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Author(s)	HORIUTI, Juro; TOYA, Tomiyuki
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## ADSORPTION ISOTHERM AND THE STATES OF ADSORPTION<sup>\*)</sup>

By

Juro HORIUTI<sup>\*\*)</sup> and Tomiyuki TOYA<sup>\*\*)</sup>

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### Abstract

Existence of the two distinctly different states, the *r*- and *s*-states, of hydrogen adatom was previously deduced from the quantum-mechanical theory of adsorption developed by one of the present authors<sup>10)</sup>. The energy of the *r*-state adsorption of a single hydrogen adatom without interaction with other adatoms (an adatom free from interaction with other ones will be termed a single adatom in what follows) was shown lower than that of *s*-state one on any crystal plane of nickel and the energy of either state is lowest on the least dense (110)-plane. Steps, kinks, and defects on a lattice plane furnish *s*-states of extraordinarily low energy.

The consequent distribution of sites over the energy of a single adatom should be uniquely deduced from isotherm observed at any temperature by the distribution function method, if the neglect of the interactions among adsorbates, implied in the latter method, were applicable at all. The distribution function exactly based on the observed isotherm was thus deduced by applying the SOMMERFELD's method of deducing the free energy of Fermi gas from the known distribution function of quantum states over energy inversely to the present problem. The distribution function of sites thus deduced for the dissociative adsorption of hydrogen shifted considerably with the observation temperature, from 0° to 300°C, of the isotherm. This contradicts the neglect of the interaction implied, since experimental facts exclude the change of the surface structure of the adsorbents over the temperature range in question from being alternatively responsible for the shift.

Experimental informations indicated that the adsorbent's surface consists of crystal planes each big enough to secure the physical identity of metal atoms on it. The interaction between *r*-adatoms was shown repulsive as caused by the exchange repulsion between hydrogen adatoms and their competition for metal electrons, besides by the dipole interaction in case of charged adatom. There exists practically no interaction between *s*-adatoms nor between *s*- and *r*-adatoms. The model of exclusive adsorption of *r*-adatoms on (110)-

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<sup>\*\*)</sup> Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan.

plane allowed for the repulsive interaction (the crystal plane model) should in consequence reproduce the bulk of the adsorption isotherm, provided that (110)-plane makes a good portion of the surface, whereas sites of low energy furnished by the imperfections are just a minority. At higher coverage the theoretical isotherm may fall too low, because the preference of the  $r$ -state adsorption on (110)-plane is more or less counterbalanced by repulsion enhanced with coverage. The experimental results were satisfactorily accounted for on the base of the above crystal plane model extended to include the additional  $s$ -state adsorption on the same plane<sup>36,37</sup>.

The preferential desorption of the portion later adsorbed observed by means of isotopic tracer<sup>13</sup>) was shown not exclusively to evidence the distribution function method but equally accounted for on the basis of the crystal plane model with proper allowance for the interaction.

The distribution function method implying the neglect of interaction was thus concluded inapplicable, whereas the crystal plane model, extended as above, was shown in accordance with the experimental results.

### Introduction

There are two schools of conception of the surface structure of adsorbents, from which isotherms are theoretically deduced, *i. e.*, that of homogeneous surface with physically identical adsorption sites originating from LANGMUIR<sup>1)</sup> and that of inhomogeneous one with sites of diverse properties especially of different heat of adsorption initiated by H. S. TAYLOR<sup>2)</sup>. The former model has been elaborated by ROBERTS<sup>3)</sup> and OKAMOTO, HORIUTI and HIROTA<sup>4)</sup> by assigning the homogeneous surface to a crystal plane of metallic adsorbent and taking account of the repulsive interaction among adsorbates, whereas the latter has been developed into that underlying the distribution function method<sup>5)</sup>, where the interaction was ignored or the energy of adsorbate taken particular to the site it occupied irrespective of the arrangements of other adsorbates. The former might be called the crystal plane model and the latter the distribution model in what follows.

It has been observed<sup>6)</sup> by field emission microscope that the surface of tungsten tip consists of a single crystal, which exposes different crystal planes each big enough to ensure the physical identity of the majority of metal atoms on it. SUHRMANN<sup>7)</sup> has observed that evaporated metal film of nickel consists of single crystals of the linear dimension of *ca.* 100 Å comparable to that on the above tungsten tip. Single crystals of the linear dimension of at least 200 Å are observed with reduced nickel powder<sup>8)</sup> or tungsten powder<sup>9)</sup> used ordinarily in the adsorption experiments. It might be admitted from these experimental results that the surface of these adsorbents consists of lattice planes each big enough in the above sense.

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We have to accept, on the other hand, that the energy of adsorbate is considerably diverse. One of the present authors<sup>10)</sup> has shown on the basis of the quantum-mechanical theory of metal electrons that there exist two distinctly different states of adsorption of hydrogen atoms; the one is that of the adsorption of usual sense with the relevant adatom being situated outside the electronic surface of metal and the other that with the adatom just inside the electronic surface, as called by him respectively the *r*- and *s*-states of adsorption<sup>10)</sup>. The energy of the *r*- and *s*-states of the same metal varies from a crystal plane to another and steps, kinks, and defects make a further difference in the energy of adatom.

It follows that the distribution model is exact, provided that the interaction among adsorbate were ignorable. If then, the distribution function of the energy of adsorbates should be concordantly deduced from any of adsorption isotherms observed at different temperatures, insofar as the thermal rearrangements of surface metal atoms of adsorbent is excluded, hence the distribution function itself remain constant. One of the present authors<sup>11)</sup> has thus investigated the consistency of the distribution model with the negative conclusion that the distribution function of hydrogen on nickel as well as on tungsten deduced from observed isotherms does shift markedly with the temperature of the observation ranging from 0°C to 300°C, where the thermal rearrangement of adsorbent's surface is precluded by experimental facts. This leads inevitably to the conclusion that the interaction among adsorbates is by no means ignorable.

It was now tried theoretically to reproduce the observed adsorption isotherm of hydrogen on nickel, allowing for the interaction and admitting the adsorbent surfaces composed of different lattice planes. It is evidenced that hydrogen is dissociated to form statistically independent adatoms on nickel at least at low coverage<sup>8)</sup>. The adatoms should then predominantly adsorb on the lattice plane, on which the energy of adatoms is sufficiently low. The *r*-adatom on (110)-plane is the lowest in energy among adatoms in the absence of interaction as shown in § 1 and the interaction is repulsive between *r*-adatoms as deduced in § 3 from every conceivable cause, whereas it exists scarcely between *s*-adatoms or between *r*- and *s*-adatoms<sup>10)</sup>. Imperfections such as steps, kinks, and defects may possibly furnish adsorptive sites of considerably low energy but probably be of little adsorptive capacity.

The isotherm of the dissociative adsorption of hydrogen on the (110)-plane was thus theoretically worked out allowing for the interaction at different temperatures from 0° to 300°C as shown in § 6 and § 7. Deviation of the theoretical isotherms is expected at extremely low coverage on the one hand

because of the contribution from the imperfections mentioned above and at higher coverage on the other hand, since the preference of  $r$ -state adsorption on the (110)-plane is more or less counterbalanced by the repulsive interaction of  $r$ -adatoms, which raises the energy of the adatoms.

The theoretical isotherms thus worked out accounts in the main quantitatively for the observed ones<sup>12)</sup> but the expected deviations reveal themselves at lower and higher extremities of coverage as shown in § 7; the deviation at lower coverages is explained qualitatively attributing it to the imperfections, whereas that at higher coverage is satisfactorily reproduced by ascribing it to the  $s$ -state adsorption on the (110)-plane.

It might now be questioned how to reconcile the above conclusion with the experimental results of the differential isotopic method<sup>13)</sup> that the portion adsorbed later is desorbed initially in preference to that adsorbed earlier as observed by isotopic tracer, which is taken as the exclusive evidence for the distribution model, on account of the inability of the crystal plane model to explain it as based on the simple assumption of the repulsive potential proportional to the coverage. It was shown by one of the present authors<sup>14)</sup> as summarised in § 8 that the experimental result of the differential isotopic method is adequately derived from the crystal plane model, if allowed properly for the repulsive interaction and for the appearance mentioned above of the  $s$ -state on the same plane at higher coverage.

On these grounds it is concluded that the distribution model is inapplicable but the crystal plane model with the above extension is the sound basis of accounting for the observed isotherms.

Detailed accounts will be given of the above points in the following sections.

### § 1. Energy of Single Adatom

Consider a hydrogen adatom in the absence of interaction on a perfect crystal plane of a metal, which will be called a single adatom in what follows. The energy  $W_r$  of a single adatom at the  $r$ -state is determined by the equation<sup>10)</sup>

$$(R_o - W_r) - \frac{1}{2} \frac{N_v |V_v|^2}{\bar{E}_+ - W_r} - \frac{1}{2} \frac{N |V_0|^2}{\bar{E}_- - W_r} = 0 \quad (1)$$

based on the quantum-mechanical theory of adsorption developed by one of the present authors<sup>10)</sup>, where

$R_o$ : repulsive potential of the adatom due to metal electrons and metal ions,  
 $\bar{E}_+$ : energy of the  $H^+$ -state of the adatom averaged over the vacant energy

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- level of the metal, to which the electron of the adatom is transferred,  
 $N_v$ : number of the vacant levels of free electrons in the metal,  
 $\bar{E}_-$ : energy of  $H^-$ -state of the adatom, inclusive of the repulsive potential due to metal atoms, averaged over the occupied levels in the metal, from which an electron removed to the adatom to form  $H^-$ ,  
 $N$ : the number of the occupied levels in the metal,  
 $|V_v|$ : mean value of the matrix element between  $1s$ -electron of the adatom and a vacant level, and  
 $|V_0|$ : mean value of the matrix element between an occupied level and the electron trapped by H.

It has been shown that the theoretical values of  $\sqrt{N_v} V_v$  and  $\sqrt{N} V_0$  yield by (1) the value of heat of adsorption of the right order of magnitude<sup>10</sup>.

We see that  $\bar{E}_- < \bar{E}_+$  for usual metallic adsorbents, for which the work function is smaller than the mean of the ionization potential 13.6 eV and the electron affinity 0.7 eV of hydrogen atom, admitting that electron is transferred from the adatom mainly to the levels near the Fermi level or reversely. Besides,  $\sqrt{N} V_0$  is found slightly larger than  $\sqrt{N_v} V_v$  as calculated for copper and nickel<sup>10</sup>. Ignoring the second term on these grounds the above equation shows qualitatively that  $W_r$  is the higher, the greater the  $\bar{E}_-$  and the  $R_0$ . The  $\bar{E}_-$  increases now with increase of the work function of the relevant crystal plane, which increases with increase of density of metal atoms on it due to the decrease of the smoothing effect as discussed by SMOLUCKOWSKI<sup>15</sup> and verified by field emission microscopic observations<sup>6</sup>. The repulsive potential  $R_0$  should increase as well with increase of the density of metal ions on the crystal plane. It follows that the energy of  $r$ -adatom is lower on a less dense crystal surface.

The above conclusion is regarded as the incorporation of the following two ones. OKAMOTO, HORIUTI and HIROTA<sup>4)</sup> have concluded that the energy of hydrogen adatom on nickel is lowest on (110)-plane taking account of the repulsion exerted by metal atoms other than that to which the adatom is bonded.

On the other hand,  $W_r$  is given by the Eley's empirical rule as<sup>16,17)</sup>

$$-W_r = \frac{1}{2} \left\{ W(M-M) + W(H-H) \right\} + 23.06 (X_M - X_H)^2 \text{ eV},$$

where  $W(M-M)$  is the bond energy between two metal atoms, as determined by dividing the heat of evaporation of solid metal by the coordination number of a metal atom,  $W(H-H)$  the dissociation energy of hydrogen molecule and  $X_M$  or  $X_H$  the electronegativity of the metal or hydrogen atom, *i. e.*, 0.355

times the work function of metal or the mean of the ionization potential and the electron affinity of hydrogen atom respectively. Admitting that  $X_M < X_H$ , it follows from the above equation, that  $W_r$  is the higher, the greater the work function. Since a dense crystal plane renders the work function greater as mentioned above, these two conclusions are consistently incorporated into that from (1).

The  $s$ -state adsorption comes into existence because the Thomas-Fermi kinetic energy  $\frac{16\pi^3\hbar^2}{5m_e} \left(\frac{3}{8\pi}\right)^{5/3} \int \rho^{5/3} d\tau$  where  $m_e$  is the mass of electron,  $\rho$  the electron density and  $d\tau$  the volume element, is reduced by bringing the peak of extra electron density around a proton along with it from the bulk of metal up to the electronic surface, where the electron density of the metal proper decays outwards<sup>10</sup>; the Thomas-Fermi kinetic energy with WEIZSÄCKER's correction\*) for the gradient of electron density plus the potential energy of the whole system results in a potential hollow of proton close to but inside the electronic surface, *i.e.*, the  $s$ -state of adatom as shown in Fig. 1. The energy of  $s$ -state adatom is also lower on a less dense crystal plane because of less repulsion exerted by metal ions and depends on the work function of the respective lattice plane<sup>10</sup>.

It follows that the energy either of the  $r$ - or the  $s$ -state on nickel is respectively lowest on the least dense crystal plane (110). It is shown in a forthcoming paper of one of the present authors<sup>19</sup> for nickel that the energy of  $r$ -state is lower than that of  $s$ -state throughout the crystal planes and that the energy of the  $s$ -state is higher than that of the  $r$ -state by 0.5 eV on (110)-plane.

It might be mentioned that steps, kinks, and defects on a lattice plane

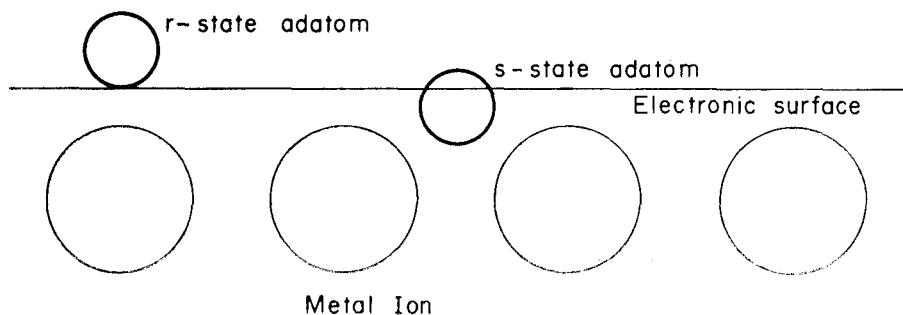
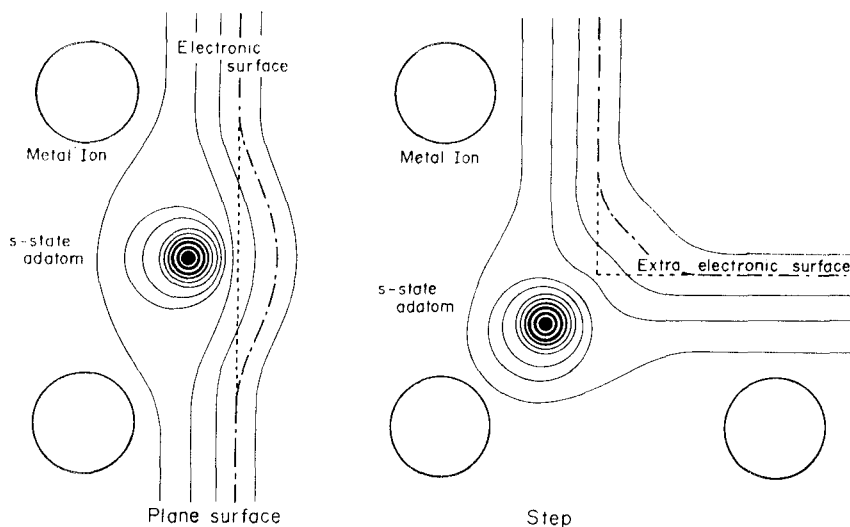


Fig. 1.  $r$ - and  $s$ -States of Adsorption

\*) The term  $\kappa \frac{\hbar^2}{8m_e} \int \frac{|\text{grad } \rho|^2}{\rho} d\tau$  additional to the Thomas-Fermi kinetic energy, where  $\kappa \approx 0.6$  (see Ref. 18).

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**Fig. 2.** Contours of  $\rho$  of  $s$ -State at Plane Surface and at Step

may provide the  $s$ -state adsorption sites of extraordinarily low energy<sup>10). The  $s$ -state adatom situated there is associated with a sharp decrease outwards of electron cloud around it, *i.e.*, the outward decrease of symmetric charge cloud around the proton superposed upon the similar outward decrease of the charge cloud of metal electron at the electronic surface of metal. The sharp decrease or the gradient of large absolute amount increases the energy of  $s$ -adatom through the WEIZSÄCKER's correction. The electron cloud of this sharp decrease is now more or less housed inside the extra electronic surfaces provided by step, kink, or defect as shown in Fig. 2 appreciably to decrease its energy.<sup>20)</sup></sup>

The sites are thus diversely distributed as a function, either continuous or discontinuous, of the energy of a single adatom. The distribution function method of adsorption may thus be applicable, provided that the energy of an adatom depends solely on the site that it occupies, as is the case, if the interaction among adatoms were ignorable.

## § 2. Distribution Function Method

The distribution function method is examined for its applicability by deriving the distribution function from isotherms observed at different temperatures from 0° to 300°C. The distribution function thus derived should be unique irrespective of temperature at which the relevant isotherm is observed, provided that the arrangement of metal atoms on the surface is prac-



tically constant. It requires  $\sim 2$  eV to make a defect or so-called damage inside metals<sup>21)</sup>, hence about one half of this amount of energy to make an imperfection on the surface. Since this amount of energy is hardly supplied thermally over the temperature range in question, we might safely exclude any possibility of rearrangements of surface metal atoms, hence admit a constant distribution of sites over the energy of single adatom independent of temperature.

One of the present authors has deduced<sup>22)</sup> the distribution function  $F(E)$  from the adsorption isotherm  $v=v(p)$  observed at different temperatures according to the equation

$$v = \int_{-\infty}^{+\infty} \theta(E, \mu) F(E) dE, \quad (2. v)$$

where  $F(E) dE$  is the number of sites with the energy of adatom lying between  $E$  and  $E+dE$  in terms of the amount of gas fully adsorbed there and  $\theta$  or  $v$  the fraction of these sites occupied or the total amount of gas adsorbed at the hydrogen pressure  $P$ . The  $\theta$  is expressed in accordance with the premised absence of interaction among adatoms by the Langmuir type function

$$\theta = \left\{ 1 + \exp \left( \frac{E - \mu}{RT} \right) \right\}^{-1} \quad (2. \theta)$$

of  $E$  and the chemical potential  $\mu$  of adatom, which equals, in equilibrium of the dissociative adsorption, one half of the chemical potential  $\mu_1 + RT \ln P$  of hydrogen molecule, as

$$\mu = \mu_1/2 + RT/2 \cdot \ln P, \quad (2. \mu)$$

where  $\mu_1$  is the chemical potential of hydrogen molecule at  $P=1$ . We deal with the range of  $v$ , which obeys the FREUNDRICH's law, *i. e.*,

$$v = v_1 P^c, \quad (2. F)$$

where  $v_1$  and  $c$  are respectively constant at constant temperature.

SIPS<sup>23)</sup> and TODES and BONDAREVA<sup>24)</sup> have deduced  $F(E)$  from  $v(p)$  of (2.  $F$ ) by applying the theory of STIELTJES or Laplace transform\*) to (2.  $v$ ). SIPS encountered, as he remarked, with the difficulty that  $F(E)$  thus obtained led to infinite sites to exist on a finite portion of adsorbent.

The latter procedure is based on an implicit assumption that (2.  $F$ ) holds over the whole range of  $P$  from zero to infinity. Alternatively  $F(E)$  was

\*) They (Refs. (23) and (24)) have applied the theory instead to the case of simple molecular adsorption, where  $\mu = \mu_1 + RT \ln P$  in place of (2.  $\mu$ ).

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deduced<sup>22)</sup> just over the range, where  $F(E)$  is directly based on the observed  $v$ , by applying the SOMMERFELD's method of evaluating  $\mu$  of Fermi gas from known  $F(E)$ , inversely to the present problem as follows. According to SOMMERFELD<sup>25)</sup>,

$$v = \int_{-\infty}^{\mu} F(E) dE + 2 \sum_{m=1}^{\infty} \frac{(\pi RT)^{2m}}{(2m)!} (2^{2m} - 1) B_m \left\{ \frac{d^{2m-1} F(E)}{dE^{2m-1}} \right\}_{E=\mu}, \quad (3. a)$$

where  $B_m$  is the Bernoulli's number, *i. e.*,  $1/6, 1/30, 1/42, \dots$  for  $m=1, 2, 3, \dots$  respectively. KEII has shown<sup>26)</sup> that the ROGINSKY's approximation<sup>5)</sup> for evaluating  $F(E)$  from observed  $v$  corresponds to the first term of (3. a) only being retained and he worked out<sup>26)</sup>  $F(E)$  and hence the heat of adsorption reserving first two terms.

It has now been shown<sup>22)</sup> retaining the whole terms that (3. a) leads with special reference to (2.  $F$ ), exactly to the equation

$$F(E)_{E=\mu} = \frac{v}{RT} \frac{\sin \pi c}{\pi}. \quad (3. b)$$

Eq. (3. b) defines the function  $F(E)$  just over the range of  $E$  equal to  $\mu$ , which is determined directly by observations by (2.  $\mu$ ), thus basing  $F(E)$  solidly upon observations.

The explicit function  $F(E)$  is obtained from (3. b) by substituting  $\mu$  from (2.  $F$ ), expressing  $P$ , thus introduced, by (2.  $\mu$ ) and identifying  $\mu$  with  $E$  for  $F(E)_{E=\mu}$ , as

$$\log_{10} F(E) = \log_{10} \frac{v_1 \sin 2\pi c}{\pi RT} - \frac{c\mu_1}{2.30RT} + \frac{2cE}{2.30RT}. \quad (4. a)$$

The  $\mu_1$  is statistical-mechanically expressed by definition as<sup>22)</sup>

$$\mu_1 = 2.303 \times 0.4918RT - 7/2RT \ln T. \quad (4. b)$$

The function  $\log_{10} F(E)$  given by (4) is numerically worked out at different temperatures from  $0^\circ$  to  $300^\circ\text{C}$  for hydrogen adsorption on nickel from the observations of KINUYAMA and KWAN<sup>12)</sup> and for that on tungsten from those of FRANKENBURG<sup>9)</sup> as shown in Figs. 3 and 4 respectively. The linear function  $\log_{10} F(E)$  of  $E$  based on the observation is bounded above and below by the upper and lower bounds of observed  $v$  according to (3. b) as shown in Figs. 3 and 4.

We see from Figs. 3 and 4 that the distribution functions of one and the same portion of adsorbent derived from isotherms observed at different temperatures deviate seriously from each other, which contradicts the applicability of the distribution function method.

We have termed  $E$  the energy of adsorbate but exactly  $E$  in accordance with (2.  $\theta$ ) is the free energy increase caused by bringing an adatom from its standard state to a definite, preliminarily evacuated site<sup>\*)</sup>, which depends in general on temperature. One might thus alternatively assume that it is the ground state energy  $\epsilon_0$  of adatoms, over which the sites are constantly distributed independent of temperature. It has now turned out<sup>22)</sup> for the sites to be distributed constantly over  $\epsilon_0$ , that adatoms must have vibrational frequencies of the magnitude of far infrared or microwave frequency, which precludes, any localization of adatom on a site<sup>22)</sup>. This contradicts the experimental results of the differential isotopic method<sup>\*\*) as well as those of GOMER<sup>27)</sup>, which verifies the practical localization of adatom. SWEET and RIDEAL<sup>28)</sup> have concluded from their observation of hydrogen adsorption on nickel that the entropy of adatom attains to remarkably high a value at higher coverage. They have inferred from this result that a part of adatoms at higher coverage are behaving as two-dimensional gas particles. Such increase</sup>

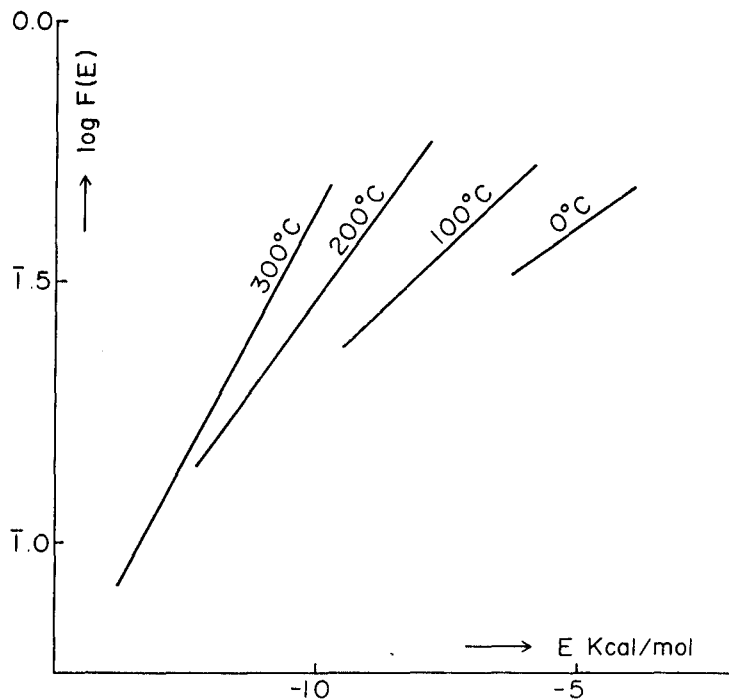


Fig. 3. Distribution Functions of  $H_2$  on Ni

\*) Cf. §5 (see Ref. 11).

\*\*) Cf. §8.

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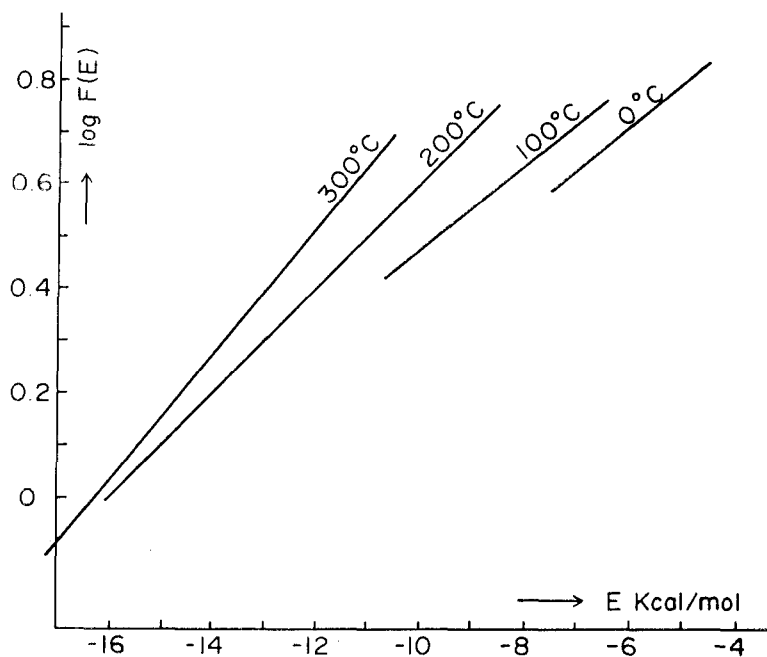


Fig. 4. Distribution Functions of  $H_2$  on W

of entropy is deduced as well from the observation of KINUYAMA and KWAN<sup>12)</sup> as shown in the Appendix but, as discussed there, these increase of entropy is accounted for on the basis of perfectly localized  $r$ -adatoms coexistent with  $s$ -adatom of the amount increasing with increase of coverage; the localized  $r$ -adatoms are in conformity with the above experimental results of the differential isotopic method<sup>13)</sup> and of GOMER<sup>27)</sup>, whereas the coexistent  $s$ -adatom is in concordance with the conclusion from the analysis of isotherms as mentioned in § 7.

It has also been shown<sup>22)</sup> that no relief is brought about either by an alternative assumption of molecular adsorption.

On these grounds it is concluded that the interaction among adatoms could not be precluded in dealing with the adsorption isotherms.

### § 3. Interaction between Hydrogen Adatoms

There are three conceivable causes of interaction between hydrogen adatoms, which are, in zeroth approximation, exclusive of each other, hence the potentials (i), (ii), and (iii) respectively appropriate to these causes make additively the overall potential of interaction. They are developed below for

two hydrogen adatoms each bonded to a surface metal atom.

(i) Exchange repulsion

The potential between the two hydrogen atoms is given quantum-mechanically as  $Q - J/2$ , where  $Q$  or  $J$  is the Coulomb or exchange integral between the two hydrogen atoms. The  $Q - J/2$  will be called the exchange repulsion in what follows. EYRING and POLANYI have evaluated<sup>29)</sup>  $Q$  or  $J$  as 10% or 90% respectively of the Morse function of hydrogen molecule in calculating the activation energy of the elementary reaction  $H + H_2 \rightarrow H_2 + H$ , on which base the exchange repulsion is -35% of the Morse function.

It is well-known that the absolute value of the Morse function of hydrogen is too large<sup>30)</sup> at distances appreciably larger than the nuclear separation of hydrogen molecule, which are now in question. The above estimate of the exchange repulsion may in consequence be too large.

(ii) Potential of interaction through metal electrons

EUCKEN<sup>31)</sup> has pointed out the repulsion between adatoms through the intermediary of metal electrons. One of the present authors formulated the interaction of this cause on the basis of the quantum-mechanical theory of adsorption<sup>10)</sup> developed by him as follows.

Metal electrons impinging the metal surface within the cross section of an adatom are trapped and reemitted thus participating in the bond formation in accordance with (1) on the one hand and increasing the electric resistance of the metal on the other hand<sup>10)</sup>. The competition for metal electrons occurs as their cross sections overlap each other, to weaken the bonds each of the adatoms with metal, hence the repulsive interaction between them. The above cross section was theoretically<sup>10)</sup> worked out at *ca.*  $4\pi r_s^2$ , where  $r_s$  is the radius of atomic sphere of metal atom, in a fair agreement with its value  $3 \sim 4\pi r_s^2$  deduced from the observed effect of adsorption on the resistance of evaporated metal film<sup>32)</sup>, which is appreciably larger than the area allotted to a surface metal atom.

(iii) Electrostatical interaction potential

Adatoms may be more or less charged to contribute to the repulsive potential by electrostatical interaction between dipoles thus formed as discussed by de BOER<sup>33)</sup>; as he remarks, however, the repulsive potential of this cause is too small to account for the overall one.

The exchange repulsion amounts to 0.1019, 0.0134, or 0.0028 eV for the distance, 2.49 Å, 3.52 Å, or 4.31 Å, which happens respectively to be the first, second, or third nearest distance between adatoms on (110)-plane<sup>\*</sup>). This value is not necessarily smaller than the overall repulsive potential at the

<sup>\*</sup>) Cf. § 4.

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respective distance, because of the possible overestimate through the Morse function as mentioned above. We have proceeded to express the overall repulsive potential  $R_I$ ,  $R_{II}$  or  $R_{III}$  at the respective distance as

$$R_I = 0.1019\lambda \text{ eV}, \quad R_{II} = 0.0134\lambda \text{ eV}, \quad R_{III} = 0.0028\lambda \text{ eV}.$$

(5. I), (5. II), (5. III)

and to adjust factor  $\lambda$  to observations as described in § 7.

#### § 4. States of Adatoms

The surface of metallic adsorbents may consist, as mentioned in the introduction, of different crystal planes associated with imperfections and any of these planes of adsorption may provide the  $r$ - and  $s$ -state adsorption sites. It may safely be assumed, however, that the imperfections provide quite a minority of adsorption sites especially those of extraordinarily low energy as referred to in § 1. This is in accordance with the experimental results of GOMER<sup>27)</sup> and SWEET and RIDEAL<sup>28)</sup> that the initial adsorption on a clean surface with extraordinary large heat of adsorption amounts just to 1.5~5.0% of the total coverage. The place of the bulk of adsorption may thus be taken as the crystal planes, each of them in general accommodating adatom with  $r$ - or  $s$ -state.

As stated in § 1 with regard to nickel, the  $r$ -state on (110)-plane is of the lowest energy among both the kinds of states on different crystal planes. It follows that the  $r$ -state adsorption on (110)-plane is a good approximation except at higher coverage, where the low energy of a single adatom on (110)-plane is more or less counterbalanced by the repulsive potential, provided that (110)-plane makes a good portion of the surface as assumed in what follows.

At higher coverage the  $s$ -state adsorption on (110)-plane or  $r$ -state one on other crystal plane should appear first to contribute comparably to the adsorption, inasmuch as the energy of a single adatom of  $r$ -state is constantly lower than that of  $s$ -state on every lattice plane as mentioned in § 1. In that case the observed amount of adsorption should deviate too high above the theoretical one based on the exclusive  $r$ -state adsorption on (110)-plane.

The latter theoretical isotherm is derived on the base of the model specified below. Every metal atom on the (110)-lattice plane provides a site of adsorption of a hydrogen adatom right above it at equal height, so that the centres of the sites of adsorption compose another (110)-plane congruent with the basic one as shown in Fig. 5. A site  $\sigma_0$  has thus two first nearest sites  $\sigma_1$  and  $\sigma_2$ , two second nearest sites,  $\sigma_3$  and  $\sigma_4$ , and four third nearest

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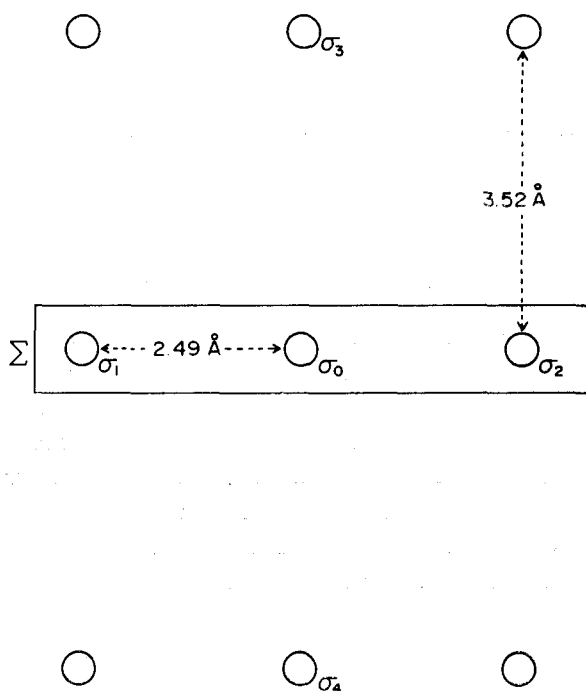


Fig. 5. (110)-Lattice of Adsorption Sites

sites indicated in the corners of the Figure.

### § 5. Statistical Mechanics of Adsorption Isotherm

Consider a macroscopic system  $C^H$  consisting of adsorbent nickel and hydrogen gas each of definite quantity, which are in equilibrium of dissociative adsorption at constant total volume and temperature. The ratio of the probability  $\theta_i$  of a site on the adsorbent being occupied to that  $1-\theta_i$  of it unoccupied is given as

$$\frac{\theta_i}{1-\theta_i} = \frac{QC_{\sigma_i(H)}^H}{QC_{\sigma_i(0)}^H}, \quad (6)$$

where  $QC_{\sigma_i(H)}^H$  or  $QC_{\sigma_i(0)}^H$  is the partition function of  $C^H$  at the particular state, where a definite site  $\sigma_i$  is occupied by a hydrogen atom H or unoccupied respectively with certainty. Let now  $QC_{\sigma_i(0)}$  be the partition function of the system derived from  $C_{\sigma_i(0)}^H$  just by removing one hydrogen atom from the latter without altering the microscopic constrained signified by  $\sigma_i(0)$ . Eq. (6) is written in the form

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$$\theta_i/(1-\theta_i) = q_{\sigma_i}^H/p^H, \quad (7. \theta)$$

where

$$q_{\sigma_i}^H = QC_{\sigma_i(H)}^H/QC_{\sigma_i(0)} \quad (7. q)$$

and

$$p^H = QC_{\sigma_i(0)}^H/QC_{\sigma_i(0)}. \quad (7. p)$$

Since any partition function is the Boltzmann factor of the relevant free energy,  $q_{\sigma_i}^H$  is the Boltzmann factor or the free energy increase of the system  $C_{\sigma_i(0)}$  caused by bringing a hydrogen atom from its standard state onto the  $\sigma_i$  preliminarily evacuated to make an adatom there or the appropriate work  $E_i$  required for the latter process keeping the system involved in the statistical mechanical equilibrium throughout, *i. e.*,

$$q_{\sigma_i}^H = \exp(-E_i/RT), \quad (8. q)$$

where  $E_i$  is allotted to mol of adatom. Such work under the statistical mechanical equilibrium of the system involved kept throughout will be called the reversible work.

The  $\mu^H$  is according to (7. *p*) the Boltzmann factor of free energy increase caused by a simple addition of a hydrogen atom to  $C_{\sigma_i(0)}$ ; ignoring the effect of the microscopic restriction  $\sigma_i(0)$ ,  $-RT \ln p^H$  is identified with the chemical potential  $\mu$  of hydrogen atom, hence

$$p^H = QC^H/QC = \exp(-\mu/RT), \quad (8. p)$$

where  $QC^H$  or  $QC$  is the partition function respectively of  $C^H$  or  $C$  derived from  $C^H$  just by removing one hydrogen atom, each without any microscopic constraint. We have from (7. *\theta*) and (8)

$$\theta_i = \left\{ 1 + \exp\left(\frac{E_i - \mu}{RT}\right) \right\}^{-1}$$

Comparing the latter equation with (2. *\theta*), we see now that  $E$  in (2. *\theta*) is the free energy rather than the energy of adatom in the definite site  $\sigma_i$  as mentioned in § 2 in distinction from in the case of the Fermi gas, where the energies of the respective states is sharply defined.

The  $E_i$  may be expressed as the sum of its part  $E_0$  required in the absence of the interaction and the rest  $E'_i$  due to the interaction with other adatoms, as

$$E_i = E_0 + E'_i,$$

hence by (8. *q*)



$$q_{\sigma_1}^H = q_0^H \exp(-E'_1/RT), \quad (9. a)$$

where

$$q_0^H = \exp(-E_0/RT). \quad (9. b)$$

Eq. (7.  $\theta$ ) is now transformed by substituting  $p^H$  and  $q_{\sigma_1}^H$  respectively from (8.  $p$ ) and (9. a) as

$$\theta_1/(1-\theta_1) = \gamma \exp(-E'_1/RT), \quad (10. \theta)$$

where

$$\gamma = q_0^H/p^H. \quad (10. \gamma)$$

The  $\gamma$  is expressed according to (9. b) and (10.  $\gamma$ ) as<sup>11,34)</sup>

$$\begin{aligned} \gamma = & \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 IkT}{h^2} \right\}^{-1/2} \prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \\ & \times \left( \frac{1.360 \times 980.5P}{kT} \right)^{1/2} \exp\left(\frac{\Delta\epsilon}{RT}\right), \end{aligned} \quad (11)$$

where  $m$  or  $I$  is the mass or the moment of inertia of hydrogen molecule,  $\nu_j$  the  $j$ -th normal vibrational frequency of hydrogen adatom,  $P$  the pressure of hydrogen gas in mmHg and  $\Delta\epsilon$  the excess energy per mol of hydrogen atom in hydrogen molecule in gas at the ground state over the energy of adatom at its ground state. The  $\gamma$  is, according to the definition of  $q_0^H$  and  $p^H$ , the factor with which  $QC_{\sigma_1(0)}^H$  is multiplied to make  $QC_{\sigma_1(H)}^H$  in the absence of the interaction between the adatom in  $\sigma_1$  and surrounding ones or the Boltzmann factor of the reversible work required to convert  $C_{\sigma_1(0)}^H$  into  $C_{\sigma_1(H)}^H$  by transposing a hydrogen atom within the system  $C^H$  from outside  $\sigma_1$  into it less its part due to the repulsive interaction. The  $\nu_j$ 's were evaluated for a single adatom on (110)-plane taking account of the repulsive interaction with other metal atoms than that to which the adatom is bonded.

In the absence of the interaction, *i. e.* for  $E'_1=0$ , we have from (10.  $\theta$ )

$$\theta/(1-\theta) = \gamma \quad (12. \theta)$$

identifying  $\theta_1$  with the coverage  $\theta$  on the ground of the premised physical identity of sites. Assuming on the other hand that the extra work  $E'_1$  is proportional to the coverage as mentioned in the introduction, we have similarly

$$\theta/(1-\theta) = \gamma \exp(U\theta/RT), \quad (12. P)$$

where  $U$  is the value of  $E'_1$  at  $\theta=1$ .

The approximation implied in (12.  $\theta$ ) or (12.  $P$ ) will be called the zeroth

or the proportional one respectively. The higher approximations resorted to Ref. (34) is exemplified by the first approximation in the next section.

## § 6. The First Approximation

The first approximation is based on the assumption that the repulsive interaction exists only between the first nearest adatoms. An adatom on  $\sigma_0$  is thus repulsed by another occupying  $\sigma_1$  or  $\sigma_2$  in the case of (110)-plane as seen in Fig. 5. Consider a set  $\Sigma$  of sites consisting of a site  $\sigma_0$  and such other sites, as an adatom occupying any of them repulses that situated on  $\sigma_0$ . The  $\Sigma$  consists thus, in this case, of  $\sigma_0$ ,  $\sigma_1$  and  $\sigma_2$ . The righthand side of (6) is evaluated constructing the respective partition functions on the base of that  $QC_{\Sigma(0)}^H$  of the system  $C^H$  at the particular state, where  $\Sigma$  is altogether unoccupied; they are thus given as

$$QC_{\sigma_0(H)}^H = QC_{\Sigma(0)}^H \gamma (1 + 2\gamma\xi\eta + \gamma^2\xi^2\eta^2) = QC_{\Sigma(0)}^H \gamma (1 + \gamma\xi\eta)^2, \quad (13. a)$$

$$QC_{\sigma_0(0)}^H = QC_{\Sigma(0)}^H (1 + 2\gamma\eta + \gamma^2\eta^2) = QC_{\Sigma(0)}^H (1 + \gamma\eta)^2, \quad (13. b)$$

since  $QC_{\sigma_0(H)}^H$  or  $QC_{\sigma_0(0)}^H$  is the sum of partition functions of all states of occupation of  $\Sigma$ , satisfying the condition that  $\sigma_0$  is respectively either occupied or unoccupied; the first term in the parentheses of the second member of (13. a) corresponds to the state of occupation that a hydrogen adatom is situated on  $\sigma_0$  but nowhere else, since the above state of adsorption is brought about from  $C_{\Sigma(0)}^H$  by transposing a hydrogen atom within the system  $C^H$  from outside  $\Sigma$  onto  $\sigma_0$ , which results in the increase of the partition function by the factor  $\gamma$  according to (10.  $\gamma$ ) by definitions of  $q_0^H$  and  $p^H$ . The term  $\gamma\xi\eta$  in the same parentheses cares for the state of occupation of  $\Sigma$ , where either  $\sigma_1$  or  $\sigma_2$ , besides  $\sigma_0$ , is occupied;  $\xi$  is the Boltzmann factor of the additional reversible work due to the repulsive interaction between the adatom to be brought to  $\sigma_1$  or  $\sigma_2$  and that situated on  $\sigma_0$ , and  $\eta$  is the Boltzmann factor of another part of the additional reversible work due to the interaction between the hydrogen atom brought to  $\sigma_1$  or  $\sigma_2$  and adatom outside  $\Sigma$ . The factor 2 corresponds to the two states each of an adatom occupying either  $\sigma_1$  or  $\sigma_2$ . The last term  $\gamma^2\xi^2\eta^2$  in the same parentheses represents the state of  $\Sigma$  completely occupied.

The first, second, or third term in the parentheses of the second member of (13. b) corresponds similarly to the state of  $\Sigma$ , which none, either or both of  $\sigma_1$  and  $\sigma_2$  are respectively occupied, leaving  $\sigma_0$  unoccupied.

Substituting  $QC_{\sigma_0(H)}^H$  and  $QC_{\sigma_0(0)}^H$  from (13) into (6), we have

$$\frac{\theta}{1-\theta} = \gamma \left( \frac{1 + \gamma\xi\eta}{1 + \gamma\eta} \right)^2, \quad (14)$$

identifying  $\theta_i$  with  $\theta$  because of the physical identity of the sites. The  $\xi$  is approximated as the Boltzmann factor of the potential  $R_i$  between adatoms\*), as

$$\xi = \exp(-R_i/RT). \quad (15)$$

The  $\eta$  is determined by identifying the partition function of  $C^H$  at the particular state of  $\sigma_1$  being empty, *i. e.*,

$$QC_{\sigma_1(0)}^H = QC_{\Sigma(0)}^H(1 + \gamma + \gamma\eta + \gamma^2\xi\eta),$$

with  $QC_{\sigma_0(0)}^H$  on the ground of the physical identity of sites in accordance with BETHE and PEIERS<sup>35)</sup>, where the first term corresponds to the state, where all sites of  $\Sigma$  are unoccupied, the second term to that of  $\sigma_0$  alone among them being occupied, the third one to that of  $\sigma_2$  alone being occupied and the fourth one to that of both  $\sigma_0$  and  $\sigma_2$  being occupied. We have thus from (13. b) and the above equation

$$(1 + \gamma\eta)^2 = 1 + \gamma + \gamma\eta + \gamma^2\xi\eta, \quad (16)$$

which determines  $\eta$  on the base of known values of  $\gamma$  and  $\xi$ . Eqs. (14), (15), (16), and (5. I) determine  $\theta$  as a function of  $\gamma$  at any temperature and value of the factor  $\lambda$  in (5).

## § 7. Higher Approximations

The second approximation includes the repulsive interactions between the second nearest adatoms as well as those between the first nearest ones. The third approximation takes account further of the repulsive interactions between the third nearest ones. The partition functions on the right-hand side of (6) is constructed for the respective cases of approximation on the base of the partition function  $QC_{\Sigma(0)}^H$ , where  $\Sigma$  is a set of sites consisting of  $\sigma_0$  and such other sites as an adatom occupying any of them repulses that situated on  $\sigma_0$  in the respective cases of the approximation;  $\Sigma$  of the second approximation consists thus of  $\sigma_0$ ,  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ , and  $\sigma_4$  in Fig. 5 and that of the third approximation consists of the latters and four ones in the corners of Fig. 5. Isotherms of hydrogen on (110)-plane were calculated<sup>34)</sup> at 50°C for  $\lambda=1$  by the third and second approximations as well as by the first, proportional, and zeroth approximations identifying the additional reversible work due to the repulsion between the second or the third nearest neighbours with  $R_{II}$  or  $R_{III}$  as in the case of (15)\*\*).

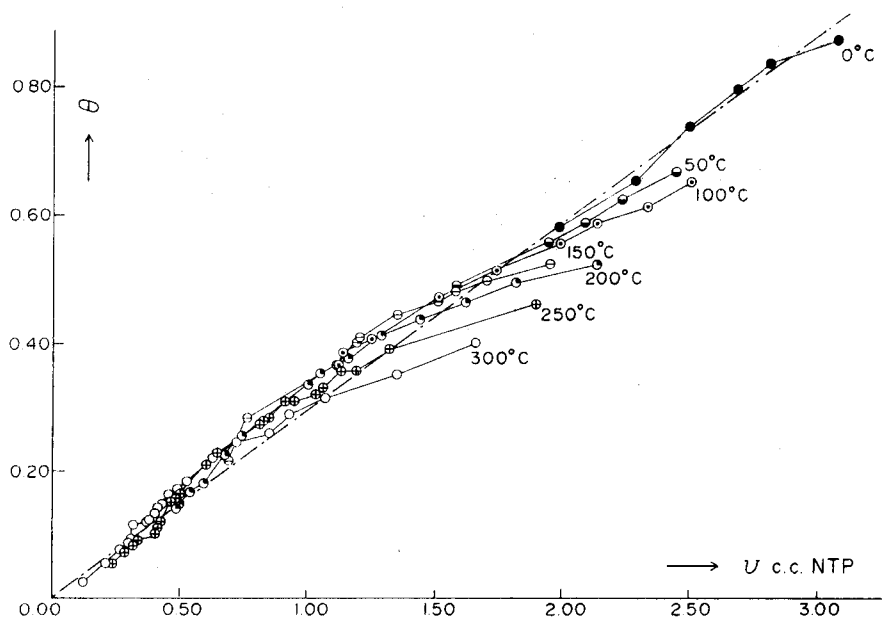
\*) Cf. § 3.

\*\*) In the case of the proportional approximation,  $U$  in (12. P) was approximated with

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The theoretical isotherms  $\theta(\gamma)$  thus obtained by the second and third approximations were almost congruent with each other, whereas that of the first approximation deviated somewhat from the former two, that of the proportional approximation wider and that of the zeroth approximation still more<sup>34)</sup>. On this ground it was plausibly concluded that the second approximation is accurate enough to substitute the third approximation, which is extremely laborious<sup>34)</sup>.

The adsorption isotherm was now computed by the second approximation at different temperatures from 0° to 300°C for different values of  $\Delta\epsilon$  and  $\lambda$  and compared with experimental results of KINUYAMA and KWAN<sup>12)</sup> as follows. The theoretical value of  $\theta(\gamma)$  corresponds to the observed value of  $v(P)$ , with reference to (11) for a given set of values of  $\Delta\epsilon$  and  $\lambda$ . The values



**Fig. 6.** Amount  $v$  of Adsorption Observed and Coverage  $\theta$  Calculated.  $r$ -type Adsorption, Second Approximation,  $\Delta\epsilon = 10.3$  kcal/mol adatom

$2R_I + 2R_{II} + 4R_{III}$ , in the case of the second approximation the additional reversible work due to the repulsion between the first and the second nearest neighbours were respectively identified with  $R_I + 2R_{III}R_I/(R_I + R_{II})$  and  $R_{II} + 2R_{III}R_{II}/(R_I + R_{II})$  proportionally allotting the ignored part  $R_{III}$  and in the case of the first approximation that between the first nearest neighbours was equated to  $R_I + R_{II} + R_{III}$ , so that the additional reversible work of an adatom at  $\theta=1$  is the same throughout the different approximations except in the zeroth one for the sake of quantitative comparison of the results.

of  $\Delta\epsilon$  and  $\lambda$  were now adjusted, so that the adsorbed amount  $v$  runs proportional to the corresponding value of  $\theta$ ; the appropriate proportionality constant  $v/\theta$  gives the amount of adsorption at full occupation, hence the number of sites of adsorption per unit area.

Fig. 6 shows the plot of  $\theta$  against  $v$  at different temperatures for the value of  $\Delta\epsilon=10.3$  kcal/mol atom and  $\lambda=1$  in (5), which is the best fit among those tried for the values of  $\Delta\epsilon$ , 10.3, 10.8, 11.3, 12.3 and 13.3 kcal/mol. ad-atom, and those of  $\lambda$ , 0.5, 1.0 and 1.2. The above value of  $\Delta\epsilon$  leads<sup>34)</sup> to the limiting value 22.0 kcal/mol  $H_2$  of the differential heat of adsorption of hydrogen at 300°C at  $\theta \rightarrow 0$ , which is compared with the experimental value 26 kcal/mol  $H_2$  observed at hydrogen pressure above  $10^{-4}$  mmHg but appreciably lower than 32 kcal/mol<sup>28)</sup> observed at extremely low hydrogen pressure around  $10^{-8}$  mmHg, whereas the proportionality constant  $v/\theta$  gives the number of surface metal atoms,  $1.1 \times 10^{15}$  per  $cm^2$  of BET-area<sup>12)</sup>, which is in fair agreement with the number of atoms on (110)-lattice plane per  $cm^2$ .

The above deviation at extremely low pressure is attributed to the imperfections as mentioned in § 4. We see, on the other hand, in Fig. 6 a common trend of deviation that  $v$  exceeds its theoretical value at higher value of  $\theta$  and the value of  $\theta$  at which the deviation begins is the lower, the higher the temperature. This deviation expected in § 4 has been discussed in a previous work<sup>38)</sup>. The present authors have now found<sup>37)</sup>, that the allowance for the  $s$ -state adsorption on the same lattice plane accounts satisfactorily for the experimental results.

The above conclusion is based on the assumption that the (110)-plane composes a good part of the adsorbent's surface as mentioned in § 4, which is supported by the above results as well as those of BEECK<sup>38)</sup> and PONEC and KNOR<sup>39)</sup>. The possibility is not however altogether excluded that the assumption does not actually hold but adsorption on some other lattice plane than (110) of a sufficient extension might have happened to conform with the present theoretical conclusion.

## § 8. The Differential Isotopic Method

ROGINSKY and KEIER<sup>13)</sup> have developed the differential isotopic method in order experimentally to investigate the states of adsorption. They have allowed isotopically labelled portions of gas to be adsorbed successively on adsorbent and found that the portion later adsorbed was desorbed preferentially. This result conformed, as they pointed out<sup>32)</sup>, to the distribution model but not to the crystal plane model allowed for the interaction by the proportional approximation, which led instead to the equal chance of desorption with the

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rate proportional to the amount of each portion adsorbed.

One of the present authors has now shown<sup>14)</sup> that the experimental result of the differential isotopic method is equally accounted for on the basis of the crystal plane model, if allowed for the interaction by a proper approximation instead by the proportional one. The underlying principle is illustrated first with the adsorption of atomic hydrogen gas on (110)-plane, allowing for the interaction of adatoms by the first approximation.

The first approximation allows for the repulsive interaction with the first nearest neighbours only, so that our problem is reduced to that of one-dimensional arrangements of adatoms on the line of adsorption sites through  $\sigma_1$ ,  $\sigma_0$ , and  $\sigma_2$  in Fig. 5 and on these parallel to it. He has calculated<sup>14)</sup> the state of the linear adsorption of hydrogen atoms at 50°C and  $\gamma = 3 \times 10^3$ , where  $\theta = 0.542$  according to § 7, by comparing the probabilities of different occupations of  $\Sigma$  according to § 6, with the following results. Among 1000 sites linearly arrayed, 542 ones are occupied and  $1000 - 542 = 458$  ones are vacant. Among 542 occupied sites, 350 ones have on directly neighbouring adatoms, 172 ones have each only one neighbouring adatom and 20 ones each two neighbouring adatom.

Among 458 vacant sites, only one has no directly neighbouring adatom, 42 have each one neighbouring adatoms and the remaining 415 have each two ones. The one unoccupied site without neighbour and 42 ones each with only one neighbour are associated with lower energies of adsorption than the 415 vacant sites each with two neighbours. These vacant sites are now supposed to be occupied by 121 new adatoms, which increases the coverage from 0.542 to 0.663. The calculation shows<sup>14)</sup>, assuming the full occupation of sites of lower energy by the new adatoms that 99 among them are obliged to take seat in the sites of highest energy, *i. e.*, those each with two neighbours.

The occupation of vacant sites raises however the energy of the previous occupants by the repulsive potential due to the new neighbours. The adatoms of the highest energy with two neighbours among the previous occupants are thus increased from 20 to 63<sup>14)</sup>. Admitting that adatoms of the highest energy are desorbed initially, both the portions first and subsequently adsorbed are recovered initially on desorption at the ratio 63:99. On the basis of the proportional approximation this ratio is just that of the respective coverages, *i. e.*, 542:121.

The above arguments may be summarized as follows. Previous occupants take easy seats of low energy occupying the linear sites alternately in the main thus avoiding the repulsive interaction, leaving cramped seats to new-

comers, as seen in the above statistics of the occupation of the previous occupants. Newcomers obliged to occupy the cramped seats are thus desorbed preferentially.

It was now shown<sup>(4)</sup> that the above situation remains valid, if the adatoms are formed by the dissociative adsorption of hydrogen molecules instead by simple adsorption of the atomic hydrogen gas, provided that the constituent hydrogen atoms are divided between the second nearest pair of sites, *e.g.*, between  $\sigma_0$  and  $\sigma_3$  or  $\sigma_4$  in Fig. 5 as concluded by OKAMOTO, HORIUTI and HIROTA.<sup>(4)</sup>

This difference in energies of the previous occupants and of newcomers should vanish altogether, however, on the basis of the present model, insofar as the *r*-state adsorption alone is concerned. Even then the higher energy of newcomers and in consequence preferential desorption of the newcomers realized along with the appearance of *s*-state adsorption at higher coverage in accordance with §§ 2, 4 and 7.

The above conclusions show that the experimental results of the differential isotopic method are by no means the exclusive evidence for the distribution model but as well in conformity with the crystal plane model allowed properly for the interaction among adatoms and the alternative *s*-state of adasorption.

We thus arrive at the conclusion that the latter model is the only sound basis of accounting for the observed isotherms.

The present authors wish to thank Mrs. R. WAKE, Mr. T. NAGAYAMA, Miss R. SUDA and Miss T. KAWAI for their help in preparing the manuscript.

### Appendix

SWEET and RIDEAL<sup>(28)</sup> concluded that the entropy of hydrogen adatom on nickel increases considerably with increase of coverage, hence suggested that the adatoms are partly conducting two-dimensional translation. This conclusion is investigated below on the basis of the statistical mechanical theory of the present work, their line of calculation being hardly traceable.

The contribution  $\bar{S}_a$  per mol adatom to the entropy of the whole system is given according to (7. *q*) as the increment per mol of entropy due to an adatom brought to a definite, preliminarily evacuated site  $\sigma_1$ , *i.e.*,

$$\bar{S}_a = (\partial RT \ln q_{\sigma_1}^H / \partial T)_\theta, \quad (i)$$

since the the entropy of the system  $C_{\sigma_1(H)}^H$  or  $C_{\sigma_1(0)}$  is the negative temperature coefficient of the appropriate free energy  $-RT \ln QC_{\sigma_1(H)}^H$  or  $-RT \ln QC_{\sigma_1(0)}$  at constant parameters, which define the respective system.

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We first consider that adatoms are exclusively at the  $r$ -state. If the  $r$ -adatoms are localized with vibrational frequencies large enough, the value of  $\bar{S}_a$  is practically zero according to the expression<sup>11,34)</sup>,  $q_{s_1}^H \equiv \prod_{j=1}^3 \{1 - \exp(-h\nu_j/kT)\}^{-1} \exp(-\varepsilon_0/kT)$ , where  $\varepsilon_0$  is the energy of the ground state of the adatom.  $\bar{S}_a$  is, on the other hand, 10 *e.u.* or 10.8 *e.u.* respectively at 25° or 50°C, if the adatoms conduct the two dimensional translation, when  $q_{s_1}^H$  is approximated as  $q_{s_1}^H = A \cdot 2\pi mkT/h^2 \cdot \exp(-\varepsilon_0/kT)$ , provided the valence vibration is stiff enough, where  $A$  is *ca.* 10 Å<sup>2</sup> area allotted to one adatom and  $m$  its mass.

The  $\bar{S}_a$  is evaluated, assuming hypothetically exclusive  $r$ -state of adatoms, from the experimental result as follows; (7.  $\theta$ ) is written as

$$\theta/(1-\theta) = q_{s_1}^H/p^H, \quad (\text{ii})$$

identifying  $\theta_1$  with the coverage  $\theta^{*})$ . The  $p^H$  is expressed for the adsorption equilibrium<sup>11,34)</sup>, as

$$p^H = \sqrt{Q_F^H/P}, \quad (\text{iii})$$

where<sup>11,34)</sup>

$$Q_F^H = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} \frac{kT}{1.36 \times 980}, \quad (\text{iv})$$

$P$  is the pressure of hydrogen gas in mmHg,  $m$  or  $I$  is the mass or the moment of inertia of hydrogen molecule and the energy its ground state is taken zero. We have from (i), (ii), (iii), and (iv)

$$\bar{S}_a = \frac{\bar{S}_g}{2} + R \ln \frac{\theta}{1-\theta} - \frac{R}{2} \ln P - \frac{RT}{2} \left( \frac{\partial \ln P}{\partial T} \right)_\theta, \quad (\text{v. a})$$

where

$$\bar{S}_g = \ln \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} \frac{kT}{1.36 \times 980} + \frac{7}{2} \cdot R \quad (\text{v. g})$$

is the entropy and  $RT^2(\partial \ln P/\partial T)_\theta$  is the isosteric heat of adsorption respectively per mol hydrogen gas.

The  $\bar{S}_a$  is calculated from the experimental data of KINUYAMA and KWAN<sup>12)</sup> at 50°C or from those of SWEET and RIDEAL<sup>28)</sup> at 25°C as

TABLE 1  $\bar{S}_a$ -Values from Observations

t (°C)	$\bar{S}_a$ cal/deg. mol. adatom					
50	$\theta$	0.458	0.56	0.59	0.625	0.665
	$\bar{S}_a$	5	5	8	8	10
25	$\theta$	0.119	0.310	0.468	0.574	0.761
	$\bar{S}_a$	~0	~0	2	7	15

\*) Cf. pp. 173 and 174.



The  $\bar{S}_a$  is zero at lower  $\theta$  within the experimental fluctuation as required by the localization with large vibrational frequencies but increases remarkably at higher  $\theta$  both in the cases of the observations:  $\bar{S}_a$ -values thus determined are approximately in accordance with those given by SWEET and RIDEAL at higher coverages<sup>28)</sup>.

The above result would appear to confirm the conclusion of SWEET and RIDEAL<sup>28)</sup>, that the adatoms behave as the two-dimensional gas, contradicting the result of GOMER on tungsten<sup>27)</sup> and that of the differential isotopic method on nickel<sup>19)</sup>. This contradiction is, however, only apparent and reconciled as below by taking account of the  $s$ -state adsorption in conformity with in the case of the theoretical deduction of isotherms.\*)

The  $s$ - and  $r$ -adatoms occupy their respective sites independently as concluded in the latter case, hence

$$\frac{\theta_s}{1-\theta_s} = \frac{q_s^H}{p^H}, \quad \frac{\theta_r}{1-\theta_r} = \frac{q_r^H}{p^H}, \quad (\text{vi. } s), (\text{vi. } r)$$

where  $\theta_s$  or  $\theta_r$  is the coverage of adsorption sites respectively of  $s$ - or  $r$ -states adatom and  $q_s^H$  or  $q_r^H$  the value of  $q_{s_i}^H$  respectively relevant to the latter and

$$\theta_s + \theta_r = \theta, \quad (\text{vi. } \theta)$$

by definition, where  $\theta$  is now the coverage directly observed. We see according to (i) and (ii) that  $\bar{S}_a$  is given, under the assumption of exclusive  $r$ -adatoms, apparently as

$$\bar{S}_a = \left( \frac{\partial RT \ln p_s^H}{\partial T} \right)_\theta + R \ln \frac{\theta}{1-\theta}. \quad (\text{vii})$$

The apparent value of  $\bar{S}_a$  is now given as below theoretically allowing for the coexistent  $r$ - and  $s$ -states. The first term of (vii) is developed by differentiating (vi) as

$$\left( \frac{\partial \theta_s}{\partial T} \right)_\theta = \theta_s(1-\theta_s) \left\{ \left( \frac{\partial \ln q_s^H}{\partial T} \right)_\theta - \left( \frac{\partial \ln p^H}{\partial T} \right)_\theta \right\}$$

and

$$\left( \frac{\partial \theta_r}{\partial T} \right)_\theta = \theta_r(1-\theta_r) \left\{ \left( \frac{\partial \ln q_r^H}{\partial T} \right)_\theta - \left( \frac{\partial \ln p^H}{\partial T} \right)_\theta \right\}$$

and noting  $(\partial \theta_s / \partial T)_\theta + (\partial \theta_r / \partial T)_\theta = 0$  by (vi.  $\theta$ ), as

$$\left( \frac{\partial \ln p^H}{\partial T} \right)_\theta = \frac{\theta_s(1-\theta_s) (\partial \ln q_s^H / \partial T)_\theta + \theta_r(1-\theta_r) (\partial \ln q_r^H / \partial T)_\theta}{\theta_s(1-\theta_s) + \theta_r(1-\theta_r)},$$

\*) Cf. p. 178 (see Ref. 37).

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hence we have referring to (vi) and (vii)

$$\begin{aligned}\bar{S}_a = R \ln \frac{\theta}{1-\theta} + \frac{\theta_s(1-\theta_s)(\partial RT \ln q_s^H/\partial T)_\theta + \theta_r(1-\theta_r)(\partial \ln q_r^H/\partial T)_\theta}{\theta_s(1-\theta_s) + \theta_r(1-\theta_r)} \\ + R \frac{\theta_s(1-\theta_s) \ln \frac{1-\theta_s}{\theta_s} + \theta_r(1-\theta_r) \ln \frac{1-\theta_r}{\theta_r}}{\theta_s(1-\theta_s) + \theta_r(1-\theta_r)}.\end{aligned}\quad (\text{viii})$$

It follows from (viii) at smaller  $\theta$ , where  $\theta_s=0$  or  $\theta=\theta_r$  practically, that

$$\bar{S}_a = \bar{S}_{a,r} \equiv (\partial RT \ln q_r^H/\partial T)_\theta.$$

$\bar{S}_a$  is, on the other hand, practically zero at smaller  $\theta$ , as deduced from experimental result in Table 1; the entropy  $\bar{S}_{a,r}$  of  $r$ -adatom is, in consequence, taken zero, hence we have by (viii)

$$\begin{aligned}\bar{S}_a = R \ln \frac{\theta}{1-\theta} + \frac{\theta_s(1-\theta_s)(\partial RT \ln q_s^H/\partial T)_\theta}{\theta_s(1-\theta_s) + \theta_r(1-\theta_r)} \\ + R \frac{\theta_s(1-\theta_s) \ln \frac{1-\theta_s}{\theta_s} + \theta_r(1-\theta_r) \ln \frac{1-\theta_r}{\theta_r}}{\theta_s(1-\theta_s) + \theta_r(1-\theta_r)}.\end{aligned}\quad (\text{ix})$$

It is now the  $s$ -state, as follows theoretically from the relevant potential energy<sup>10,37)</sup>, that should be treated as the two-dimensional translation. The vibration normal to the electronic surface of metal is estimated at *ca.* 1000  $\text{cm}^{-1}$  wave number, which makes the relevant vibrational entropy negligible. We have thus 10.8 *e. u.* for the entropy  $(\partial RT \ln q_s^H/\partial T)_\theta$  of  $s$ -adatom at 50°C.

The  $\bar{S}_a$  is thus calculated by (ix) for hydrogen adsorption on nickel at 50°C as shown in Table 2.

TABLE 2  $\bar{S}_a$  allowed for  $s$ -State Adsorption  
H on Ni, 50°C

$\theta$	$\theta_r$	$\theta_s (= \theta - \theta_a)$	$\bar{S}_a$ cal/mol degree.
0.310	0.310	0.000	0.0
	0.250	0.060	3.8
	0.200	0.110	5.7
0.574	0.500	0.074	3.6
	0.400	0.174	5.8
	0.300	0.274	7.2
0.769	0.600	0.169	9.3
	0.500	0.269	10.3
	0.400	0.369	11.0

The values of  $\theta_r$  in the Table are those arbitrarily taken around the probable range of its value for the theoretical presentation of the adsorption isotherms<sup>37)</sup> and of the effect of adsorption on the electric resistance<sup>32)</sup>. The above values of  $\bar{S}_a$  is in satisfactory agreement with those derived from observation in Table 1; the apparent contradiction is thus reconciled, whereas the s-state of adatom is established.

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