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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 KWAN¹⁾ and recently by RIDEAL and SWEET²⁾. 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^{3,4)} 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 conductivity⁴⁾, the work function of adsorbent⁴⁾, and the infrared absorption of adatoms⁵⁾. 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 discussed⁶⁾ 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

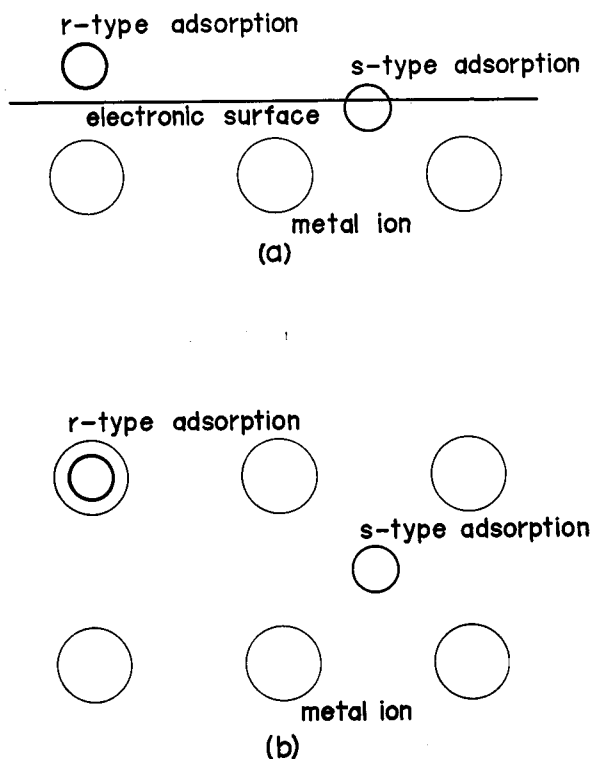


Fig. 1. Two types of adsorption. The r-type adatom is slightly negatively polarized, and its equilibrium position right above a metal ion at *ca.* 1Å outside the electronic surface of the metal. The equilibrium position of s-type adsorption is interstitial and *ca.* 0.5Å inside the electronic surface.

inferences^{3,5)}.

I) The equilibrium position of r-atom is situated right above a metal atom on a lattice plane exposed at the surface of metallic adsorbent, *ca.* 1Å outside its electronic surface⁶⁾, whereas that of s-atom is in an interstitial surface site, *ca.* 0.5Å inside the electronic surface⁶⁾ 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-atom 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^{1,6)}, 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-atom specified in the above inferences is essentially the same as adatom hitherto conceived regardless of the dual state of adatom^{7,8)}.

III) Both r- and s-atom 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-atom vibrates with frequencies comparable with those of bending vibrations, whereas s-atom conducts practically two dimensional translational motion parallel to the surface^{5,6)}.

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^{7,9,10)*}.

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 MACRAE¹⁰⁾ 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 μ^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 μ^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 ΩC or ΩC^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^{7,11)}

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

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 σ 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 σ .

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 σ 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

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

provided that σ is either occupied by one H or unoccupied exclusively. Denoting $\Omega C_{\sigma(\text{H})}^{\text{H}}/\Omega C^{\text{H}}$ by θ^{H} we have from the above two equations¹¹⁾

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

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

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

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

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

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

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.*

$$S_{\text{I}}^{\text{H}} = (\partial RT \ln p^{\text{H}}/\partial T)_{\theta}, \quad (8)$$

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

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

where

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

and

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

The S_{I}^{H} is obtained as a function of T and θ according to (9), by determining q^{r} and q^{s} , as respective functions of T and θ .

§ 2. Formulation of q^{r}

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

preliminarily evacuated site σ 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 ΩC_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 σ . 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 cm^{-1} deduced from the DEBYE temperature of the adsorbent nickel is sufficiently low as compared with the estimated lowest frequency^{*)} 417 cm^{-1} of the r-adatom and the approximately covalent nature of the bond of r-adatom⁴⁾ 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 ϵ_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 Ωr in the above equation is developed in accordance with III) in the introduction as⁷⁾

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

as previously deduced from the above mentioned potential field of r-adatom⁷⁾, 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).

$$q_0^r = \prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \exp\left(-\frac{\varepsilon^r}{kT}\right), \quad (14. q)$$

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^{11,12,13)} 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 method¹⁴⁾. 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 $W(T, \gamma)$ of T and γ , *i. e.*

$$\gamma = q_0^r/p^H \quad (15)$$

by eliminating η_I and η_{II} between the three simultaneous equations

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

and

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

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_0^r of (11), with that of adding an s-adatom on a bare adsorbent C_0 , as

$$q^s = \Omega C_{\sigma(s),0}^s / \Omega C_0 \quad (18)$$

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

$$\Omega C_{\sigma(s),0}^s = \Omega C_0 \cdot \Omega s \cdot \exp(-\varepsilon_0^s/kT), \quad (19)$$

where Ωs or ε_0^s is the partition function or the minimum potential energy of s-adatom in the potential field of C_0 , which corresponds to Ωr or ε_0^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 Ωs 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 σ , m the effective mass of the translation and ν the frequency of the valence vibration normal to the electronic surface.

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

$$q^s = A \frac{2\pi mkT}{h^2} \exp\left(-\frac{\varepsilon_0^s}{kT}\right) \left\{1 - \exp\left(-\frac{h\nu}{kT}\right)\right\}^{-1}, \quad (21. a)$$

where

$$\varepsilon^s = \varepsilon_0^s + h\nu/2 \quad (21. b)$$

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

The A in (21. a) is estimated as follows. Let θ^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. ΩC of C retaining N^s-1 s-adatoms is given as

$$\Omega C = \Omega C_0 (Q^s)^{N^s-1} / (N^s-1)!, \quad (22. a)$$

where

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

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 ΩC^s of C^s formed by adding another s-adatom to C is given similar to ΩC 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 θ^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 / θ^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 \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 γ according to (16) and (17) with parameters R_I and R_{II} , *i. e.*

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

where γ is connected with θ^r by (6. r), (10) and (15) as

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

It follows from (26. a) and (26. b) that W is given as a function of T and θ^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^{12)*}.

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)

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

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

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

and noting the condition of constant θ in accordance with (7), *i. e.*

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

we have

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

The $(\partial \theta^r/\partial T)_\theta$ is determined computing $d \ln(q_\theta^r/q^\theta)/dT$ by (14. q) and (21. a) on the base of parameters $\nu_1, \nu_2, \nu_3, \nu, \varepsilon^r$ and ε^θ 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^θ .

The q^r is given as a function of γ 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 γ with parameters ν_1, ν_2, ν_3 and ϵ^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 ν_1, ν_2 and ν_3 have previously been estimated with special reference to (110)-lattice plane of nickel as⁷⁾

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

and ν as^{4,6)}

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

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-adatoms⁷⁾. Recent theoretical investigation by one of the present authors^{3,4)} has shown that the repulsive potential must be considerably greater than the repulsion of the above amount⁷⁾, 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 α in place of the two, *i. e.* R_I and R_{II} .

The theoretical investigation⁴⁾ has shown further that ϵ^r must be lower than ϵ^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 α in (31) by adjusting them to observed adsorption isotherms by the following procedure¹⁵⁾. Eliminating $q^r, q^s, \gamma, \theta^s$ and θ^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 α , ϵ^r and ϵ^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⁽¹⁾

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

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 ϵ^r and ϵ^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 θ . The parameters α , ϵ^r and ϵ^s are thus adjusted to the required proportionality

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

with reference to the observation of KINUYAMA and KWAN⁽¹⁾ 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, $\alpha = 1.200$.

Temperature °C	q^r	q^s	log r									
			Quantit.	-1	0	1	2	3	4	5	6	
0	3.603×10^8	1.063×10^5	W cal/mol	1.311×10^2	5.998×10^2	1.468×10^3	2.559×10^3	3.723×10^3	4.853×10^3	5.819×10^3	6.442×10^3	
			q^r	2.830×10^8	1.193×10^8	2.410×10^7	3.233×10^6	3.786×10^5	4.721×10^4	7.966×10^3	2.527×10^3	
			θ^r	0.07282	0.2488	0.4008	0.4729	0.5123	0.5671	0.6885	0.8752	
			θ^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	
			$(\partial W/\partial \theta^r)_T$	2.00×10^3	3.80×10^3	9.65×10^3	22.70×10^3	30.85×10^3	13.55×10^3	4.90×10^3	2.50×10^3	
			$-(\partial \theta^r/\partial T)_\theta$	1.052×10^{-6}	1.026×10^{-5}	9.098×10^{-5}	3.132×10^{-4}	1.015×10^{-4}	-1.450×10^{-4}	-1.704×10^{-4}	-2.900×10^{-5}	
			$-(\partial W/\partial T)_\theta$	-0.4049	-1.673	-2.862	3.279	5.601	2.403	1.483	0.6675	
50	1.510×10^7	2.303×10^4	W cal/mol	1.497×10^2	6.953×10^2	1.719×10^3	2.995×10^3	4.318×10^3	5.503×10^3	6.319×10^3	6.629×10^3	
			q^r	1.196×10^7	5.115×10^6	1.039×10^6	1.424×10^5	1.814×10^4	2.868×10^3	8.051×10^2	4.970×10^2	
			θ^r	0.07339	0.2530	0.4076	0.4853	0.5457	0.6550	0.8420	0.9705	
			θ^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	
			$(\partial W/\partial \theta^r)_T$	2.35×10^3	4.10×10^3	11.60×10^3	23.30×10^3	16.55×10^3	7.00×10^3	3.00×10^3	2.10×10^3	
			$-(\partial \theta^r/\partial T)_\theta$	4.048×10^{-6}	3.863×10^{-5}	2.645×10^{-4}	3.099×10^{-4}	4.037×10^{-5}	-1.353×10^{-4}	-3.092×10^{-5}	-3.504×10^{-6}	
			$-(\partial W/\partial T)_\theta$	-0.3925	-1.441	-0.3414	5.360	3.596	2.013	0.8203	0.1346	

100	1.437×10^6	7.230×10^3	W cal/mol	1.680×10^2	7.876×10^2	1.961×10^3	3.405×10^3	4.839×10^3	5.974×10^3	6.542×10^3	6.670×10^3
			q^r	1.146×10^6	4.969×10^5	1.022×10^5	1.456×10^4	2.107×10^3	4.559×10^2	2.120×10^2	1.782×10^2
			θ^r	0.07389	0.2569	0.4155	0.5032	0.5945	0.7603	0.9365	0.9920
			θ^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
			$(\partial W/\partial \theta^r)_T$	2.70×10^3	4.70×10^3	11.15×10^3	20.30×10^3	11.25×10^3	4.20×10^3	2.70×10^3	1.80×10^3
			$-(\partial \theta^r/\partial T)_{\theta}$	1.037×10^{-5}	9.457×10^{-5}	4.273×10^{-4}	2.307×10^{-4}	-1.526×10^{-5}	-3.852×10^{-5}	-5.935×10^{-6}	6.268×10^{-7}
			$-(\partial W/\partial T)_{\theta}$	0.3420	-1.036	2.012	4.943	2.680	1.168	0.2940	0.02887
150	2.326×10^5	2.885×10^3	W cal/mol	1.843×10^2	8.765×10^2	2.192×10^3	3.784×10^3	5.273×10^3	6.275×10^3	6.624×10^3	6.677×10^3
			q^r	1.869×10^5	8.204×10^4	1.717×10^4	2.586×10^3	4.402×10^2	1.336×10^2	8.822×10^1	8.287×10^1
			θ^r	0.07435	0.2607	0.4246	0.5264	0.6542	0.8517	0.9743	0.9972
			θ^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
			$(\partial W/\partial \theta^r)_T$	2.90×10^3	5.15×10^3	12.50×10^3	17.60×10^3	7.90×10^3	3.40×10^3	2.50×10^3	1.80×10^3
			$-(\partial \theta^r/\partial T)_{\theta}$	1.772×10^{-5}	1.468×10^{-4}	3.902×10^{-4}	8.780×10^{-5}	8.711×10^{-5}	-2.722×10^{-5}	3.211×10^{-6}	-3.215×10^{-7}
			$-(\partial W/\partial T)_{\theta}$	-0.2656	-0.5939	2.680	2.785	1.241	0.5475	0.1020	0.01942
200	5.420×10^4	1.358×10^3	W cal/mol	2.002×10^2	9.616×10^2	2.411×10^3	4.127×10^3	5.619×10^3	6.448×10^3	6.654×10^3	6.668×10^3
			q^r	4.381×10^4	1.949×10^4	4.171×10^3	6.729×10^2	1.376×10^2	5.700×10^1	4.577×10^1	4.511×10^1
			θ^r	0.07478	0.2645	0.4349	0.5539	0.7174	0.9131	0.9883	0.9988
			θ^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
			$(\partial W/\partial \theta^r)_T$	3.10×10^3	5.80×10^3	12.85×10^3	13.30×10^3	6.30×10^3	3.40×10^3	2.50×10^3	2.20×10^3
			$-(\partial \theta^r/\partial T)_{\theta}$	2.842×10^{-5}	2.104×10^{-4}	3.495×10^{-4}	5.239×10^{-5}	-4.957×10^{-5}	-1.011×10^{-5}	-1.120×10^{-6}	1.122×10^{-7}
			$-(\partial W/\partial T)_{\theta}$	0.1559	0.02732	2.887	2.197	0.9877	0.2546	0.02720	0.002753

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_0^r	q_0^s	log r Quantit.	-1	0	1	2	3	4	5	6
250	1.640×10^4	7.208×10^2	W cal/mol	2.155×10^2	1.043×10^3	2.618×10^3	4.433×10^3	5.885×10^3	6.542×10^3	6.674×10^3	6.651×10^3
			q^r	1.333×10^4	6.015×10^3	1.321×10^3	2.307×10^2	5.703×10^1	3.032×10^1	2.672×10^1	2.731×10^1
			θ^r	0.07519	0.2684	0.4462	0.5845	0.7767	0.9487	0.9939	0.9994
			θ^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
			$(\partial W/\partial \theta^r)_T$	3.30×10^3	6.00×10^3	12.90×10^3	10.9×10^3	4.75×10^3	3.10×10^3	2.80×10^3	2.70×10^3
			$-(\partial \theta^r/\partial T)_\theta$	4.055×10^{-5}	2.616×10^{-4}	3.012×10^{-4}	1.619×10^{-4}	2.527×10^{-5}	4.199×10^{-6}	4.590×10^{-7}	3.915×10^{-8}
			$-(\partial W/\partial T)_\theta$	-0.0862	0.4894	2.866	3.201	0.7230	0.1220	0.01272	0.001894
300	6.022×10^3	4.183×10^2	W cal/mol	2.294×10^2	1.120×10^3	2.812×10^3	4.704×10^3	6.083×10^3	6.593×10^3	6.676×10^3	6.825×10^3
			q^r	4.924×10^3	2.254×10^3	5.098×10^2	9.690×10^1	2.885×10^1	1.844×10^1	1.715×10^1	1.505×10^1
			θ^r	0.07558	0.2723	0.4584	0.6167	0.8273	0.9684	0.9965	0.9996
			θ^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
			$(\partial W/\partial \theta^r)_T$	3.50×10^3	6.35×10^3	12.30×10^3	9.90×10^3	4.40×10^3	3.10×10^3	2.95×10^3	2.90×10^3
			$-(\partial \theta^r/\partial T)_\theta$	5.274×10^{-5}	2.935×10^{-4}	2.655×10^{-4}	1.433×10^{-5}	1.281×10^{-5}	1.922×10^{-6}	1.970×10^{-7}	1.634×10^{-8}
			$-(\partial W/\partial T)_\theta$	-0.03542	0.8537	2.625	1.569	0.5237	0.08104	0.005419	0.0009526

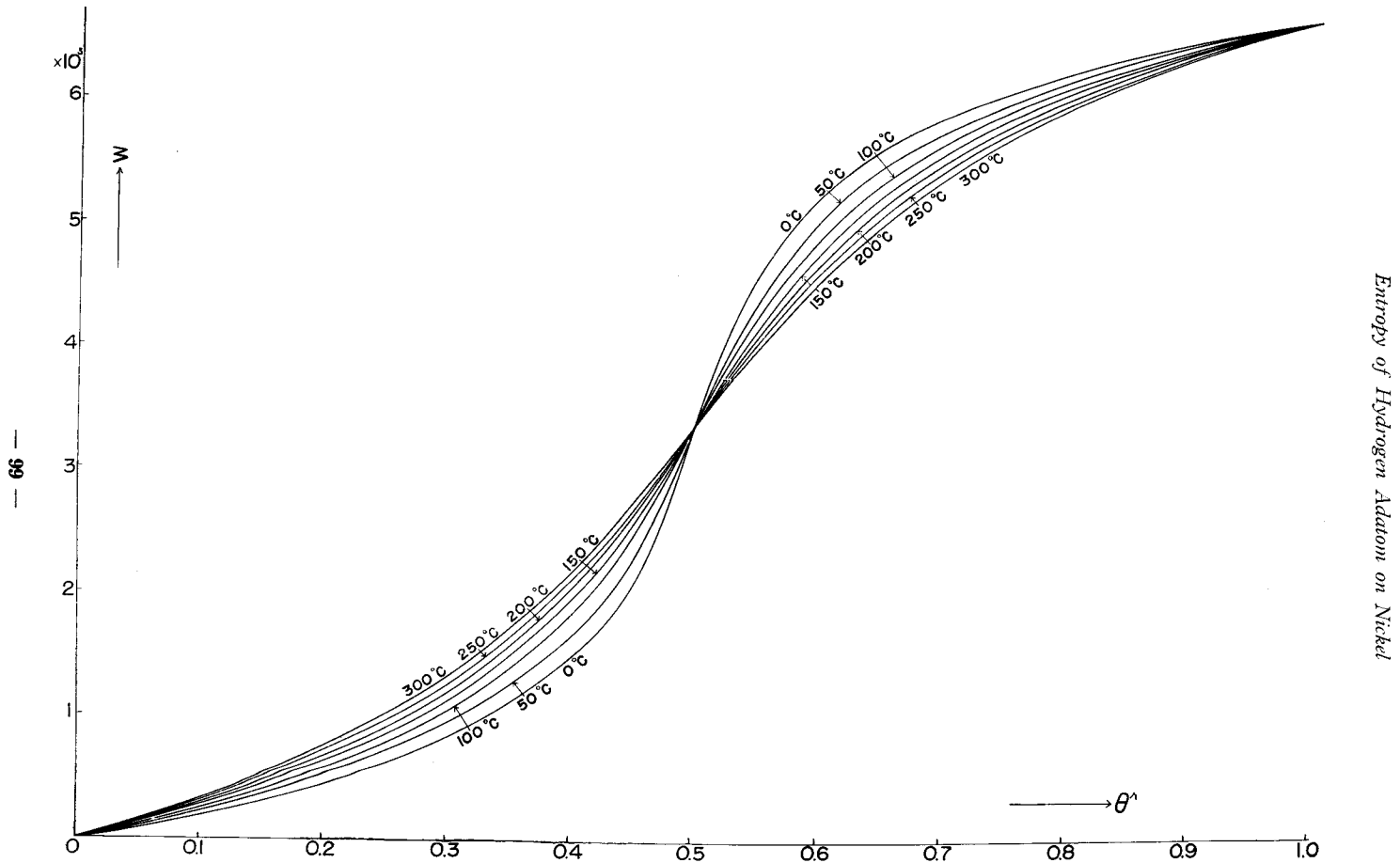


Fig. 2. Free Energy of Repulsion W cal/mol of Hydrogen Adatom on (110)-lattice Plane of f.c.c. Ni Crystal
 $R_I = 0.1019 \times 1.200 \text{ ev}$, $R_{II} = 0.0134 \times 1.200 \text{ ev}$.

TABLE 2. $S_I^H \equiv$

Temperature °C	$\frac{dRT \ln q_0^r}{dT}$	$\frac{dRT \ln q_0^s}{dT}$	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
					6.752×10^{-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
				2.951×10^{-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
					6.800×10^{-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
				1.525×10^{-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
					6.843×10^{-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
				5.025×10^{-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
					6.882×10^{-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
				1.237×10^{-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
1.869×10^{-1}	2.402×10^{-1}	2.493×10^{-1}	2.499×10^{-1}	2.455×10^{-1}	2.145×10^{-1}	1.092×10^{-1}
22.511	17.936	13.360	8.784	4.209	-0.367	-4.941
2.949×10^{-4}	2.934×10^{-3}	2.784×10^{-2}	1.759×10^{-1}	1.890×10^{-1}	3.171×10^{-2}	3.369×10^{-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
1.890×10^{-1}	2.415×10^{-1}	2.498×10^{-1}	2.479×10^{-1}	2.260×10^{-1}	1.330×10^{-1}	2.863×10^{-2}
19.581	15.005	10.430	5.854	1.278	-3.298	-7.859
1.521×10^{-3}	1.480×10^{-2}	1.148×10^{-1}	2.392×10^{-1}	5.774×10^{-2}	6.468×10^{-3}	6.596×10^{-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
1.909×10^{-1}	2.429×10^{-1}	2.500×10^{-1}	2.411×10^{-1}	1.822×10^{-1}	5.947×10^{-2}	7.936×10^{-3}
17.496	12.920	8.345	3.769	-0.7701	-5.387	-9.946
4.980×10^{-3}	4.560×10^{-2}	2.227×10^{-1}	1.383×10^{-1}	1.911×10^{-2}	1.976×10^{-3}	2.000×10^{-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
1.927×10^{-1}	2.443×10^{-1}	2.493×10^{-1}	2.262×10^{-1}	1.263×10^{-1}	2.504×10^{-2}	2.792×10^{-3}
15.953	11.377	6.801	2.226	-2.350	-6.915	-11.517
1.210×10^{-2}	9.817×10^{-2}	2.471×10^{-1}	6.905×10^{-2}	7.936×10^{-3}	8.093×10^{-4}	7.999×10^{-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	$\theta = \theta^r + \theta^s$		0.07728
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$		6.013
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$		0.5337
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$		5.532
					6.919×10^{-2}
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$		19.352
				2.494×10^{-3}	
250	0.6485	7.650	$\theta = \theta^r + \theta^s$		0.07957
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$		6.309
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$		0.5623
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$		5.549
					6.954×10^{-2}
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$		18.435
				4.357×10^{-3}	
300	0.5927	7.832	$\theta = \theta^r + \theta^s$		0.08248
			$S_I^H = \frac{\theta^r(1-\theta^r)S^r + \theta^s(1-\theta^s)S^s}{\theta^r(1-\theta^r) + \theta^s(1-\theta^s)}$		6.621
			$R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta = \frac{dRT \ln q_0^r}{dT} - \left(\frac{\partial W}{\partial T}\right)_\theta$		0.5573
			$S^r = R\left(\frac{\partial T \ln q^r}{\partial T}\right)_\theta + R \ln \frac{1-\theta^r}{\theta^r}$		5.533
					6.987×10^{-2}
			$S^s = R\left(\frac{\partial T \ln q^s}{\partial T}\right)_\theta + R \ln \frac{1-\theta^s}{\theta^s}$		17.708
				6.850×10^{-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), ξ_I and ξ_{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
1.945×10^{-1}	2.458×10^{-1}	2.471×10^{-1}	2.027×10^{-1}	7.935×10^{-2}	1.156×10^{-2}	1.199×10^{-3}
14.777	10.201	5.625	1.049	-3.528	-8.096	-12.673
2.385×10^{-2}	1.602×10^{-1}	2.039×10^{-1}	3.690×10^{-2}	3.954×10^{-3}	3.998×10^{-4}	4.000×10^{-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
1.964×10^{-1}	2.471×10^{-1}	2.429×10^{-1}	1.734×10^{-1}	4.867×10^{-2}	6.063×10^{-3}	5.996×10^{-4}
13.859	9.283	4.708	-0.060	-4.444	-8.997	-13.851
4.033×10^{-2}	2.121×10^{-1}	1.510×10^{-1}	2.175×10^{-2}	2.265×10^{-3}	2.300×10^{-4}	2.000×10^{-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
1.982×10^{-1}	2.483×10^{-1}	2.364×10^{-1}	1.429×10^{-1}	3.060×10^{-2}	3.488×10^{-3}	3.998×10^{-4}
13.132	8.556	3.980	-0.596	-5.168	-9.802	-15.047
6.073×10^{-2}	2.419×10^{-1}	1.100×10^{-1}	1.399×10^{-2}	1.438×10^{-3}	1.400×10^{-4}	1.000×10^{-5}

values of q_0^r calculated as above. The q^r , q^s and p^H thus evaluated decide θ^r and θ^s by (6), hence θ by (7). Fig. 2 shows W thus calculated as a function of T and θ^r . W being thus given as a function of T and θ^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 θ and T according to (27) and (28). Table 1 shows the values of W , q_0^r , q^s , q^r , θ^r , θ^s , θ ,

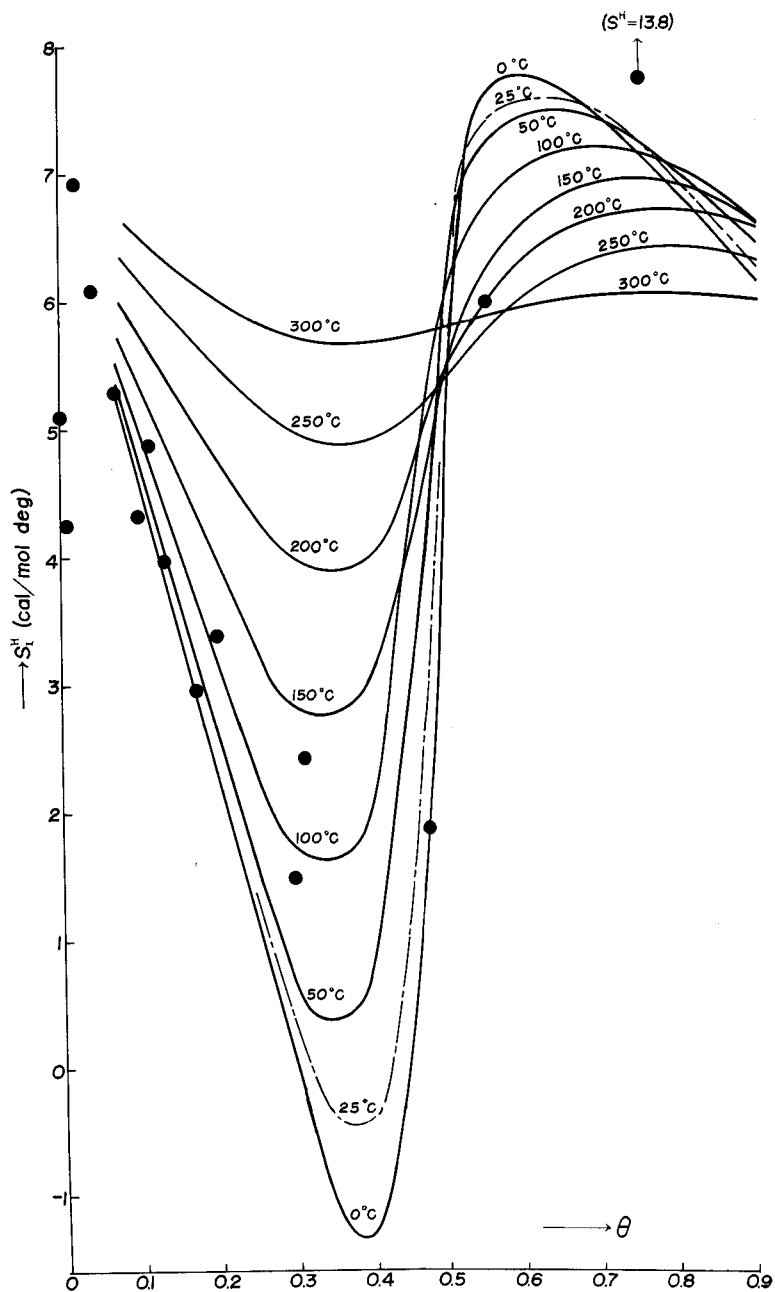


Fig. 3. Calculated Entropy S_I^H on Homogeneous Model and Observed Entropy S^H .
 Lines: S_I^H at signified temperatures (S_I^H at 25°C interpolated).
 Solid circles: S^H at 25°C observed by RIDEAL and SWEETT²⁾.

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

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 θ 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 μ^H implied in (1) is expressed according to (33. a) in terms of hydrogen pressure P as

$$\mu^H = 1/2 \cdot \mu_1^{H_2} + 1/2 \cdot RT \ln P,$$

where $\mu_1^{H_2}$ is the value of μ^{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)

$$S^H = 1/2 \cdot S_1^{H_2} + 1/2 \cdot (\partial RT \ln P/\partial T)_v, \quad (41)$$

where

$$S_1^{H_2} = -d\mu_1^{H_2}/dT$$

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

The $S_1^{H_2}$ -values were directly taken or interpolated from those in literature¹⁶⁾. The $(\partial RT \ln P/\partial T)_v$ was determined from the experimental results of KINUYAMA and KWAN¹⁾ at the v -value relevant to the specified θ -value according to (39) from the observed relation $v=v(T, P)$ and the S^H thus determined from the observation¹⁾ 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 observation¹⁾.

S^H at 25°C was derived from observations of RIDEAL and SWEETT²⁾, 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 θ 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 θ . At higher θ , S_I^H passes through a maximum and then decreases with increase of θ , 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 boundaries¹⁷⁾, while the first small portion of adsorbed hydrogen is accommodated with extraordinary high heat of adsorption^{2,9)}. The present authors have previously inferred⁶⁾ 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^{*)}. 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 θ_h^r or θ_h^s respectively and that of *i*-sites by *s*-adatoms by θ_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)

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

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

It follows that θ_h^r , θ_h^s and $\theta_h = \theta_h^r + \theta_h^s$ are respectively equal to θ^r , θ^s and $\theta = \theta^r + \theta^s$ on the homogeneous model for the same value of p^H . We see from Table 1 that θ^s is negligibly small as compared with θ^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 , ε_i^s and ν_i respectively corresponding to A , ε^s and ν 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 θ 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

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

and

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

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 LUNDY⁹⁾ and that

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

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 θ_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 θ_i^s over θ_h^r as well as the proximity of θ_i^s to θ/x is enhanced, as θ gets smaller^{*}.

The factors η_I and η_{II} in (16) are essentially positive by definition [cf. Appendix 2] and τ is positive as well according to (15), (2) and (11). The ξ_I and ξ_{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)

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

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 θ_h^r and θ_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 θ_h^r and θ_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 θ^* . 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°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 ν_i in (43. b) respectively with A and ν given by (24) and (30. s) as

^{*}) Cf. footnote ^{**}) 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_{II}^{H} approaches S_i^s according to the above, as θ decreases.

The above value of entropy on the revised model is compared with the entropy on the homogeneous model for the same value of θ , *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

$$S^r = RdT \ln q_0^r/dT - (\partial W/\partial T)_{\theta^r} + R \ln \left\{ (1 - \theta^r)/\theta^r \right\},$$

noting that q_0^r is a sole function of temperature and the differentiation at constant θ is equivalent in this case to that at constant θ^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_{I}^{H} to S_{II}^{H} as much as 5 cal/mol deg for θ less than to cover the *i*-sites completely. The A_i and ν_i have been identified with A and ν in the above calculation of S_i^s . The variation of ν_i around ν has little effect on S_i^s , since the factor $1 - \exp(-h\nu_i/kT)$ remains close to unity insofar as ν_i is as large as ν given by (30. s), whereas that of A_i may make difference. Since A_i is identified with A , the value of S_{II}^{H} in (52. a) is its upper bound and hence the above value 5 cal/mol deg of the depression from S_{I}^{H} to S_{II}^{H} is its lower bound.* This accounts reasonably for the depression of the observed value of S^{H} from S_{I}^{H} as seen in Fig. 3. The conclusion remains unchanged, if the low energy of *i*-sites is inhomogeneous instead.

§ 11. S_{II}^{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_{II}^{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 θ_h^r and θ_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 , θ_i^s being nearly unity. It is readily shown that the predominance of weight of S_h^r and the proximity of θ_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 θ increases from a value lower than x to that higher.

§ 12. Isotheric 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 results²⁾.

*) $(\partial W/\partial T)_{\theta_h^r}$ involved in the calculation is determined from (26. c) identifying θ_h^r with θ^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 θ_i^s , θ_h^r and θ by (44. b) increase or decrease simultaneously at constant temperature, noting that W is positive and monotonously increases with increase of θ_h^r as seen in Fig. 2. Both θ_h^r and θ_i^s increase in consequence monotonously with increase of θ . As θ_i^s is not very near to unity, θ_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 θ_i^s/θ_h^r increases with decrease of θ_i^s , hence of θ . 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 θ as mentioned on p. 108.

As θ increases and in consequence θ_i^s and θ_h^r simultaneously increase according to (44. b), θ_i^s approaches unity sooner than θ_h^r does. In case where θ_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 θ_i^s . This proximity of θ_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 θ .

It is now investigated whether (46. q) be compatible with the observation of isosteric heat of adsorption by RIDEAL and SWEETT²⁾. 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 SWEETT²⁾. 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

$$Q_i^H = H_1^H - \bar{H}_i^H, \quad Q_h^H = H_1^H - \bar{H}_h^H,$$

where H_1^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 μ^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 θ_h^s is negligibly small as

*) The ϵ^r and ϵ_i^s are expressed in units of cal/mol in this section.

compared with θ_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 θ_h^r or θ_h^s varies with θ_h identically as θ^r or θ^s does with θ 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*). $RT^2 d \ln q_o^r/dT$ is calculated by (60. b) on the base of parameters given by (30. r) as

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

we have now from (59), (60. a), (61) and (62. r) identifying θ_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 ν_i respectively identified with A in (24) and ν 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 θ_h^r as given by (51. r), so that $RT^2(\partial \ln q_h^r/\partial T)_\theta$ equals practically $RT^2 d \ln q_o^r/dT$. 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),

*) $W - T(\partial W/\partial T)_\theta$ for the homogeneous model is not unconditionally identifiable with that for the revised model, inasmuch as the suffixed constant θ is that of (7) or (44. b) in the respective case. In the specified range of θ , however, θ^s is negligibly small in case of the homogeneous model, while θ_i^s is practically unity in case of the revised model. The constant θ renders θ^r or θ_h^r constant according to (7) or (44. b) in the respective case. The θ^r is thus practically equal to θ in case of homogeneous model. The θ_h^r equals on the other hand nearly θ 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 θ_h^r and θ 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 SWEETT²⁾ 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 result²⁾ 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 θ and $\theta_h = \theta_h^r + \theta_h^s$ is practically ignorable in the region of θ in question**, while θ_h^r or θ_h^s varies with θ_h identically as θ^r or θ^s does with θ 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 θ 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°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 θ in question, and S^s itself decreases with increase of θ 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 ν_i in (43. b) are identified respectively with A and ν in (21. a); *cf.* § 9.

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

term on the right of (9. r) decreasing with increase of θ 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 $-(\partial W/\partial T)_\theta^r$ 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 θ 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 θ , 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 θ 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 θ^r and θ^s approach unity with increase of θ . In the present approximation, where the repulsion among s-adatoms is ignored, θ^s approaches unity more readily than in case, where the repulsion were taken into account. Table 1 shows that θ^s is 0.9966 for $\theta^r=0.8752$. The depression of S_I^H at higher θ is thus mainly due to the ready approach of θ^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 θ^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 θ , 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 θ^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^{4,5,6)} 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^{4,5,6}) 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 θ .

It has been pointed out that the steep rise of entropy with increase of θ around $\theta=0.45$ is due to that of the entropy of repulsion $-(\partial W/\partial T)_\theta = -(\partial W/\partial T)_{\theta^r} - (\partial W/\partial \theta^r)_r (\partial \theta^r/\partial T)_\theta$, 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 θ . The observed rapid rise of entropy with θ 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 θ 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 θ of the adsorbed quantity over that at -195°C and 1.5×10^{-3} mmHg pressure²⁾. In Fig. 3 the observed entropy is plotted against the latter experimental value of θ . The general agreement between the observed and the experimental entropy plotted against the respective values of θ would suggest that the adsorbed quantity at -195°C and 1.5×10^{-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 θ should exceed unity at higher temperature and higher hydrogen pressure. With regard to the latter two points, *i.e.* the behavior of entropy at θ beyond the steep rise and the suggested excess of θ 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 θ as

$$\begin{aligned} (\partial \theta^r / \partial T)_\theta &= \theta^r (1 - \theta^r) \left\{ (\partial \ln q^r / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \right\}, \\ (\partial \theta^s / \partial T)_\theta &= \theta^s (1 - \theta^s) \left\{ (\partial \ln q^s / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \right\}, \end{aligned}$$

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

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

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

$$\begin{aligned} (\partial \theta_h^r / \partial T)_\theta &= \theta_h^r (1 - \theta_h^r) \left\{ (\partial \ln q_h^r / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \right\}, \\ (\partial \theta_i^s / \partial T)_\theta &= \theta_i^s (1 - \theta_i^s) \left\{ (\partial \ln q_i^s / \partial T)_\theta - (\partial \ln p^H / \partial T)_\theta \right\}, \end{aligned}$$

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

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

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 HIROTA¹²⁾ 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 Σ of sites on C^* , consisting of a site σ_0 of interest on (110)-lattice plane, two first nearest sites, σ_1 and σ_2 , and two second nearest sites, σ_3 and σ_4 , respectively to σ_0 as shown in Fig. 4. The q^r is written, according to (4) with special reference to σ_0 , as

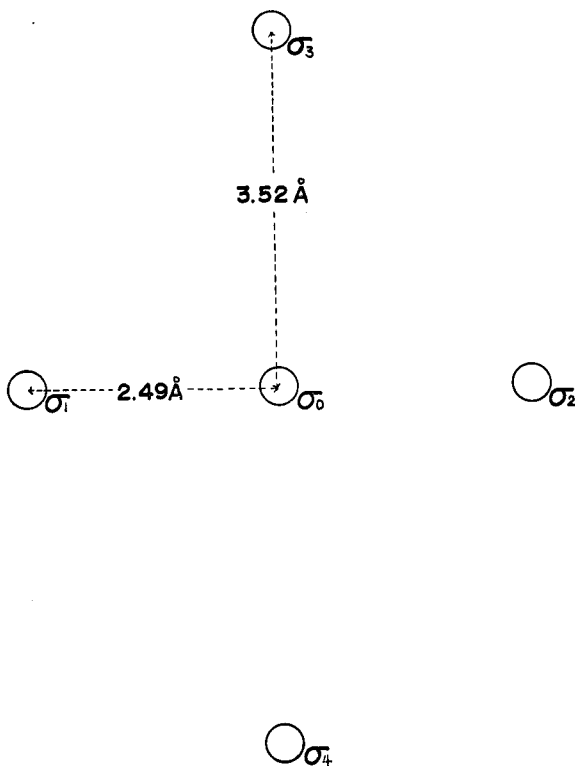


Fig. 4. Group Σ of Sites of r-Adatoms.

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

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

The $\mathfrak{Q}C_{\sigma_0(r)}^r$ and $\mathfrak{Q}C_{\sigma_0(0)}$ are now developed in terms of the partition function $\mathfrak{Q}C_{\Sigma(0)}$ of the particular state $C_{\Sigma(0)}$ of C , where Σ is completely unoccupied. The $C_{\sigma_0(0)}$ comprises five states which differ in the number n of occupied sites among the four ones envrioning σ_0 in Σ . The partition function $\mathfrak{Q}C_{\sigma_0(0)}$ is the total sum of the partition function of the five different states, *i. e.*

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

$\mathfrak{Q}C_{\Sigma(0,n)}$ is the partition function of the state $C_{\Sigma(0,n)}$ of C , which has n r-adatoms on four sites envrioning σ_0 but none on σ_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 envrioning sites, so that $\mathfrak{Q}C_{\Sigma(0,n)}$ is the sum of the partition functions of the appropriate particular states.

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

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

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

where r_1 *etc.* signifies r-adatom on σ_1 *etc.* respectively. The particular state $C_{\Sigma(0,r_1)}$ is derived from $C_{\Sigma(0)}$ by extracting one r-adatom from outside Σ and putting it in σ_1 . The former step of extraction changes the partition function of the system from $\mathfrak{Q}C_{\Sigma(0)}$ to $\mathfrak{Q}C_{\Sigma(0)}/p^H$ in accordance with (2), ignoring the effect on p^H of the microscopic constraint signified by $\Sigma(0)$, whereas the subsequent one from $\mathfrak{Q}C_{\Sigma(0)}/p^H$ to $\mathfrak{Q}C_{\Sigma(0)}q_{\Sigma(0,r_1)}^r/p^H$ in accordance with (4), hence

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

bold letter r_1 characterizing the r-adatom brought to σ_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 Σ . 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)

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

Similar reasoning shows that $\mathfrak{Q}C_{\Sigma(0,r_2)}$ is identical with $\mathfrak{Q}C_{\Sigma(0,r_1)}$ because of the symmetry of Σ 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 Σ . 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, σ_1 and σ_2 , *etc.*, but none of others inside Σ 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 Σ to σ_2 ; the partition function thus changes from $\Omega C_{\Sigma(0,r_1)}$ to $\Omega C_{\Sigma(0,r_1)} q_{\Sigma(r_1,r_2)}^r / p^H$, 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 σ_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 Σ is identical with $-kT \ln \eta_I$ in (iv. b), because of symmetry of Σ 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

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

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 $\Omega C_{\sigma_0^{(r)}}$ 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 σ_0 as well as n sites among those envrioning σ_0 are occupied, leaving other sites inside Σ unoccupied, *i. e.*

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

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 σ_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 Σ to σ_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 σ_1 , *i. e.* r_1 , in the presence of r_0 on σ_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

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

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

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

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

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

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

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

where ξ_{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)

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

Extending the above reasoning, we have

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

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

and

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

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

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

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

$$q^r = q_0^r \frac{(1 + \gamma \eta_I \xi_I)^2 (1 + \gamma \eta_{II} \xi_{II})^2}{(1 + \gamma \eta_I)^2 (1 + \gamma \eta_{II})^2}.$$

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

The determination of $W(T, \gamma)$ requires those of ξ_I , ξ_{II} , η_I and η_{II} implied in (16. a). The ξ_I and ξ_{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 η_I and η_{II} are determined by equating $\Omega C_{\sigma_0(\sigma)}$, in accordance with the BETHE and PEIERLS' method¹⁴⁾, with the partition functions $\Omega C_{\sigma_1(\sigma)}$ and $\Omega C_{\sigma_3(\sigma)}$ respectively of the states $C_{\sigma_1(\sigma)}$ and $C_{\sigma_3(\sigma)}$, where σ_1 and σ_3 are respectively unoccupied with certainty, as

$$\Omega C_{\sigma_0(\sigma)} = \Omega C_{\sigma_1(\sigma)} = \Omega C_{\sigma_3(\sigma)}. \quad (\text{xx})$$

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

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

and

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

Eq. (16. b) is obtained from (xii), (xx) and (xxi), which decides η_I and η_{II} as respective functions of γ , ξ_I and ξ_{II} . The W is in consequence determined as a function of T and γ by (16) with reference to (17).

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