1}{\theta^s(1 - \theta^s)} + \frac{(\partial W/\partial \theta^r)_T}{RT} \right\}. \quad (28)$$

The  $(\partial \theta^r/\partial T)_\theta$  is determined computing  $d \ln(q_0^r/q^s)/dT$  by (14. q) and (21. a) on the base of parameters  $\nu_1, \nu_2, \nu_3, \nu, \varepsilon^r$  and  $\varepsilon^s$  given in § 6 and by substituting  $(\partial W/\partial T)_{\theta^r}$  and  $(\partial W/\partial \theta^r)_T$  evaluated as above into (28), hence  $(\partial W/\partial T)_\theta$  by (27). The negative of  $(\partial W/\partial T)_\theta$  will be called the *entropy of repulsion* in what follows.

## § 6. Evaluation of Parameters in $q^r$ and $q^s$ .

The  $q^r$  is given as a function of  $r$  and  $T$  according to (10), (14. q) and

\*) Cf. § 7.

(26. a) with parameters  $\nu_1, \nu_2, \nu_3, \epsilon^r, R_I$  and  $R_{II}$ , *i.e.*

$$q^r = q^r(T, \gamma; \nu_1, \nu_2, \nu_3, \epsilon^r, R_I, R_{II}) \quad (29. r)$$

and  $q^s$  similarly as

$$q^s = q^s(T; m, \nu, \epsilon^s). \quad (29. s)$$

The  $p^H$  in (6) is according to (15) and (14. q) a function of  $T$  and  $\gamma$  with parameters  $\nu_1, \nu_2, \nu_3$  and  $\epsilon^r$  *i.e.*

$$p^H = p^H(T, \gamma; \nu_1, \nu_2, \nu_3, \epsilon^r). \quad (29. p)$$

The parameters implied in (29) are  $\nu_1, \nu_2, \nu_3, \nu, \epsilon^r, \epsilon^s, m, R_I$  and  $R_{II}$ , which are all that required for the evaluation of  $q^r$  and  $q^s$ . The frequencies  $\nu_1, \nu_2$  and  $\nu_3$  have previously been estimated with special reference to (110)-lattice plane of nickel as<sup>7)</sup>

$$\tilde{\nu}_1 = 419 \text{ cm}^{-1}, \quad \tilde{\nu}_2 = 479 \text{ cm}^{-1}, \quad \tilde{\nu}_3 = 1900 \text{ cm}^{-1}, \quad (30. r)$$

and  $\nu$  as<sup>4,6)</sup>

$$\tilde{\nu} = 1000 \text{ cm}^{-1}. \quad (30. s)$$

The estimated values of (30) will be used as they are, since, insofar as they are so hard, the inaccuracies, if any, would hardly effect the numerical values of  $q^r$  and  $q^s$  as seen in (14. q) and (21. a). The effective mass  $m$  is simply identified with the mass of proton.

The  $R_I$  and  $R_{II}$  were previously estimated at 0.1019 *ev* and 0.0134 *ev* respectively as the quantum mechanical repulsions between unbonded s-electrons of the relevant r-adatoms<sup>7)</sup>. Recent theoretical investigation by one of the present authors<sup>3,4)</sup> has shown that the repulsive potential must be considerably greater than the repulsion of the above amount<sup>7)</sup>, although not estimated with sufficient accuracy. The  $R_I$  and  $R_{II}$  are assumed at the moment respectively proportional to the above values, *i.e.*

$$R_I = 0.1019 \alpha \text{ ev}, \quad R_{II} = 0.0134 \alpha \text{ ev} \quad (31. I), (31. II)$$

introducing a single parameter  $\alpha$  in place of the two, *i.e.*  $R_I$  and  $R_{II}$ .

The theoretical investigation<sup>4)</sup> has shown further that  $\epsilon^r$  must be lower than  $\epsilon^s$  by a few tenth of an electron volt but neither of them has been determined with sufficient accuracy. These quantities have been determined together with  $\alpha$  in (31) by adjusting them to observed adsorption isotherms by the following procedure<sup>15)</sup>. Eliminating  $q^r, q^s, \gamma, \theta^s$  and  $\theta^r$  from six equations of (6), (7) and (29), we have

$$f(p^H, T, \theta; \alpha, \epsilon^r, \epsilon^s) = 0, \quad (32)$$

where  $\alpha$ ,  $\epsilon^r$  and  $\epsilon^s$  are parameters yet to be determined. We have on the other hand for adsorption isotherms,

$$\mu^H = \mu^{H_2}/2 \quad (33. a)$$

or

$$p^H = \sqrt{p^{H_2}} \quad (33. b)$$

in accordance with (3) and the similar relation  $\mu^{H_2} = RT \ln p^{H_2}$ . The  $p^{H_2}$  is expressed on the other hand as<sup>(1)</sup>

$$p^{H_2} = Q^{H_2}/N^{H_2}, \quad (34. p)$$

where

$$Q^{H_2} = \frac{(2\pi m^{H_2} kT)^{3/2}}{h^3} \cdot \frac{4\pi^2 I kT}{h^2} \quad (34. Q)$$

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 molecules in adsorption equilibrium and  $m^{H_2}$  or  $I$  is the mass or the moment of inertia of the molecule; the energy of the ground state is taken zero, to which the values of  $\epsilon^r$  and  $\epsilon^s$  are referred.  $N^{H_2}$  is connected with hydrogen pressure  $P$  in mmHg as

$$P = kTN^{H_2}/980.5 \times 1.360. \quad (35)$$

Eliminating  $p^{H_2}$ ,  $N^{H_2}$  and  $Q^{H_2}$  from the four equations (33. b), (34) and (35), we have

$$p^H = \left\{ \frac{(2\pi m^{H_2} kT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} \frac{kT}{980.5 \times 1.360 P} \right\}^{1/2} \quad (36)$$

and further by eliminating  $p^H$  from (32) and (36), the theoretical adsorption isotherm

$$\theta = \theta(P, T; \alpha, \epsilon^r, \epsilon^s). \quad (37)$$

The experimental isotherm is given on the other hand as

$$v = v(P, T), \quad (38)$$

while the homogeneous model requires that  $v$  varies proportional to  $\theta$ . The parameters  $\alpha$ ,  $\epsilon^r$  and  $\epsilon^s$  are thus adjusted to the required proportionality

$$v = v_1 \theta \quad (39. a)$$

with reference to the observation of KINUYAMA and KWAN<sup>(1)</sup> as

$$v_1 = 2.2 \text{ cc NTP/gm Ni}, \quad (39. b)$$

$$\epsilon^r = -0.468 \text{ ev}, \quad \epsilon^s = -0.230 \text{ ev}, \quad \alpha = 1.200.$$

$$(40. r), (40. s), (40. \alpha)$$

TABLE 1. Free Energy  $W$  and Entropy  $-(\partial W/\partial T)_\theta$  of Repulsion and Associated Quantities  
 $\epsilon^r = 10.80$  kcal/mol,  $\epsilon^s = 5.30$  kcal/mol,  $\alpha = 1.200$ .

Tempera- ture °C	$q^r$	$q^s$	$\log r$ Quantit.	-1	0	1	2	3	4	5	6
0	$3.603 \times 10^8$	$1.063 \times 10^5$	$W$ cal/mol	$1.311 \times 10^2$	$5.998 \times 10^2$	$1.468 \times 10^3$	$2.559 \times 10^3$	$3.723 \times 10^3$	$4.853 \times 10^3$	$5.819 \times 10^3$	$6.442 \times 10^3$
			$q^r$	$2.830 \times 10^8$	$1.193 \times 10^8$	$2.410 \times 10^7$	$3.233 \times 10^6$	$3.786 \times 10^5$	$4.721 \times 10^4$	$7.966 \times 10^3$	$2.527 \times 10^3$
			$\theta^r$	0.07282	0.2488	0.4008	0.4729	0.5123	0.5671	0.6885	0.8752
			$\theta^s$	0.00003	0.0003	0.0029	0.0287	0.2279	0.7469	0.9672	0.9966
			$\theta = \theta^r + \theta^s$	0.07285	0.2491	0.4037	0.5016	0.7402	1.3140	1.6557	1.8718
			$-(\partial W/\partial T)_{\theta^r}$	-0.407	-1.712	-3.740	-3.830	2.470	4.368	2.318	0.740
			$(\partial W/\partial \theta^r)_T$	$2.00 \times 10^3$	$3.80 \times 10^3$	$9.65 \times 10^3$	$22.70 \times 10^3$	$30.85 \times 10^3$	$13.55 \times 10^3$	$4.90 \times 10^3$	$2.50 \times 10^3$
			$-(\partial \theta^r/\partial T)_\theta$	$1.052 \times 10^{-6}$	$1.026 \times 10^{-5}$	$9.098 \times 10^{-5}$	$3.132 \times 10^{-4}$	$1.015 \times 10^{-4}$	$-1.450 \times 10^{-4}$	$-1.704 \times 10^{-4}$	$-2.900 \times 10^{-5}$
			$-(\partial W/\partial T)_\theta$	-0.4049	-1.673	-2.862	3.279	5.601	2.403	1.483	0.6675
50	$1.510 \times 10^7$	$2.303 \times 10^4$	$W$ cal/mol	$1.497 \times 10^2$	$6.953 \times 10^2$	$1.719 \times 10^3$	$2.995 \times 10^3$	$4.318 \times 10^3$	$5.503 \times 10^3$	$6.319 \times 10^3$	$6.629 \times 10^3$
			$q^r$	$1.196 \times 10^7$	$5.115 \times 10^6$	$1.039 \times 10^6$	$1.424 \times 10^5$	$1.814 \times 10^4$	$2.868 \times 10^3$	$8.051 \times 10^2$	$4.970 \times 10^2$
			$\theta^r$	0.07339	0.2530	0.4076	0.4853	0.5457	0.6550	0.8420	0.9705
			$\theta^s$	0.00015	0.0015	0.0150	0.1323	0.6040	0.9385	0.9935	0.9993
			$\theta = \theta^r + \theta^s$	0.07354	0.2545	0.4226	0.6176	1.1497	1.5935	1.8355	1.9698
			$-(\partial W/\partial T)_{\theta^r}$	-0.402	-1.599	-3.409	-1.860	2.928	2.960	0.913	0.142
			$(\partial W/\partial \theta^r)_T$	$2.35 \times 10^3$	$4.10 \times 10^3$	$11.60 \times 10^3$	$23.30 \times 10^3$	$16.55 \times 10^3$	$7.00 \times 10^3$	$3.00 \times 10^3$	$2.10 \times 10^3$
			$-(\partial \theta^r/\partial T)_\theta$	$4.048 \times 10^{-6}$	$3.863 \times 10^{-5}$	$2.645 \times 10^{-4}$	$3.099 \times 10^{-4}$	$4.037 \times 10^{-5}$	$-1.353 \times 10^{-4}$	$-3.092 \times 10^{-5}$	$-3.504 \times 10^{-6}$
			$-(\partial W/\partial T)_\theta$	-0.3925	-1.441	-0.3414	5.360	3.596	2.013	0.8203	0.1346

100	$1.437 \times 10^6$	$7.230 \times 10^3$	$W$ cal/mol	$1.680 \times 10^2$	$7.876 \times 10^2$	$1.961 \times 10^3$	$3.405 \times 10^3$	$4.839 \times 10^3$	$5.974 \times 10^3$	$6.542 \times 10^3$	$6.670 \times 10^3$
			$q^r$	$1.146 \times 10^6$	$4.969 \times 10^5$	$1.022 \times 10^5$	$1.456 \times 10^4$	$2.107 \times 10^3$	$4.559 \times 10^2$	$2.120 \times 10^2$	$1.782 \times 10^2$
			$\theta^r$	0.07389	0.2569	0.4155	0.5032	0.5945	0.7603	0.9365	0.9920
			$\theta^s$	0.00050	0.0050	0.0479	0.3347	0.8342	0.9802	0.9980	0.9998
			$\theta = \theta^r + \theta^s$	0.07439	0.2619	0.4634	0.8379	1.4287	1.7405	1.9345	1.9918
			$-(\partial W / \partial T)_{\theta^r}$	-0.370	1.480	-2.752	0.260	2.852	1.330	0.310	0.030
			$(\partial W / \partial \theta^r)_T$	$2.70 \times 10^3$	$4.70 \times 10^3$	$11.15 \times 10^3$	$20.30 \times 10^3$	$11.25 \times 10^3$	$4.20 \times 10^3$	$2.70 \times 10^3$	$1.80 \times 10^3$
			$-(\partial \theta^r / \partial T)_{\theta}$	$1.037 \times 10^{-5}$	$9.457 \times 10^{-5}$	$4.273 \times 10^{-4}$	$2.307 \times 10^{-4}$	$-1.526 \times 10^{-5}$	$-3.852 \times 10^{-5}$	$-5.935 \times 10^{-6}$	$6.268 \times 10^{-7}$
			$-(\partial W / \partial T)_{\theta}$	0.3420	-1.036	2.012	4.943	2.680	1.168	0.2940	0.02887
150	$2.326 \times 10^5$	$2.885 \times 10^3$	$W$ cal/mol	$1.843 \times 10^2$	$8.765 \times 10^2$	$2.192 \times 10^3$	$3.784 \times 10^3$	$5.273 \times 10^3$	$6.275 \times 10^3$	$6.624 \times 10^3$	$6.677 \times 10^3$
			$q^r$	$1.869 \times 10^5$	$8.204 \times 10^4$	$1.717 \times 10^4$	$2.586 \times 10^3$	$4.402 \times 10^2$	$1.336 \times 10^2$	$8.822 \times 10^1$	$8.287 \times 10^1$
			$\theta^r$	0.07435	0.2607	0.4246	0.5264	0.6542	0.8517	0.9743	0.9972
			$\theta^s$	0.00128	0.0123	0.1103	0.5536	0.9254	0.9920	0.9992	0.9999
			$\theta = \theta^r + \theta^s$	0.07563	0.2730	0.5349	1.0800	1.5796	1.8437	1.9735	1.9971
			$-(\partial W / \partial T)_{\theta^r}$	-0.317	-1.350	-2.198	1.240	1.929	0.640	0.110	0.020
			$(\partial W / \partial \theta^r)_T$	$2.90 \times 10^3$	$5.15 \times 10^3$	$12.50 \times 10^3$	$17.60 \times 10^3$	$7.90 \times 10^3$	$3.40 \times 10^3$	$2.50 \times 10^3$	$1.80 \times 10^3$
			$-(\partial \theta^r / \partial T)_{\theta}$	$1.772 \times 10^{-5}$	$1.468 \times 10^{-4}$	$3.902 \times 10^{-4}$	$8.780 \times 10^{-5}$	$8.711 \times 10^{-5}$	$-2.722 \times 10^{-5}$	$3.211 \times 10^{-6}$	$-3.215 \times 10^{-7}$
			$-(\partial W / \partial T)_{\theta}$	-0.2656	-0.5939	2.680	2.785	1.241	0.5475	0.1020	0.01942
200	$5.420 \times 10^4$	$1.358 \times 10^3$	$W$ cal/mol	$2.002 \times 10^2$	$9.616 \times 10^2$	$2.411 \times 10^3$	$4.127 \times 10^3$	$5.619 \times 10^3$	$6.448 \times 10^3$	$6.654 \times 10^3$	$6.668 \times 10^3$
			$q^r$	$4.381 \times 10^4$	$1.949 \times 10^4$	$4.171 \times 10^3$	$6.729 \times 10^2$	$1.376 \times 10^2$	$5.700 \times 10^1$	$4.577 \times 10^1$	$4.511 \times 10^1$
			$\theta^r$	0.07478	0.2645	0.4349	0.5539	0.7174	0.9131	0.9883	0.9988
			$\theta^s$	0.00250	0.0245	0.2004	0.7148	0.9616	0.9960	0.9996	1.0000
			$\theta = \theta^r + \theta^s$	0.07728	0.2890	0.6353	1.2687	1.6790	1.9091	1.9879	1.9988
			$-(\partial W / \partial T)_{\theta^r}$	-0.244	-1.193	-1.604	1.500	1.300	0.289	0.030	0.003
			$(\partial W / \partial \theta^r)_T$	$3.10 \times 10^3$	$5.80 \times 10^3$	$12.85 \times 10^3$	$13.30 \times 10^3$	$6.30 \times 10^3$	$3.40 \times 10^3$	$2.50 \times 10^3$	$2.20 \times 10^3$
			$-(\partial \theta^r / \partial T)_{\theta}$	$2.842 \times 10^{-5}$	$2.104 \times 10^{-4}$	$3.495 \times 10^{-4}$	$5.239 \times 10^{-5}$	$-4.957 \times 10^{-5}$	$-1.011 \times 10^{-5}$	$-1.120 \times 10^{-6}$	$1.122 \times 10^{-7}$
			$-(\partial W / \partial T)_{\theta}$	0.1559	0.02732	2.887	2.197	0.9877	0.2546	0.02720	0.002753

Entropy of Hydrogen Atom on Nickel

TABLE 1. Free Energy  $W$  and Entropy  $-(\partial W/\partial T)_\theta$  of Repulsion and Associated Quantities (continued)  
 $\epsilon^r = 10.80$  kcal/mol,  $\epsilon^s = 5.30$  kcal/mol,  $\alpha = 1.200$ .

Temperature (°C)	$q^r$	$q^s$	$\log r$ Quantit.	-1	0	1	2	3	4	5	6
250	$1.640 \times 10^4$	$7.208 \times 10^2$	$W$ cal/mol	$2.155 \times 10^2$	$1.043 \times 10^3$	$2.618 \times 10^3$	$4.433 \times 10^3$	$5.885 \times 10^3$	$6.542 \times 10^3$	$6.674 \times 10^3$	$6.651 \times 10^3$
			$q^r$	$1.333 \times 10^4$	$6.015 \times 10^3$	$1.321 \times 10^3$	$2.307 \times 10^2$	$5.703 \times 10^1$	$3.032 \times 10^1$	$2.672 \times 10^1$	$2.731 \times 10^1$
			$\theta^r$	0.07519	0.2684	0.4462	0.5845	0.7767	0.9487	0.9939	0.9994
			$\theta^s$	0.00438	0.0421	0.3054	0.8147	0.9798	0.9977	0.9998	1.0000
			$\theta = \theta^r + \theta^s$	0.07957	0.3105	0.7516	1.3992	1.7565	1.9464	1.9937	1.9994
			$-(\partial W/\partial T)_{\theta^r}$	-0.220	-1.080	-1.020	1.436	0.843	0.135	0.014	0.002
			$(\partial W/\partial \theta^r)_T$	$3.30 \times 10^3$	$6.00 \times 10^3$	$12.90 \times 10^3$	$10.9 \times 10^3$	$4.75 \times 10^3$	$3.10 \times 10^3$	$2.80 \times 10^3$	$2.70 \times 10^3$
			$-(\partial \theta^r/\partial T)_\theta$	$4.055 \times 10^{-5}$	$2.616 \times 10^{-4}$	$3.012 \times 10^{-4}$	$1.619 \times 10^{-4}$	$2.527 \times 10^{-5}$	$4.199 \times 10^{-6}$	$4.590 \times 10^{-7}$	$3.915 \times 10^{-8}$
			$-(\partial W/\partial T)_\theta$	-0.0862	0.4894	2.866	3.201	0.7230	0.1220	0.01272	0.001894
300	$6.022 \times 10^3$	$4.183 \times 10^2$	$W$ cal/mol	$2.294 \times 10^2$	$1.120 \times 10^3$	$2.812 \times 10^3$	$4.704 \times 10^3$	$6.083 \times 10^3$	$6.593 \times 10^3$	$6.676 \times 10^3$	$6.825 \times 10^3$
			$q^r$	$4.924 \times 10^3$	$2.254 \times 10^3$	$5.098 \times 10^2$	$9.690 \times 10^1$	$2.885 \times 10^1$	$1.844 \times 10^1$	$1.715 \times 10^1$	$1.505 \times 10^1$
			$\theta^r$	0.07558	0.2723	0.4584	0.6167	0.8273	0.9684	0.9965	0.9996
			$\theta^s$	0.00690	0.0649	0.4099	0.8742	0.9858	0.9986	0.9999	1.0000
			$\theta = \theta^r + \theta^s$	0.08248	0.3372	0.8683	1.4909	1.8131	1.9670	1.9964	1.9996
			$-(\partial W/\partial T)_{\theta^r}$	0.220	-1.010	-0.640	1.427	0.580	0.087	0.006	0.001
			$(\partial W/\partial \theta^r)_T$	$3.50 \times 10^3$	$6.35 \times 10^3$	$12.30 \times 10^3$	$9.90 \times 10^3$	$4.40 \times 10^3$	$3.10 \times 10^3$	$2.95 \times 10^3$	$2.90 \times 10^3$
			$-(\partial \theta^r/\partial T)_\theta$	$5.274 \times 10^{-5}$	$2.935 \times 10^{-4}$	$2.655 \times 10^{-4}$	$1.433 \times 10^{-5}$	$1.281 \times 10^{-5}$	$1.922 \times 10^{-6}$	$1.970 \times 10^{-7}$	$1.634 \times 10^{-8}$
			$-(\partial W/\partial T)_\theta$	-0.03542	0.8537	2.625	1.569	0.5237	0.08104	0.005419	0.0009526



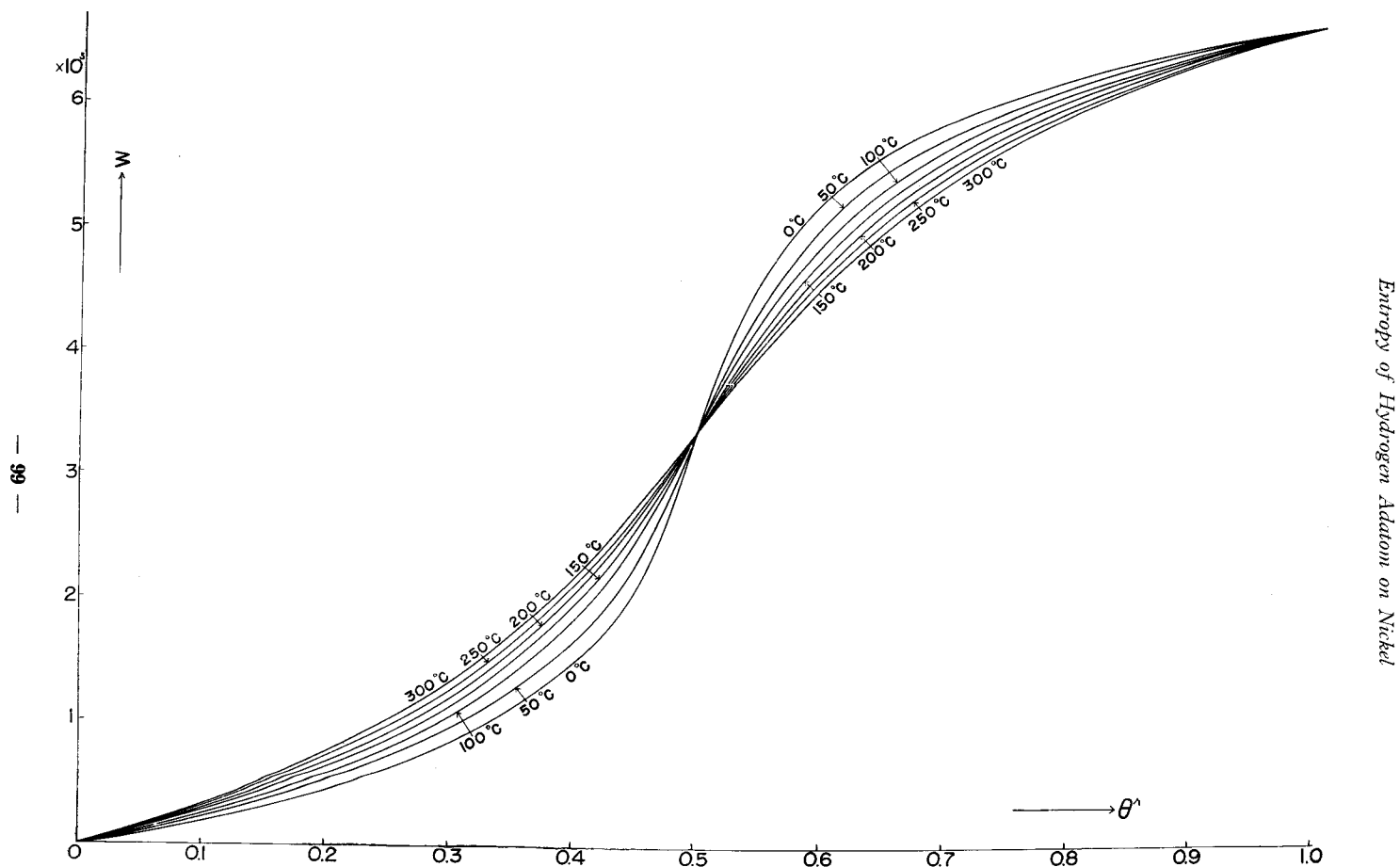


Fig. 2. Free Energy of Repulsion  $W$  cal/mol of Hydrogen Adatom on (110)-lattice Plane of f.c.c. Ni Crystal  
 $R_I = 0.1019 \times 1.200 \text{ ev}$ ,  $R_{II} = 0.0134 \times 1.200 \text{ ev}$ .

TABLE 2.  $S_I^H \equiv$ 

Temperature °C	$\frac{dRT \ln q_0^r}{dT}$	$\frac{dRT \ln q^s}{dT}$	Quantities $\log \tau$	-1
0	0.5808	6.359	$\theta = \theta^r + \theta^s$	0.07258
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$	5.244
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$	0.1759
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$	5.232
			$\theta^r(1-\theta^r)$	$6.752 \times 10^{-2}$
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$	27.087
			$\theta^s(1-\theta^s)$	$2.951 \times 10^{-5}$
50	0.6653	6.693	$\theta = \theta^r + \theta^s$	0.07354
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$	5.354
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$	0.2728
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$	5.312
			$\theta^r(1-\theta^r)$	$6.800 \times 10^{-2}$
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$	24.157
			$\theta^s(1-\theta^s)$	$1.525 \times 10^{-4}$
100	0.7056	6.979	$\theta = \theta^r + \theta^s$	0.07439
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$	5.510
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$	0.3636
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$	5.388
			$\theta^r(1-\theta^r)$	$6.843 \times 10^{-2}$
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$	22.072
			$\theta^s(1-\theta^s)$	$5.025 \times 10^{-4}$
150	0.7108	7.229	$\theta = \theta^r + \theta^s$	0.07563
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$	5.721
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$	0.4452
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$	5.456
			$\theta^r(1-\theta^r)$	$6.882 \times 10^{-2}$
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$	20.457
			$\theta^s(1-\theta^s)$	$1.237 \times 10^{-3}$

*Entropy of Hydrogen Adatom on Nickel*

$$\frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)} \quad \text{cal/mol deg}$$

0	1	2	3	4	5	6
0.2491	0.4037	0.5016	0.7402	1.3140	1.6557	1.8718
1.137	-1.248	5.008	7.199	3.213	0.3776	-2.692
-1.092	-2.281	3.860	6.182	2.984	2.064	1.248
1.104	-1.482	4.076	6.084	2.447	0.4876	-2.622
$1.869 \times 10^{-1}$	$2.402 \times 10^{-1}$	$2.493 \times 10^{-1}$	$2.499 \times 10^{-1}$	$2.455 \times 10^{-1}$	$2.145 \times 10^{-1}$	$1.092 \times 10^{-1}$
22.511	17.936	13.360	8.784	4.209	-0.367	-4.941
$2.949 \times 10^{-4}$	$2.934 \times 10^{-3}$	$2.784 \times 10^{-2}$	$1.759 \times 10^{-1}$	$1.890 \times 10^{-1}$	$3.171 \times 10^{-2}$	$3.369 \times 10^{-3}$
0.2545	0.4226	0.6176	1.1497	1.5935	1.8355	1.9698
1.522	1.872	7.493	4.858	1.378	-1.907	-6.181
-0.7757	0.3239	6.026	4.262	2.678	1.486	0.8000
1.376	1.067	6.142	3.897	1.404	-1.839	-6.142
$1.890 \times 10^{-1}$	$2.415 \times 10^{-1}$	$2.498 \times 10^{-1}$	$2.479 \times 10^{-1}$	$2.260 \times 10^{-1}$	$1.330 \times 10^{-1}$	$2.863 \times 10^{-2}$
19.581	15.005	10.430	5.854	1.278	-3.298	-7.859
$1.521 \times 10^{-3}$	$1.480 \times 10^{-2}$	$1.148 \times 10^{-1}$	$2.392 \times 10^{-1}$	$5.774 \times 10^{-2}$	$6.468 \times 10^{-3}$	$6.596 \times 10^{-4}$
0.2619	0.4634	0.8379	1.4287	1.7405	1.9345	1.9918
2.111	4.901	6.906	3.042	-0.4534	-4.382	-8.896
-0.3300	2.718	5.649	3.386	1.874	0.9995	0.7344
1.709	3.396	5.642	2.626	-0.4201	-4.348	-8.844
$1.909 \times 10^{-1}$	$2.429 \times 10^{-1}$	$2.500 \times 10^{-1}$	$2.411 \times 10^{-1}$	$1.822 \times 10^{-1}$	$5.947 \times 10^{-2}$	$7.936 \times 10^{-3}$
17.496	12.920	8.345	3.769	-0.7701	-5.387	-9.946
$4.980 \times 10^{-3}$	$4.560 \times 10^{-2}$	$2.227 \times 10^{-1}$	$1.383 \times 10^{-1}$	$1.911 \times 10^{-2}$	$1.976 \times 10^{-3}$	$2.000 \times 10^{-4}$
0.2730	0.5349	1.0800	1.5796	1.8437	1.9735	1.9971
3.001	6.111	5.036	1.045	-2.223	-6.427	-10.961
0.1170	3.391	3.496	1.952	1.258	0.8128	0.7303
2.188	3.995	3.286	0.685	-2.215	-6.411	-10.945
$1.927 \times 10^{-1}$	$2.443 \times 10^{-1}$	$2.493 \times 10^{-1}$	$2.262 \times 10^{-1}$	$1.263 \times 10^{-1}$	$2.504 \times 10^{-2}$	$2.792 \times 10^{-3}$
15.953	11.377	6.801	2.226	-2.350	-6.915	-11.517
$1.210 \times 10^{-2}$	$9.817 \times 10^{-2}$	$2.471 \times 10^{-1}$	$6.905 \times 10^{-2}$	$7.936 \times 10^{-3}$	$8.093 \times 10^{-4}$	$7.999 \times 10^{-5}$

TABLE 2.  $S_I^H \equiv$

Temperature °C	$\frac{dRT \ln q^r}{dT}$	$\frac{dRT \ln q^s}{dT}$	Quantities $\log r$	-1
200	0.6896	7.451	$\theta = \theta^r + \theta^s$ $S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$ $R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$ $S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$ $\theta^r(1-\theta^r)$ $S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$ $\theta^s(1-\theta^s)$	0.07728 6.013 0.5337 5.532 $6.919 \times 10^{-2}$ 19.352 $2.494 \times 10^{-3}$
250	0.6485	7.650	$\theta = \theta^r + \theta^s$ $S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$ $R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$ $S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$ $\theta^r(1-\theta^r)$ $S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$ $\theta^s(1-\theta^s)$	0.07957 6.309 0.5623 5.549 $6.954 \times 10^{-2}$ 18.435 $4.357 \times 10^{-3}$
300	0.5927	7.832	$\theta = \theta^r + \theta^s$ $S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$ $R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$ $S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$ $\theta^r(1-\theta^r)$ $S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$ $\theta^s(1-\theta^s)$	0.08248 6.621 0.5573 5.533 $6.987 \times 10^{-2}$ 17.708 $6.850 \times 10^{-3}$

### § 7. Statistical Mechanical Entropy $S_I^H$ on the Homogeneous Model

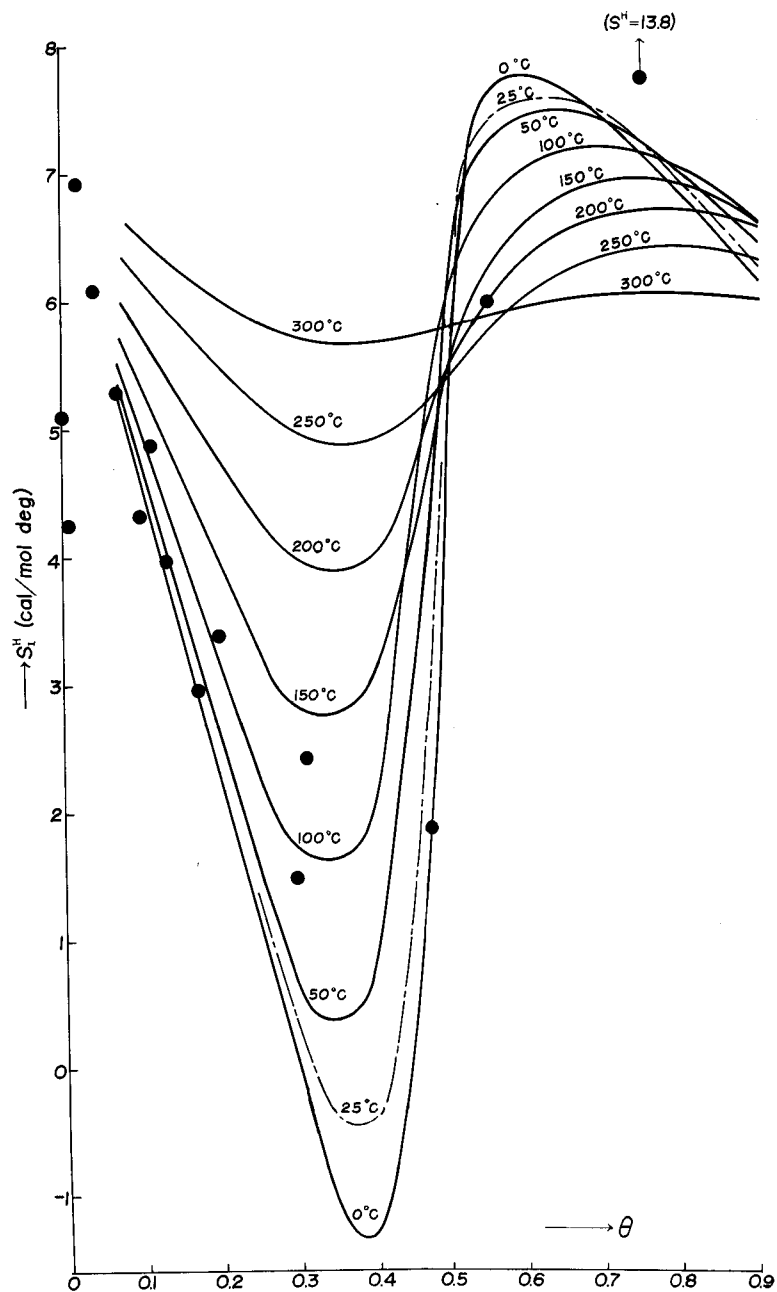
For any prescribed value of  $T$  and  $r$ ,  $q_0^r$  is calculated by (14.  $q$ ),  $q^s$  by (21. a),  $\xi_I$  and  $\xi_{II}$  by (17),  $W$  by (16) on the base of the parameter values in (30), (31) and (40);  $q^r$  is hence determined by (10) and  $p^H$  by (15) from the

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$$\frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)} \quad \text{cal/mol deg (continued)}$$

0	1	2	3	4	5	6
0.2890	0.6353	1.2687	1.6790	1.9091	1.9879	1.9988
4.063	6.506	3.889	0.01439	-3.720	-8.099	-12.670
0.7167	3.577	2.886	1.677	0.9442	0.7168	0.6924
2.749	4.097	2.456	-0.1740	-3.730	8.099	-12.670
$1.945 \times 10^{-1}$	$2.458 \times 10^{-1}$	$2.471 \times 10^{-1}$	$2.027 \times 10^{-1}$	$7.935 \times 10^{-2}$	$1.156 \times 10^{-2}$	$1.199 \times 10^{-3}$
14.777	10.201	5.625	1.049	-3.528	-8.096	-12.673
$2.385 \times 10^{-2}$	$1.602 \times 10^{-1}$	$2.039 \times 10^{-1}$	$3.690 \times 10^{-2}$	$3.954 \times 10^{-3}$	$3.998 \times 10^{-4}$	$4.000 \times 10^{-5}$
0.3105	0.7516	1.3992	1.7565	1.9464	1.9937	1.9994
4.959	6.406	3.760	-0.9891	-5.001	-9.443	-14.083
1.1379	3.514	3.849	1.371	0.7704	0.6612	0.6504
3.131	3.944	3.171	-1.106	-5.027	-9.460	-14.091
$1.964 \times 10^{-1}$	$2.471 \times 10^{-1}$	$2.429 \times 10^{-1}$	$1.734 \times 10^{-1}$	$4.867 \times 10^{-2}$	$6.063 \times 10^{-3}$	$5.996 \times 10^{-4}$
13.859	9.283	4.708	-0.060	-4.444	-8.997	-13.851
$4.033 \times 10^{-2}$	$2.121 \times 10^{-1}$	$1.510 \times 10^{-1}$	$2.175 \times 10^{-2}$	$2.265 \times 10^{-3}$	$2.300 \times 10^{-4}$	$2.000 \times 10^{-5}$
0.3373	0.8683	1.4909	1.8131	1.9670	1.9964	1.9996
5.683	6.022	2.096	-1.871	-6.085	-10.600	-14.956
1.446	3.218	2.162	1.116	0.6738	0.5981	0.5937
3.399	3.549	1.217	-1.997	-6.127	-10.633	-14.954
$1.982 \times 10^{-1}$	$2.483 \times 10^{-1}$	$2.364 \times 10^{-1}$	$1.429 \times 10^{-1}$	$3.060 \times 10^{-2}$	$3.488 \times 10^{-3}$	$3.998 \times 10^{-4}$
13.132	8.556	3.980	-0.596	-5.168	-9.802	-15.047
$6.073 \times 10^{-2}$	$2.419 \times 10^{-1}$	$1.100 \times 10^{-1}$	$1.399 \times 10^{-2}$	$1.438 \times 10^{-3}$	$1.400 \times 10^{-4}$	$1.000 \times 10^{-5}$

values of  $q_o^r$  calculated as above. The  $q^r$ ,  $q^s$  and  $p^H$  thus evaluated decide  $\theta^r$  and  $\theta^s$  by (6), hence  $\theta$  by (7). Fig. 2 shows  $W$  thus calculated as a function of  $T$  and  $\theta^r$ .  $W$  being thus given as a function of  $T$  and  $\theta^r$ , the differential coefficients  $(\partial W / \partial T)_{\theta^r}$  and  $(\partial W / \partial \theta^r)_T$  are now determined, hence the entropy of repulsion  $-(\partial W / \partial T)_{\theta}$  is evaluated as a function of  $\theta$  and  $T$  according to (27) and (28). Table 1 shows the values of  $W$ ,  $q_o^r$ ,  $q^s$ ,  $q^r$ ,  $\theta^r$ ,  $\theta^s$ ,  $\theta$ ,



**Fig. 3.** Calculated Entropy  $S_I^H$  on Homogeneous Model and Observed Entropy  $S^H$ .  
 Lines:  $S_I^H$  at signified temperatures ( $S_I^H$  at 25°C interpolated).  
 Solid circles:  $S^H$  at 25°C observed by RIDEAL and SWEETT<sup>2)</sup>.

$-(\partial W/\partial T)_\theta$ ,  $(\partial W/\partial \theta)_T$ ,  $-(\partial \theta^r/\partial T)_\theta$ , and  $-(\partial W/\partial T)_\theta$  thus obtained at different temperatures. We see from the Table that  $\theta^s$  vanishes practically at low  $\theta$ .

We are now ready to calculate  $S_I^H$  by (9. S). Table 2 shows

$$S_I^H = \left\{ \theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s \right\} / \left\{ \theta^r(1-\theta^r) + \theta^s(1-\theta^s) \right\}$$

$S^r = (\partial RT \ln q^r / \partial T)_\theta + R \ln \{(1-\theta^r)/\theta^r\}$ ,  $S^s = dRT \ln q^s / dT + R \ln \{(1-\theta^s)/\theta^s\}$ ,  $\theta^r(1-\theta^r)$ , and  $\theta^s(1-\theta^s)$ , which are derived from data given in Table 1.

The value of  $S_I^H$  in Table 2 is plotted against  $\theta$  in Fig. 3.

### § 8. Observed Value of $S^H$ as Compared with $S_I^H$

The observed value of  $S^H$  is derived thermodynamically from experimental results as follows. The  $\mu^H$  implied in (1) is expressed according to (33. a) in terms of hydrogen pressure  $P$  as

$$\mu^H = 1/2 \cdot \mu_i^{H_2} + 1/2 \cdot RT \ln P,$$

where  $\mu_i^{H_2}$  is the value of  $\mu^{H_2}$  at  $P=1$  or GIBBS free energy of one mol hydrogen gas at unit pressure. We have from the above equation and (1)

$$S^H = 1/2 \cdot S_i^{H_2} + 1/2 \cdot (\partial RT \ln P / \partial T)_v, \quad (41)$$

where

$$S_i^{H_2} = -d\mu_i^{H_2}/dT$$

is the entropy of hydrogen gas per mol at unit pressure and at the temperature of adsorption equilibrium.

The  $S_i^{H_2}$ -values were directly taken or interpolated from those in literature<sup>16)</sup>. The  $(\partial RT \ln P / \partial T)_v$  was determined from the experimental results of KINUYAMA and KWAN<sup>1)</sup> at the  $v$ -value relevant to the specified  $\theta$ -value according to (39) from the observed relation  $v=v(T, P)$  and the  $S^H$  thus determined from the observation<sup>1)</sup> was found to reproduce its statistical mechanical value fairly well, as it should, inasmuch as the parameters involved, *i. e.* those of (39. b) and (40), have been determined from the same observation<sup>1)</sup>.

$S^H$  at 25°C was derived from observations of RIDEAL and SWEETT<sup>2)</sup>, which numerically confirmed  $S^H$  as deduced by the latter authors from the same observations formally in different way. The data of  $S^H$  thus confirmed are plotted in Fig. 3 as shown by solid circles. The general features of the variation of  $S^H$  with coverage  $\theta$  is reproduced, as seen in Fig. 3, by that of  $S_I^H$  inclusive of the minimum around  $\theta=0.3$ , except that the former runs appreciably lower than the latter at extremely low  $\theta$ . At higher  $\theta$ ,  $S_I^H$  passes through a maximum and then decreases with increase of  $\theta$ , although observed  $S^H$  is not thus far available. These aspects will be discussed in subsequent sections.

### § 9. Entropy Allowed for Lattice Imperfections

It is well-known that the catalyst surface is associated with lattice imperfections, *i.e.* steps, kinks, defects and grain boundaries<sup>17)</sup>, while the first small portion of adsorbed hydrogen is accommodated with extraordinary high heat of adsorption<sup>2,9)</sup>. The present authors have previously inferred<sup>6)</sup> that these lattice imperfections provide *s*-sites alone, where *s*-adatoms assume appreciably low energy even lower than that of *r*-adatoms on the homogeneous model<sup>\*)</sup>. In accordance with these conclusions the homogeneous model is revised as below, on which basis the discrepancy mentioned in § 8 between the observed  $S^H$  and  $S_I^H$  at lower coverage is accounted for. The revised model is composed of *h*-sites and a small proportion of *i*-sites; the *h*-sites are physically identical with those of the homogeneous model, hence consist of sites for *r*-adatoms, physically identical with each other and those for *s*-adatoms similarly physically identical with each other; the number of sites for *r*-adatoms equals that for *s*-adatoms as well as the number of the metal atoms on the surface lattice plane; *i*-sites are those provided by lattice imperfections, which are assumed, for the first approximation, physically identical with each other and accommodate *s*-adatoms only, at lower energy than that either of *r*- or *s*-adatom on *h*-sites. The coverage of sites for *r*- or *s*-adatom of *h*-sites by the latter will be denoted by  $\theta_h^r$  or  $\theta_h^s$  respectively and that of *i*-sites by *s*-adatoms by  $\theta_i^s$ .

We define  $q^r$  and  $q^s$  with special reference to *h*-sites similar to those of the homogeneous model and denote them by  $q_h^r$  and  $q_h^s$  respectively, although they are respectively identical with  $q^r$  and  $q^s$  of the homogeneous model according to the premise. We have hence from (6) and (10)

$$q_h^r/p^H = \theta_h^r/(1-\theta_h^r), \quad q_h^s/p^H = \theta_h^s/(1-\theta_h^s), \quad (42. r), (42. s)$$

$$\text{and} \quad q_h^r = q_0^r \exp(-W/RT). \quad (42. q)$$

It follows that  $\theta_h^r$ ,  $\theta_h^s$  and  $\theta_h = \theta_h^r + \theta_h^s$  are respectively equal to  $\theta^r$ ,  $\theta^s$  and  $\theta = \theta^r + \theta^s$  on the homogeneous model for the same value of  $p^H$ . We see from Table 1 that  $\theta^s$  is negligibly small as compared with  $\theta^r$  for  $\theta < 0.4$  at 0°C and 50°C. Adatoms on *h*-sites consist in consequence practically exclusively of *r*-adatom for  $\theta_h < 0.4$ .

Defining  $q_i^s$  for *s*-adatom on *i*-sites similar to  $q^s$  on the homogeneous model, we have in accordance with (6. s)

$$q_i^s/p^H = \theta_i^s/(1-\theta_i^s); \quad (43. a)$$

\*) On the homogeneous model the energy of *s*-adatom is higher than that of *r*-adatom as seen from (40. r) and (40. s).



$q_i^s$  is given in accordance with (21. a) in terms of  $A_i$ ,  $\varepsilon_i^s$  and  $\nu_i$  respectively corresponding to  $A$ ,  $\varepsilon^s$  and  $\nu$  as\*)

$$q_i^s = A_i \frac{2\pi mkT}{h^2} \exp\left(-\frac{\varepsilon_i^s}{kT}\right) \left\{1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right\}^{-1} \quad (43. b)$$

Let  $G_i$  or  $G_h$  be the number of  $i$ -sites or  $h$ -sites. The overall coverage  $\theta$  is expressed admitting  $\theta_h^s = 0$  for  $\theta_h < 0.4$  as

$$\theta = (G_i\theta_i^s + G_h\theta_h^r)/(G_i + G_h) \quad (44. a)$$

or as

$$\theta = x\theta_i^s + (1-x)\theta_h^r, \quad (44. b)$$

where

$$x = G_i/(G_i + G_h). \quad (44. c)$$

The entropy  $S_{II}^H$  on the revised model is now deduced as shown in Appendix 1 as

$$S_{II}^H = \frac{x\theta_i^s(1-\theta_i^s)S_i^s + (1-x)\theta_h^r(1-\theta_h^r)S_h^r}{x\theta_i^s(1-\theta_i^s) + (1-x)\theta_h^r(1-\theta_h^r)}, \quad (45. S)$$

where

$$S_i^s = R(\partial T \ln q_i^s / \partial T)_\theta + R \ln \{(1-\theta_i^s)/\theta_i^s\} \quad (45. i)$$

and

$$S_h^r = R(\partial T \ln q_h^r / \partial T)_\theta + R \ln \{(1-\theta_h^r)/\theta_h^r\}. \quad (45. h)$$

Eq. (45) thus obtained for  $\theta_h = \theta_h^r < 0.4$  on the revised model is now discussed in two particular cases in the following sections, assuming that

$$x = 0.01 \quad (46. x)$$

according to WORTMAN, GOMER and LUNDY<sup>9)</sup> and that

$$q_i^s/q_o^r = 10^4, \quad (46. q)$$

which is *a posteriori* confirmed in § 12.

### §10. $S_{II}^H$ for $\theta < x$

This particular case will first be investigated by specifying further that

$$2\theta = x. \quad (47)$$

It follows from (46) and (47) as shown below that

$$\theta_h^r = 0.000096, \quad \theta_i^s = 0.4905 \quad (48. r), (48. s)$$

\*) The s-adatom is accommodated with narrower phase space in  $i$ -site than in  $h$ -site as remarked in ref. 6, which may be allowed for formally by a smaller  $A_i$  than  $A$  in (21. a).

or in words that adatoms are predominantly s-adatoms on  $i$ -sites. The  $\theta_i^s$ -value of (48. s) is close to  $\theta_i^s=0.5000$ , which would be the case according to (44. b) and (47), if adatoms were entirely s-adatoms on  $i$ -sites. It is readily shown that the predominance of  $\theta_i^s$  over  $\theta_h^r$  as well as the proximity of  $\theta_i^s$  to  $\theta/x$  is enhanced, as  $\theta$  gets smaller<sup>\*</sup>.

The factors  $\eta_I$  and  $\eta_{II}$  in (16) are essentially positive by definition [cf. Appendix 2] and  $r$  is positive as well according to (15), (2) and (11). The  $\xi_I$  and  $\xi_{II}$  are both positive and less than unity by definition (17). It follows that the denominator of the argument of the logarithm in (16. a) is less than the numerator, hence positive  $W$ . The  $q_h^r$  is in consequence smaller than  $q_i^r$  by (42. q). It follows hence from (46. q) that

$$q_i^s/q_h^r > 10^4 \quad (49. a)$$

or according to (42. r) and (43. a)

$$6\theta_i^s/(1-\theta_i^s) > 10^4 \theta_h^r/(1-\theta_h^r). \quad (49. b)$$

We have on the other hand from (44. b),  $x\theta_i^s < \theta$ , hence according to (47),  $\theta_i^s < 1/2$  or

$$1-\theta_i^s > 1/2 \quad (50. a)$$

or by (49. b)

$$\theta_i^s > 1/2 \cdot 10^4 \theta_h^r/(1-\theta_h^r)$$

and in consequence

$$\theta_i^s > 1/2 \cdot 10^4 \theta_h^r. \quad (50. b)$$

It follows from (50. b), (44. b), (46. x) and (47) that

$$\theta_h^r < 0.98 \times 10^{-4}.$$

The corresponding value of  $W$  is determined by (42. r), (42. q), (15), (16) and (17) as less than  $2.85 \times 10^{-4} RT$ , which makes the difference of  $q_h^r$  from  $q_i^r$  according to (42. q) only less than 0.0285 per cent. Neglecting this difference, we have from (46. q)  $q_i^s/q_h^r = 10^4$ , hence  $\theta_h^r/(1-\theta_h^r) = 10^{-4} \theta_i^s/(1-\theta_i^s)$  in place of inequalities (49. a) and (49. b) respectively. Solving the last equation and (44. b) simultaneously for  $\theta_h^r$  and  $\theta_i^s$  with reference to (46. x) and (47), we arrive at (48).

The relative weight  $(1-x)\theta_h^r(1-\theta_h^r)$  and  $x\theta_i^s(1-\theta_i^s)$  respectively of  $S_h^r$  and  $S_i^s$  in (45. S) is calculated from the above values of  $\theta_h^r$  and  $\theta_i^s$  and (46. x) as  $(1-x)\theta_h^r(1-\theta_h^r) = 0.097 \times 10^{-3}$  and  $x\theta_i^s(1-\theta_i^s) = 2.499 \times 10^{-3}$ . It is readily inferred that the latter weight predominates the more over the former, the lower the  $\theta^*$ . The  $S_h^r$  implied in (45. S) is evaluated by (45. h) and (14. q) for  $\theta_h^r = 0.98 \times 10^{-4}$  and  $25^\circ\text{C}$ , identifying  $q_h^r$  with  $q_i^r$  according to the above, as

$$S_h^r = 19.94 \text{ cal/mol deg}, \quad \theta_h^r = 0.000096, \quad 25^\circ\text{C}. \quad (51. r)$$

The  $S_i^s$  at  $\theta_i^s=0.4905$  is calculated by (45. i) and (43. b), identifying  $A_i$  and  $\nu_i$  in (43. b) respectively with  $A$  and  $\nu$  given by (24) and (30. s) as

<sup>\*</sup>) Cf. footnote <sup>\*\*</sup>) on p. 110.

$$S_i^s = 6.70 \text{ cal/mol deg}, \quad \theta_i^s = 0.4905, \quad 25^\circ\text{C}. \quad (51. s)$$

The weighted mean of (45. S) gives now

$$S_{\text{II}}^{\text{H}} = 7.18 \text{ cal/mol deg}, \quad \theta = 0.005, \quad 25^\circ\text{C}, \quad (52. a)$$

which is somewhat higher than the value of  $S_i^s$  of (51. s).  $S_{\text{II}}^{\text{H}}$  approaches  $S_i^s$  according to the above, as  $\theta$  decreases.

The above value of entropy on the revised model is compared with the entropy on the homogeneous model for the same value of  $\theta$ , *i.e.*  $\theta = 0.005$  according to (46. x) and (47). For such low coverage, adatoms on the homogeneous model consist practically exclusively of r-adatoms as remarked in § 9, *i.e.* according to (7) and (9. S),  $\theta = \theta^r$ ,  $S_{\text{I}}^{\text{H}} = S^r$ , where  $S^r$  is expressed by (9. r) and (10) as

$$S^r = R dT \ln q_r^r / dT - (\partial W / \partial T)_{\theta^r} + R \ln \{ (1 - \theta^r) / \theta^r \},$$

noting that  $q_r^r$  is a sole function of temperature and the differentiation at constant  $\theta$  is equivalent in this case to that at constant  $\theta^r$ . The first term of the above equation is calculated by (14. q) and (30. r), and the second terms by (16), (31), (40. a), (17) and (26. b). The result is

$$S_{\text{I}}^{\text{H}} = S^r = 12.12 \text{ cal/mol deg}, \quad \theta = 0.005, \quad 25^\circ\text{C}. \quad (52. b)$$

We see from (52) that the allowance for the lattice imperfection causes a depression from  $S_{\text{I}}^{\text{H}}$  to  $S_{\text{II}}^{\text{H}}$  as much as 5 cal/mol deg for  $\theta$  less than to cover the *i*-sites completely. The  $A_i$  and  $\nu_i$  have been identified with  $A$  and  $\nu$  in the above calculation of  $S_i^s$ . The variation of  $\nu_i$  around  $\nu$  has little effect on  $S_i^s$ , since the factor  $1 - \exp(-h\nu_i/kT)$  remains close to unity insofar as  $\nu_i$  is as large as  $\nu$  given by (30. s), whereas that of  $A_i$  may make difference. Since  $A_i$  is identified with  $A$ , the value of  $S_{\text{II}}^{\text{H}}$  in (52. a) is its upper bound and hence the above value 5 cal/mol deg of the depression from  $S_{\text{I}}^{\text{H}}$  to  $S_{\text{II}}^{\text{H}}$  is its lower bound.\*<sup>1)</sup> This accounts reasonably for the depression of the observed value of  $S^{\text{H}}$  from  $S_{\text{I}}^{\text{H}}$  as seen in Fig. 3. The conclusion remains unchanged, if the low energy of *i*-sites is inhomogeneous instead.

### § 11. $S_{\text{II}}^{\text{H}}$ for $\theta > x$

We investigate now the distribution of adatoms over *i*- and *h*-sites of the revised model and the appropriate value of  $S_{\text{II}}^{\text{H}}$  in case where  $0.4 > \theta > x$ .

We assume, besides (46), first that

$$\theta = 2x \quad (53)$$

in place of (47) for the sake of numerical investigation. Eqs. (42. r), (42. q), (43. a), (44. b), (46) and (53) are now solved simultaneously for  $\theta_h^r$  and  $\theta_i^s$ ,

\* Cf. footnote on p. 107.

evaluating  $W$  as in § 10, as

$$\theta_h^r = 0.01019, \quad \theta_i^s = 0.992. \quad (54. r), (54. s)$$

Appropriate values of  $S_h^r$  and  $S_i^s$  are determined by (45. h) and (45. i) with reference to (42. q), (14. q) and (43. b) as\*)

$$S_h^r = 10.75, \quad S_i^s = -3.04 \text{ cal/mol deg.} \quad (55. r), (55. s)$$

The weights of  $S_h^r$  and  $S_i^s$  in (45. S) are calculated from (46. x) and (54) as

$$(1-x)\theta_h^r(1-\theta_h^r) = 0.999 \times 10^{-2}, \quad x\theta_i^s(1-\theta_i^s) = 0.79 \times 10^{-4} \quad (56. r), (56. s)$$

We have now from (45. S), (55) and (56),

$$S_{II}^H = 10.63 \text{ cal/mol deg.} \quad (57)$$

The weight of  $S_h^r$  is so predominating that  $S_{II}^H$  is almost equal to  $S_h^r$ ,  $\theta_i^s$  being nearly unity. It is readily shown that the predominance of weight of  $S_h^r$  and the proximity of  $\theta_i^s$  to unity are enhanced with increase of  $\theta^{**})$ .

We see from (52) and (57) that  $S_{II}^H$  switches over almost from  $S_i^s$  to  $S_h^r$  as  $\theta$  increases from a value lower than  $x$  to that higher.

## § 12. Isosteric Heat of Adsorption

We have premised (46. q), from which  $S_{II}^H$  has been deduced on the basis of the revised model reasonably in accordance with the experimental results<sup>2)</sup>.

\*)  $(\partial W / \partial T)_{\theta_h^r}$  involved in the calculation is determined from (26. c) identifying  $\theta_h^r$  with  $\theta^r$  implied in  $W$  in accordance with the physical identity of  $h$ -sites with sites of homogeneous model as premised in § 9.

\*\*) We have from (42. r), (42. q), (43. a) and (46. q)

$$\theta_i^s / (1 - \theta_i^s) = 10^4 \exp(W/RT) \theta_h^r / (1 - \theta_h^r)$$

from which it follows that  $\theta_i^s > \theta_h^r$  and that  $\theta_i^s$ ,  $\theta_h^r$  and  $\theta$  by (44. b) increase or decrease simultaneously at constant temperature, noting that  $W$  is positive and monotonously increases with increase of  $\theta_h^r$  as seen in Fig. 2. Both  $\theta_h^r$  and  $\theta_i^s$  increase in consequence monotonously with increase of  $\theta$ . As  $\theta_i^s$  is not very near to unity,  $\theta_h^r$  is negligibly small as compared with unity according to the above equation and hence  $W$  is ignorable. We have then from the above equation  $\theta_i^s / \theta_h^r = 10^4 (1 - \theta_i^s)$ , i.e. that the ratio  $\theta_i^s / \theta_h^r$  increases with decrease of  $\theta_i^s$ , hence of  $\theta$ . It follows that the weight  $x\theta_i^s(1 - \theta_i^s)$  of  $S_i^s$  predominates over that  $(1-x)\theta_h^r(1 - \theta_h^r)$  of  $S_h^r$  the more, the lower the  $\theta$  as mentioned on p. 108.

As  $\theta$  increases and in consequence  $\theta_i^s$  and  $\theta_h^r$  simultaneously increase according to (44. b),  $\theta_i^s$  approaches unity sooner than  $\theta_h^r$  does. In case where  $\theta_i^s$  is close to unity, the increase of  $\theta_h^r / (1 - \theta_h^r)$  on the right-hand side of the above equation concerted by that of  $W$  is balanced by the increase of the left-hand side through the decrease of its denominator  $1 - \theta_i^s$  rather than by the increase of the numerator  $\theta_i^s$ . This proximity of  $\theta_i^s$  to unity and in consequence the predominance of the weight  $(1-x)\theta_h^r(1 - \theta_h^r)$  of  $S_h^r$  over that  $x\theta_i^s(1 - \theta_i^s)$  of  $S_i^s$  are thus amplified with increase of  $\theta$ .

It is now investigated whether (46. q) be compatible with the observation of isosteric heat of adsorption by RIDEAL and SWEETT<sup>2)</sup>. Eq. (46. q) leads as shown below to the difference between the isosteric heat over the region where the adsorption occurs predominantly on *i*-sites and that over the region where *i*-sites are nearly filled up and the fresh adsorption takes place predominantly on *h*-sites, and the difference thus obtained is compared with the experimental one by RIDEAL and SWEETT<sup>2)</sup>. These regions of adsorption dealt with in § 10 and § 11 will be called *i*- and *h*-regions respectively.

The isosteric (differential) heat of adsorption  $Q_i^H$  or  $Q_h^H$  observed respectively in the *i*- or *h*-region is expressed thermodynamically as

$$Q_i^H = H_i^H - \bar{H}_i^H, \quad Q_h^H = H_i^H - \bar{H}_h^H,$$

where  $H_i^H$  is the enthalpy of hydrogen gas to be adsorbed per unit gram atom hydrogen and  $\bar{H}_i^H$  or  $\bar{H}_h^H$  the partial molal enthalpy of hydrogen adatom in the respective region. We have from the above two equations

$$Q_i^H - Q_h^H = \bar{H}_h^H - \bar{H}_i^H. \quad (58)$$

$\bar{H}_h^H$  or  $\bar{H}_i^H$  represented by  $\bar{H}^H$  is given in terms of the chemical potential  $\mu^H$  of hydrogen adatom as

$$\bar{H}^H = \mu^H - T(\partial\mu^H/\partial T)_\theta$$

or according to (3) as

$$\bar{H}^H = RT^2(\partial\ln p^H/\partial T)_\theta.$$

The  $(\partial\ln p^H/\partial T)_\theta$  is determined by differentiating (42. r), (43. a) and (44. b) and eliminating  $d\theta_h^s$  and  $d\theta_i^s$  similarly as in case of (45. S), as

$$\bar{H}^H = RT^2 \frac{x\theta_i^s(1-\theta_i^s)d\ln q_i^s/dT + (1-x)\theta_h^s(1-\theta_h^s)(\partial\ln q_h^s/\partial T)_\theta}{x\theta_i^s(1-\theta_i^s) + (1-x)\theta_h^s(1-\theta_h^s)}, \quad (59)$$

noting that  $q_i^s$  is a sole function of temperature.  $\bar{H}_h^H$  and  $\bar{H}_i^H$  are the particular values of  $\bar{H}^H$  respectively appropriate to *h*- or *i*-region in accordance with (59). We have from (42. q) and (14. q)\*)

$$RT^2(\partial\ln q_h^s/\partial T)_\theta = RT^2 d\ln q_h^s/dT + W - T(\partial W/\partial T)_\theta, \quad (60. a)$$

$$RT^2 d\ln q_h^s/dT = RT \sum_{j=1}^3 (h\nu_j/kT) \left\{ \exp(h\nu_j/kT) - 1 \right\}^{-1} + \epsilon^r \quad (60. b)$$

and from (43. b)

$$RT^2 d\ln q_i^s/dT = RT \left[ 1 + (h\nu_i/kT) \left\{ \exp(h\nu_i/kT) - 1 \right\}^{-1} \right] + \epsilon_i^s \quad (60. c)$$

The specification of *h*-region implies now that  $\theta_h^s$  is negligibly small as

\*) The  $\epsilon^r$  and  $\epsilon_i^s$  are expressed in units of cal/mol in this section.

compared with  $\theta_h^r$ , which is satisfied, in particular, at  $\theta_h = \theta_h^r + \theta_h^s = 0.2$  and  $\theta_h = 0.3$  as seen with reference to Table 1, noting that  $\theta_h^r$  or  $\theta_h^s$  varies with  $\theta_h$  identically as  $\theta^r$  or  $\theta^s$  does with  $\theta$  on the homogeneous model as mentioned in § 9.  $W - T(\partial W/\partial T)_\theta$  was now interpolated from Table 1 at  $\theta = \theta^r = 0.2$  and 0.3 at 25°C, as

$$W - T(\partial W/\partial T)_\theta = 0.08 \text{ kcal/mol}, \quad \theta = 0.2, 25^\circ\text{C}, \quad (61. a)$$

and

$$W - T(\partial W/\partial T)_\theta = 0.21 \text{ kcal/mol}, \quad \theta = 0.3, 25^\circ\text{C}, \quad (61. b)$$

which are identified with those on the revised model<sup>\*</sup>.  $RT^2 d \ln q_0^r/dT$  is calculated by (60. b) on the base of parameters given by (30. r) as

$$RT^2 d \ln q_0^r/dT = \varepsilon^r + 0.33 \text{ kcal}, \quad 25^\circ\text{C}, \quad (62. r)$$

we have now from (59), (60. a), (61) and (62. r) identifying  $\theta_i^s$  with unity

$$\bar{H}_h^H = \varepsilon^r + 0.41 \text{ kcal}, \quad \theta = 0.2, 25^\circ\text{C}; \quad \bar{H}_h^H = \varepsilon^r + 0.54 \text{ kcal}, \quad \theta = 0.3, 25^\circ\text{C}. \quad (63. h)$$

$\bar{H}_i^H$  is now determined for the  $i$ -region specified by (47) allowing for the weight of  $(\partial \ln q_h^r/\partial T)_\theta$  in (59). The  $RT^2 d \ln q_i^s/dT$  is obtained from (60. c) on the base of the parameters  $A_i$  and  $\nu_i$  respectively identified with  $A$  in (24) and  $\nu$  in (30. s), as

$$RT^2 d \ln q_i^s/dT = \varepsilon_i^s + 0.62 \text{ kcal}, \quad 25^\circ\text{C}. \quad (62. s)$$

$W - T(\partial W/\partial T)_\theta$  is shown to be negligible at such low value of  $\theta_h^r$  as given by (51. r), so that  $RT^2(\partial \ln q_h^r/\partial T)_\theta$  equals practically  $RT^2 d \ln q_0^r/dT$ . We have from (59) and (62) with reference to (46. x), (47) and (48)

$$\bar{H}_i^H = \frac{0.2499 \times (\varepsilon_i^s + 0.62) + 0.0095(\varepsilon^r + 0.33)}{0.2499 + 0.0095}, \quad (63. i)$$

hence from (58) and (63),

<sup>\*</sup>)  $W - T(\partial W/\partial T)_\theta$  for the homogeneous model is not unconditionally identifiable with that for the revised model, inasmuch as the suffixed constant  $\theta$  is that of (7) or (44. b) in the respective case. In the specified range of  $\theta$ , however,  $\theta^s$  is negligibly small in case of the homogeneous model, while  $\theta_i^s$  is practically unity in case of the revised model. The constant  $\theta$  renders  $\theta^r$  or  $\theta_h^r$  constant according to (7) or (44. b) in the respective case. The  $\theta^r$  is thus practically equal to  $\theta$  in case of homogeneous model. The  $\theta_h^r$  equals on the other hand nearly  $\theta$  in case of revised model as seen from the equation  $\theta_h^r = (\theta - x)/(1 - x)$ , as derived from (44. b) for  $\theta_i^s = 1$ , which gives  $\theta_h^r = 0.192$  or  $0.293$  respectively for  $\theta = 0.200$  or  $0.300$

On these grounds,  $W - T(\partial W/\partial T)_\theta$  for the revised model at the specified condition is directly interpolated, ignoring the difference between  $\theta_h^r$  and  $\theta$  on the revised model, from Table 1 for the homogeneous model as in the text.

$$Q_i^H - Q_h^H = 0.963(\epsilon^r - \epsilon_i^s) - 0.20 \text{ kcal}, \quad \theta = 0.2, \quad (64. a)$$

$$Q_i^H - Q_h^H = 0.963(\epsilon^r - \epsilon_i^s) - 0.07 \text{ kcal}, \quad \theta = 0.3. \quad (64. b)$$

The premise (46. q) leads on the other hand to the value of  $\epsilon^r - \epsilon_i^s$ , with reference to (14. q), (43. b)\*), (30), (46. q) and (24), *i. e.*

$$\epsilon^r - \epsilon_i^s = 4.24 \text{ kcal/mol adatom, } 25^\circ\text{C}. \quad (65)$$

We have from (64) and (65)

$$Q_i^H - Q_h^H = 3.9 \text{ kcal/mol adatom, } \theta_h = \theta_h^r = 0.2,$$

$$Q_i^H - Q_h^H = 4.0 \text{ kcal/mol adatom, } \theta_h = \theta_h^r = 0.3.$$

The experimental value of  $Q_i^H - Q_h^H$  is determined from the smoothed curve in Fig. 3 of the paper of RIDEAL and SWEETT<sup>2)</sup> at 3.9 kcal/mol at  $\theta=0.2$  and 4.2 kcal/mol at  $\theta=0.3$ , which confirms the premise (46. q). The experimental result<sup>2)</sup> is thus consistently explained on the basis of the revised model advanced in § 9, that the sites of hydrogen adatoms consist of the majority of *h*-sites, which are physically identical with those on the homogeneous model and the minority of *i*-sites, which admit *s*-adatoms only with distinctly higher heat of adsorption.

### § 13. Entropy at Higher Coverage

We now investigate the course of entropy at higher coverage beyond  $\theta=0.3$  on the bases of the revised model. Difference between  $\theta$  and  $\theta_h = \theta_h^r + \theta_h^s$  is practically ignorable in the region of  $\theta$  in question\*\*, while  $\theta_h^r$  or  $\theta_h^s$  varies with  $\theta_h$  identically as  $\theta^r$  or  $\theta^s$  does with  $\theta$  on the homogeneous model as mentioned in the foregoing section. The course of entropy is hence dealt with on the basis of the revised model identifying  $\theta_h, \theta_h^r, \theta_h^s, S_h^r, S_h^s$  and  $S_{II}^H$  respectively with  $\theta, \theta^r, \theta^s, S^r, S^s$  and  $S_I^H$ , thus directly referring to Table 1. The steep rise of  $S_I^H$  with  $\theta$  and the subsequent maximum theoretically predicted as seen in Fig. 3 are thus discussed below respectively under the heading (A) and (B). The data at  $0^\circ\text{C}$  will be exclusively referred to for the sake of definiteness.

(A) The steep rise of  $S^H$  around  $\theta=0.45$  shown in Fig. 3 is due to that of  $S^r$  rather than that of  $S^s$ , since the weight  $\theta^s(1-\theta^s)$  of the latter in (9. S) is extremely small in the range of  $\theta$  in question, and  $S^s$  itself decreases with increase of  $\theta$  as seen from (9. s). The rapid rise of  $S^r$  is now due to that of the entropy of repulsion  $-(\partial W/\partial T)_\theta$  according to (9. r) and (25. a), the second

\*) The parameters  $A_i$  and  $\nu_i$  in (43. b) are identified respectively with  $A$  and  $\nu$  in (21. a); *cf.* § 9.

\*\*) *Cf.* footnote on p. 112.

term on the right of (9. r) decreasing with increase of  $\theta$  as seen in Table 1, while the first term on the right of (25. a) remaining constant in accordance with (25. b). The rapid increase of the entropy of repulsion is, as seen in Table 1, due to both the contributions  $-(\partial W/\partial T)_\theta$  and  $-(\partial W/\partial \theta^r)_T (\partial \theta^r/\partial T)_\theta$ , to  $-(\partial W/\partial T)_\theta$  according to (27); the first factor  $(\partial W/\partial \theta^r)_T$  of the second contribution has a large positive value over the range of  $\theta$  in question as seen in Fig. 2 and its second factor with negative sign, *i. e.*  $-(\partial \theta^r/\partial T)_\theta$  does as well, as seen in Table 1, which makes the second contribution appreciable. It may be noted that large positive value of  $(-\partial \theta^r/\partial T)_\theta$  originates from the replacement of r-adatoms by s-adatoms with rise of temperature at constant  $\theta$ , indicating that the dual state of adatom, on which premise the present theory is developed, is essential to the rapid rise of  $S^H$ .

(B)  $S_I^H$  is depressed at higher  $\theta$  through the second terms  $R \ln \{(1 - \theta^r)/\theta^r\}$  and  $R \ln \{(1 - \theta^s)/\theta^s\}$  respectively in (9. r) and (9. s), which tend both to minus infinity as  $\theta^r$  and  $\theta^s$  approach unity with increase of  $\theta$ . In the present approximation, where the repulsion among s-adatoms is ignored,  $\theta^s$  approaches unity more readily than in case, where the repulsion were taken into account. Table 1 shows that  $\theta^s$  is 0.9966 for  $\theta^r = 0.8752$ . The depression of  $S_I^H$  at higher  $\theta$  is thus mainly due to the ready approach of  $\theta^s$  to unity. The neglect of the repulsive interaction results, besides, in too large a value of  $-(\partial \theta^r/\partial T)_\theta$ , which equals  $(\partial \theta^s/\partial T)_\theta$ , *i. e.* the rate of increase of  $\theta^s$  according to (7). Too large a value of  $-(\partial \theta^r/\partial T)_\theta$  renders  $-(\partial W/\partial T)_\theta$  and hence  $S^r$  too large according to (27), (25. a) and (9. r), and in consequence the theoretical value of  $S_I^H$  too large according to (9. s) over the region of  $\theta$ , where  $(\partial W/\partial \theta^r)_T$  is appreciably large as seen in Fig. 2.

The allowance for the repulsive interaction among s-adatoms is thus expected, to make the increase of  $\theta^s$  more reluctant and in consequence the rise of  $S_I^H$  toward the maximum less steep and the depression at higher coverage less sharp, hence to shift the maximum toward higher coverage.

#### § 14. Concluding Remarks

The observed entropy of hydrogen on nickel was accounted for on the basis of the previous conclusion<sup>4,5,6)</sup> that hydrogen adatoms exists both in r- and s-state, and of the model of the adsorbent that the adsorption sites consists of a majority of *h*-sites and a minority of *i*-sites. The *h*-sites are composed of a group of sites for r-adatoms and another group of those for s-adatoms, both the groups are equal in number to metal atom in (110)-lattice plane at the surface and sites of each group are respectively physically identical with each other. The *i*-sites are the sites provided by the lattice imperfections,



which accommodate s-adatoms alone with distinctly lower energy than that of adatoms of any kind on *h*-site. The repulsive interactions among r-adatoms were taken into account, whereas those among s-adatoms<sup>4,5,6</sup>) ignored idealizing the theoretical conclusion that the latter interactions are weaker than the former.

The theoretical conclusions have been experimentally verified as far as the rapid rise of entropy around  $\theta=0.45$ , predicting beyond, that the entropy passes through a maximum and then decreases with further increase of  $\theta$ .

It has been pointed out that the steep rise of entropy with increase of  $\theta$  around  $\theta=0.45$  is due to that of the entropy of repulsion  $-(\partial W/\partial T)_\theta = -(\partial W/\partial T)_{\theta^r} - (\partial W/\partial \theta^r)_T (\partial \theta^r/\partial T)_\theta$ , which is enhanced by the replacement of r-adatoms by s-adatoms with rise of temperature through the factor  $-(\partial \theta^r/\partial T)_\theta$  and that the allowance for the repulsive interaction among s-adatoms would shift the maximum of entropy toward higher  $\theta$ . The observed rapid rise of entropy with  $\theta$  around  $\theta=0.45$  thus verifies the previous conclusion on the dual state of adatoms on which basis present theory has been developed.

It may be noted that  $\theta$  runs up to 2 theoretically because of the premised dual state apart from a slight deviation due to the presence of *i*-sites, whereas the observed entropy is referred to the fraction  $\theta$  of the adsorbed quantity over that at  $-195^\circ\text{C}$  and  $1.5 \times 10^{-3}$  mmHg pressure<sup>2)</sup>. In Fig. 3 the observed entropy is plotted against the latter experimental value of  $\theta$ . The general agreement between the observed and the experimental entropy plotted against the respective values of  $\theta$  would suggest that the adsorbed quantity at  $-195^\circ\text{C}$  and  $1.5 \times 10^{-3}$  mmHg mentioned above corresponds just to  $\theta=1$  on the theoretical base. This is possible from the present theoretical point of view, if the s-state of adatoms is practically inhibited at low temperature perhaps by a higher activation energy. If then, the experimental value of  $\theta$  should exceed unity at higher temperature and higher hydrogen pressure. With regard to the latter two points, *i.e.* the behavior of entropy at  $\theta$  beyond the steep rise and the suggested excess of  $\theta$  over unity, it is desirable to observe the entropy at higher coverage.

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### Appendix 1

Derivation of Eqs. (9) and (45)

Eq. (8) is written as

$$S^H = R \ln p^H + RT(\partial \ln p^H / \partial T)_\theta. \quad (i)$$

The second term on the right-hand side of the above equation is obtained by differentiating (6) with respect to  $T$  at constant  $\theta$  as

$$(\partial \theta^r / \partial T)_\theta = \theta^r (1 - \theta^r) \{ (\partial \ln q^r / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \},$$

$$(\partial \theta^s / \partial T)_\theta = \theta^s (1 - \theta^s) \{ (\partial \ln q^s / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \},$$

and solving the above two equations for  $(\partial \ln p^H / \partial T)_\theta$ , noting  $(\partial \theta^r / \partial T)_\theta + (\partial \theta^s / \partial T)_\theta = 0$  according to (7), as

$$RT \left( \frac{\partial \ln p^H}{\partial T} \right)_\theta = \frac{\theta^r (1 - \theta^r) RT (\partial \ln q^r / \partial T)_\theta + \theta^s (1 - \theta^s) RT (\partial \ln q^s / \partial T)_\theta}{\theta^r (1 - \theta^r) + \theta^s (1 - \theta^s)}. \quad (ii)$$

The first term  $R \ln p^H$  in (i) developed on the other hand according to (6) as

$$\begin{aligned} R \ln p^H &= \frac{R \theta^r (1 - \theta^r) \ln p^H + R \theta^s (1 - \theta^s) \ln p^H}{\theta^r (1 - \theta^r) + \theta^s (1 - \theta^s)}, \\ &= \frac{R \theta^r (1 - \theta^r) \ln q^r + R \theta^s (1 - \theta^s) \ln q^s}{\theta^r (1 - \theta^r) + \theta^s (1 - \theta^s)} \\ &\quad + \frac{R \theta^r (1 - \theta^r) \ln \{ (1 - \theta^r) / \theta^r \} + R \theta^s (1 - \theta^s) \ln \{ (1 - \theta^s) / \theta^s \}}{\theta^r (1 - \theta^r) + \theta^s (1 - \theta^s)}. \quad (iii) \end{aligned}$$

Eq. (9) is obtained by substituting  $RT(\partial \ln p^H / \partial T)_\theta$  and  $R \ln p^H$  respectively from (ii) and (iii) into (i).

In case of (45), where r-adatoms on  $h$ -sites and s-adatoms on  $i$ -sites are exclusively dealt with, we have from (42. r), (43. a) and (44. b) by differentiation

$$(\partial \theta_h^r / \partial T)_\theta = \theta_h^r (1 - \theta_h^r) \{ (\partial \ln q_h^r / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \},$$

$$(\partial \theta_i^s / \partial T)_\theta = \theta_i^s (1 - \theta_i^s) \{ (\partial \ln q_i^s / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \},$$

and

$$x(\partial \theta_i^s / \partial T)_\theta + (1 - x)(\partial \theta_h^r / \partial T)_\theta = 0.$$

Eliminating  $(\partial \theta_h^r / \partial T)_\theta$  and  $(\partial \theta_i^s / \partial T)_\theta$  from the above three equations, we have

$$RT \left( \frac{\partial \ln p^H}{\partial T} \right)_\theta = \frac{(1 - x) \theta_h^r (1 - \theta_h^r) (\partial \ln q_h^r / \partial T)_\theta + x \theta_i^s (1 - \theta_i^s) (\partial \ln q_i^s / \partial T)_\theta}{(1 - x) \theta_h^r (1 - \theta_h^r) + x \theta_i^s (1 - \theta_i^s)}.$$

Equation similar to (iii) is obtained by developing  $R \ln p^H$  with reference to (42. r) and (43. a) as

$$\begin{aligned} R \ln p^H &= \frac{R(1 - x) \theta_h^r (1 - \theta_h^r) \ln q_h^r + R x \theta_i^s (1 - \theta_i^s) \ln q_i^s}{(1 - x) \theta_h^r (1 - \theta_h^r) + x \theta_i^s (1 - \theta_i^s)} \\ &\quad + \frac{R(1 - x) \theta_h^r (1 - \theta_h^r) \ln \{ (1 - \theta_h^r) / \theta_h^r \} + R x \theta_i^s (1 - \theta_i^s) \ln \{ (1 - \theta_i^s) / \theta_i^s \}}{(1 - x) \theta_h^r (1 - \theta_h^r) + x \theta_i^s (1 - \theta_i^s)}. \end{aligned}$$

Substituting  $RT(\partial \ln p^H / \partial T)_\theta$  and  $R \ln p^H$  from the above two equations into the general equation (i), we have (45).

## Appendix 2

### Second Approximation of Free Energy of Repulsion $W$ .

HORIUTI and HIROTA<sup>12)</sup> previously presented the second approximation of the adsorption isotherm as a special case of the third approximation, referring to a mathematical equivalent of the free energy  $W$  of repulsion advanced in the present paper. The  $W$  of the second approximation is derived below in direct connection with the present treatment.

Consider a particular group  $\Sigma$  of sites on  $C^*$ , consisting of a site  $\sigma_0$  of interest on (110)-lattice plane, two first nearest sites,  $\sigma_1$  and  $\sigma_2$ , and two second nearest sites,  $\sigma_3$  and  $\sigma_4$ , respectively to  $\sigma_0$  as shown in Fig. 4. The  $q^r$  is written, according to (4) with special reference to  $\sigma_0$ , as

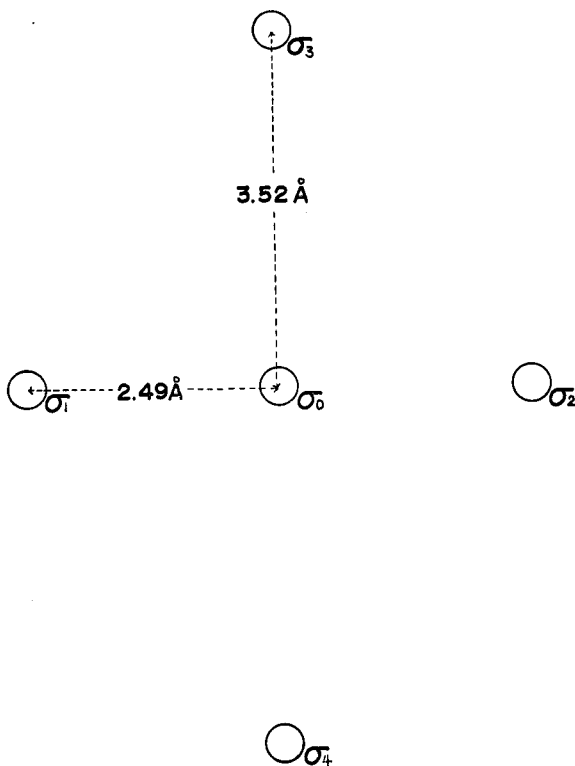


Fig. 4. Group  $\Sigma$  of Sites of r-Adatoms.

\*)  $C$  is, as mentioned in §1, a macroscopic adsorbent retaining a definite amount of adsorbate.

$$q^r = \Omega C_{\sigma_0(r)}^r / \Omega C_{\sigma_0(0)} \quad (\text{i})$$

The  $\Omega C_{\sigma_0(r)}^r$  and  $\Omega C_{\sigma_0(0)}$  are now developed in terms of the partition function  $\Omega C_{\Sigma(0)}$  of the particular state  $C_{\Sigma(0)}$  of  $C$ , where  $\Sigma$  is completely unoccupied. The  $C_{\sigma_0(0)}$  comprises five states which differ in the number  $n$  of occupied sites among the four ones environing  $\sigma_0$  in  $\Sigma$ . The partition function  $\Omega C_{\sigma_0(0)}$  is the total sum of the partition function of the five different states, *i.e.*

$$\Omega C_{\sigma_0(0)} = \sum_{n=0}^4 \Omega C_{\Sigma(0,n)} \quad (\text{ii})$$

$\Omega C_{\Sigma(0,n)}$  is the partition function of the state  $C_{\Sigma(0,n)}$  of  $C$ , which has  $n$  r-adatoms on four sites environing  $\sigma_0$  but none on  $\sigma_0$ . Each state specified by  $n$  consists now of a group of particular states, which differ in arrangement of  $n$  r-adatoms over the four environing sites, so that  $\Omega C_{\Sigma(0,n)}$  is the sum of the partition functions of the appropriate particular states.

$\Omega C_{\Sigma(0,0)}$  for  $n=0$  is of course  $\Omega C_{\Sigma(0)}$  itself.

$\Omega C_{\Sigma(0,1)}$  for  $n=1$  is the sum of partition functions of the four particular states

$$\Omega C_{\Sigma(0,1)} = \Omega C_{\Sigma(0,r_1)} + \Omega C_{\Sigma(0,r_2)} + \Omega C_{\Sigma(0,r_3)} + \Omega C_{\Sigma(0,r_4)} \quad (\text{iii})$$

where  $r_1$  *etc.* signifies r-adatom on  $\sigma_1$  *etc.* respectively. The particular state  $C_{\Sigma(0,r_1)}$  is derived from  $C_{\Sigma(0)}$  by extracting one r-adatom from outside  $\Sigma$  and putting it in  $\sigma_1$ . The former step of extraction changes the partition function of the system from  $\Omega C_{\Sigma(0)}$  to  $\Omega C_{\Sigma(0)}/p^H$  in accordance with (2), ignoring the effect on  $p^H$  of the microscopic constraint signified by  $\Sigma(0)$ , whereas the subsequent one from  $\Omega C_{\Sigma(0)}/p^H$  to  $\Omega C_{\Sigma(0)} q_{\Sigma(0,r_1)}^r / p^H$  in accordance with (4), hence

$$\Omega C_{\Sigma(0,r_1)} = \Omega C_{\Sigma(0)} q_{\Sigma(0,r_1)}^r / p^H, \quad (\text{iv. a})$$

bold letter  $r_1$  characterizing the r-adatom brought to  $\sigma_1$  by the relevant operation;  $-kT \ln q_{\Sigma(0,r_1)}^r$  is the appropriate free energy increase, expressed as

$$-kT \ln q_{\Sigma(0,r_1)}^r = -kT \ln q_0^r - kT \ln \eta_1, \quad (\text{iv. b})$$

where  $-kT \ln \eta_1$  is the additional free energy increase due to the interaction between  $r_1$  and r-adatoms outside  $\Sigma$ . We have from the above equation

$$q_{\Sigma(0,r_1)}^r = q_0^r \eta_1, \quad (\text{iv. c})$$

hence from (iv. a) with reference to (15)

$$\Omega C_{\Sigma(0,r_1)} = \Omega C_{\Sigma(0)} \eta_1. \quad (\text{v. a})$$

Similar reasoning shows that  $\Omega C_{\Sigma(0,r_2)}$  is identical with  $\Omega C_{\Sigma(0,r_1)}$  because of the symmetry of  $\Sigma$  and the physical identity of sites, hence

$$\Omega C_{\Sigma(0,r_2)} = \Omega C_{\Sigma(0)} \gamma \eta_I \quad (\text{v. b})$$

and that  $\Omega C_{\Sigma(0,r_3)}$  and  $\Omega C_{\Sigma(0,r_4)}$  are similarly identical with each other and expressed respectively as  $\Omega C_{\Sigma(0)} \gamma \eta_{II}$ , *i. e.*

$$\Omega C_{\Sigma(0,r_3)} = \Omega C_{\Sigma(0,r_4)} = \Omega C_{\Sigma(0)} \gamma \eta_{II}, \quad (\text{v. c})$$

the relevant free energy increase  $-kT \ln \eta_{II}$  being that due to the interaction between  $r_3$  or  $r_4$  and adatoms outside  $\Sigma$ . We have from (iii) and (v)

$$\Omega C_{\Sigma(0,1)} = 2\Omega C_{\Sigma(0)} \gamma (\eta_I + \eta_{II}). \quad (\text{vi})$$

$\Omega C_{\Sigma(0,2)}$  is the sum of the partition functions respectively of six particular states of  $C_{\Sigma(0,2)}$ , *i. e.*

$$\begin{aligned} \Omega C_{\Sigma(0,2)} &= \Omega C_{\Sigma(0,r_1,r_2)} + \Omega C_{\Sigma(0,r_3,r_4)} + \Omega C_{\Sigma(0,r_1,r_3)} \\ &+ \Omega C_{\Sigma(0,r_1,r_4)} + \Omega C_{\Sigma(0,r_2,r_3)} + \Omega C_{\Sigma(0,r_2,r_4)}. \end{aligned} \quad (\text{vii})$$

$\Omega C_{\Sigma(0,r_1,r_2)}$  *etc.* are respectively the partition functions of the particular states  $C_{\Sigma(0,r_1,r_2)}$  *etc.* of  $C_{\Sigma(0,2)}$ , where the pair of sites,  $\sigma_1$  and  $\sigma_2$ , *etc.*, but none of others inside  $\Sigma$  are occupied. The particular state  $C_{\Sigma(0,r_1,r_2)}$  is derived from  $C_{\Sigma(0,r_1)}$  by transferring a r-adatom from outside  $\Sigma$  to  $\sigma_2$ ; the partition function thus changes from  $\Omega C_{\Sigma(0,r_1)}$  to  $\Omega C_{\Sigma(0,r_1)} q_{\Sigma(0,r_1,r_2)}^r / p^H$ , hence

$$\Omega C_{\Sigma(0,r_1,r_2)} = \Omega C_{\Sigma(0,r_1)} q_{\Sigma(0,r_1,r_2)}^r / p^H$$

as in the case of (iv. a), where  $q_{\Sigma(0,r_1,r_2)}^r$  is the BOLZMANN factor of the free energy increase  $-kT \ln q_{\Sigma(0,r_1,r_2)}^r$  caused by the r-adatom  $r_2$  added to  $\sigma_2$  in the presence of  $r_1$ . The latter free energy increase is given similarly as in the case of (iv. b) as

$$-kT \ln q_{\Sigma(0,r_1,r_2)}^r = -kT \ln q_0^r - kT \ln \eta_I,$$

inasmuch as the additional free energy increase due to the interaction between  $r_2$  and r-adatoms outside  $\Sigma$  is identical with  $-kT \ln \eta_I$  in (iv. b), because of symmetry of  $\Sigma$  and the physical identity of sites; the interaction between  $r_1$  and  $r_2$ , is not taken into account in the present approximation, they being the fourth nearest neighbours as seen in Fig. 4. We have from the last two equations with reference to (15)

$$\Omega C_{\Sigma(0,r_1,r_2)} = \Omega C_{\Sigma(0,r_1)} \gamma \eta_I$$

or according to (v. a)

$$\Omega C_{\Sigma(0,r_1,r_2)} = \Omega C_{\Sigma(0)} \gamma^2 \eta_I^2. \quad (\text{viii. a})$$

The similar reasoning leads to the equations

$$\Omega C_{\Sigma(0,r_3,r_4)} = \Omega C_{\Sigma(0)} \gamma^2 \eta_{II}^2 \quad (\text{viii. b})$$

and

$$\Omega C_{\Sigma(0, r_1, r_3)} = \Omega C_{\Sigma(0, r_1, r_4)} = \Omega C_{\Sigma(0, r_2, r_3)} = \Omega C_{\Sigma(0, r_2, r_4)} = \Omega C_{\Sigma(0)} \gamma^2 \eta_I \eta_{II}. \quad (\text{viii. c})$$

We have from (vii) and (viii)

$$\Omega C_{\Sigma(0, 2)} = \Omega C_{\Sigma(0)} \gamma^2 (\eta_I^2 + \eta_{II}^2 + 4\eta_I \eta_{II}). \quad (\text{ix})$$

Similarly we have

$$\Omega C_{\Sigma(0, 3)} = 2\Omega C_{\Sigma(0)} \gamma^3 \eta_I \eta_{II} (\eta_I + \eta_{II}) \quad (\text{x})$$

and

$$\Omega C_{\Sigma(0, 4)} = \Omega C_{\Sigma(0)} \gamma^4 \eta_I^2 \eta_{II}^2, \quad (\text{xi})$$

hence from (ii), (vi), (ix), (x) and (xi)

$$\Omega C_{\sigma_0(0)} = \Omega C_{\Sigma(0)} (1 + \gamma \eta_I)^2 (1 + \gamma \eta_{II})^2. \quad (\text{xii})$$

The partition function  $\Omega C_{\sigma_0(r)}^r$  in (i) is constructed similarly as in the case of  $\Omega C_{\sigma_0(0)}$  as the sum of the partition functions  $\Omega C_{\Sigma(r_0, n)}$  of the states  $C_{\Sigma(r_0, n)}^r$  of  $C^r$ , where  $\sigma_0$  as well as  $n$  sites among those envrioning  $\sigma_0$  are occupied, leaving other sites inside  $\Sigma$  unoccupied, *i. e.*

$$\Omega C_{\sigma_0(r)}^r = \sum_{n=0}^4 \Omega C_{\Sigma(r_0, n)}^r; \quad (\text{xiii})$$

each state  $C_{\Sigma(r_0, n)}^r$  consists, similarly as in the case of  $C_{\Sigma(0, n)}$ , of the group of particular states, which differ from each other in arrangement of  $n$  r-adatoms, so that the partition function  $\Omega C_{\Sigma(r_0, n)}^r$  is the sum of those of the appropriate particular states.

The partition function  $\Omega C_{\Sigma(r_0, 0)}^r$  is derived from  $\Omega C_{\Sigma(0)}$  by accounting for the change of the partition function caused by addition of one r-adatom to  $C_{\Sigma(0)}$  as

$$\Omega C_{\Sigma(r_0, 0)}^r = \Omega C_{\Sigma(0)} q_{\Sigma(r_0)}^r;$$

the factor  $1/p^H$  is absent here in distinction from in the case of (iv. a), inasmuch as  $C_{\Sigma(r_0, 0)}^r$  is derived from  $C_{\Sigma(0)}$  by definition by net addition to  $C_{\Sigma(0)}$  of one r-adatom brought from outside. The appropriate free energy increase  $-kT \times \ln q_{\Sigma(r_0, 0)}^r$  equals now  $-kT \ln q_0^r$  in accordance with (10), inasmuch as no interaction between  $r_0$  and other r-adatoms exists because of the absence of any interaction of r-adatom on the four sites envrioning  $\sigma_0$  taken into account in the present approximation. We have in consequence

$$\Omega C_{\Sigma(r_0, 0)}^r = \Omega C_{\Sigma(0)} q_0^r. \quad (\text{xiv})$$

The partition function  $\Omega C_{\Sigma(r_0, 1)}^r$  is, similarly as in the case of  $\Omega C_{\Sigma(0, 1)}$  in

(iii), the sum of the partition functions of four particular states, *i. e.*

$$\Omega C_{\Sigma(r_0,1)}^r = \Omega C_{\Sigma(r_0,r_1)}^r + \Omega C_{\Sigma(r_0,r_2)}^r + \Omega C_{\Sigma(r_0,r_3)}^r + \Omega C_{\Sigma(r_0,r_4)}^r. \quad (\text{xv})$$

The particular state  $C_{\Sigma(r_0,r_1)}^r$  is derived from  $C_{\Sigma(r_0,0)}^r$  by transferring an r-adatom from outside  $\Sigma$  to  $\sigma_1$ ; the relevant partition function thus changes from  $\Omega C_{\Sigma(r_0,0)}^r$  to  $\Omega C_{\Sigma(r_0,0)}^r q_{\Sigma(r_0,r_1)}^r / p^H$  as in the case of (iv. a),  $q_{\Sigma(r_0,r_1)}^r$  being the BOLTZMANN factor of the free energy increase  $-kT \ln q_{\Sigma(r_0,r_1)}^r$  caused by the r-adatom added at  $\sigma_1$ , *i. e.*  $r_1$ , in the presence of  $r_0$  on  $\sigma_0$ . The latter free energy increase is expressed as

$$-kT \ln q_{\Sigma(r_0,r_1)}^r = -kT \ln q_0^r - kT \ln \eta_1 - kT \ln \xi_1,$$

where  $-kT \ln \xi_1$  is its part, not present in (iv. b), due to the repulsive interaction between  $r_0$  and  $r_1$ . We have from the above equation

$$q_{\Sigma(r_0,r_1)}^r = q_0^r \eta_1 \xi_1,$$

hence

$$\Omega C_{\Sigma(r_0,r_1)}^r = \Omega C_{\Sigma(r_0,0)}^r \eta_1 \eta_1 \xi_1$$

with reference to (15) or according to (xiv)

$$\Omega C_{\Sigma(r_0,r_1)}^r = \Omega C_{\Sigma(0)}^r q_0^r \eta_1 \eta_1 \xi_1. \quad (\text{xvi. a})$$

The  $\Omega C_{\Sigma(r_0,r_2)}^r$  is similarly expressed, identically with  $\Omega C_{\Sigma(r_0,r_1)}^r$ , as

$$\Omega C_{\Sigma(r_0,r_2)}^r = \Omega C_{\Sigma(0)}^r q_0^r \eta_1 \eta_1 \xi_1 \quad (\text{xvi. b})$$

and  $\Omega C_{\Sigma(r_0,r_3)}^r$  and  $\Omega C_{\Sigma(r_0,r_4)}^r$  identically as

$$\Omega C_{\Sigma(r_0,r_3)}^r = \Omega C_{\Sigma(r_0,r_4)}^r = \Omega C_{\Sigma(0)}^r q_0^r \eta_1 \eta_1 \xi_{II}, \quad (\text{xvi. c})$$

where  $\xi_{II}$  is the BOLTZMANN factor of the free energy increase due to the repulsion between  $r_3$  or  $r_4$  and  $r_0$ . We have from (xv) and (xvi)

$$\Omega C_{\Sigma(r_0,1)}^r = 2 \Omega C_{\Sigma(0)}^r q_0^r (\eta_1 \xi_1 + \eta_1 \xi_{II}). \quad (\text{xvii})$$

Extending the above reasoning, we have

$$\Omega C_{\Sigma(r_0,2)}^r = \Omega C_{\Sigma(0)}^r q_0^r \gamma^2 (\eta_1^2 \xi_1^2 + \eta_{II}^2 \xi_{II}^2 + 4 \eta_1 \eta_{II} \xi_1 \xi_{II}), \quad (\text{xviii. a})$$

$$\Omega C_{\Sigma(r_0,3)}^r = 2 \Omega C_{\Sigma(0)}^r q_0^r \gamma^3 \eta_1 \eta_{II} \xi_1 \xi_{II} (\eta_1 \xi_1 + \eta_{II} \xi_{II}) \quad (\text{xviii. b})$$

and

$$\Omega C_{\Sigma(r_0,4)}^r = \Omega C_{\Sigma(0)}^r q_0^r \gamma^4 \eta_1^2 \eta_{II}^2 \xi_1^2 \xi_{II}^2, \quad (\text{xviii. c})$$

hence from (xiii), (xvii) and (xviii)

$$\Omega C_{\sigma_0(r)}^r = \Omega C_{\Sigma(0)}^r q_0^r (1 + \gamma \eta_1 \xi_1)^2 (1 + \gamma \eta_{II} \xi_{II})^2. \quad (\text{xix})$$

Eqs. (i), (xii) and (xix) lead to the expression of  $q^r$ , *i. e.*

$$q^r = q_o^r \frac{(1 + \gamma \eta_I \xi_I)^2 (1 + \gamma \eta_{II} \xi_{II})^2}{(1 + \gamma \eta_I)^2 (1 + \gamma \eta_{II})^2}.$$

Eq. (16. a) is obtained by comparing the above equation with (10).

The determination of  $W(T, \gamma)$  requires those of  $\xi_I$ ,  $\xi_{II}$ ,  $\eta_I$  and  $\eta_{II}$  implied in (16. a). The  $\xi_I$  and  $\xi_{II}$  are approximated as (17) by identifying the relevant free energy increase  $-kT \ln \xi_I$  and  $-kT \ln \xi_{II}$  respectively with the repulsive potentials  $R_I$  and  $R_{II}$ . The  $\eta_I$  and  $\eta_{II}$  are determined by equating  $\Omega C_{\sigma_o(o)}$ , in accordance with the BETHE and PEIERLS' method<sup>14)</sup>, with the partition functions  $\Omega C_{\sigma_1(o)}$  and  $\Omega C_{\sigma_3(o)}$  respectively of the states  $C_{\sigma_1(o)}$  and  $C_{\sigma_3(o)}$ , where  $\sigma_1$  and  $\sigma_3$  are respectively unoccupied with certainty, as

$$\Omega C_{\sigma_o(o)} = \Omega C_{\sigma_1(o)} = \Omega C_{\sigma_3(o)}. \quad (\text{xx})$$

$\Omega C_{\sigma_1(o)}$  and  $\Omega C_{\sigma_3(o)}$  are derived by similar reasoning as

$$\Omega C_{\sigma_1(o)} = \Omega C_{\Sigma(o)} \left\{ (1 + \gamma \eta_I) (1 + \gamma \eta_{II})^2 + \gamma (1 + \gamma \eta_I \xi_I) (1 + \gamma \eta_{II} \xi_{II})^2 \right\} \quad (\text{xxi. a})$$

and

$$\Omega C_{\sigma_3(o)} = \Omega C_{\Sigma(o)} \left\{ (1 + \gamma \eta_I)^2 (1 + \gamma \eta_{II}) + \gamma (1 + \gamma \eta_I \xi_I)^2 (1 + \gamma \eta_{II} \xi_{II}) \right\}. \quad (\text{xxi. b})$$

Eq. (16. b) is obtained from (xii), (xx) and (xxi), which decides  $\eta_I$  and  $\eta_{II}$  as respective functions of  $\gamma$ ,  $\xi_I$  and  $\xi_{II}$ . The  $W$  is in consequence determined as a function of  $T$  and  $\gamma$  by (16) with reference to (17).

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