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Title	THEORY OF HYDROGEN ADSORPTION ON PLATINUM
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 10(3), 236-260
Issue Date	1962-12
Doc URL	<a href="https://hdl.handle.net/2115/24767">https://hdl.handle.net/2115/24767</a>
Type	departmental bulletin paper
File Information	10(3)_P236-260.pdf



# THEORY OF HYDROGEN ADSORPTION ON PLATINUM.\*)

By

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(Received December 26, 1962)

## Summary

The effects of adsorbed hydrogen on the work function and the electric resistance of the evaporated platinum film were recently investigated by MIGNOLET, SUHRMANN, WEDLER and GENTSCH and SACHTLER and DORGELO. On the other hand, PLISKIN and EISCHEMS observed the infrared absorption spectra of the adsorbed hydrogen on platinum. The above observations are discussed theoretically to elucidate the hydrogen adsorption on platinum.

It is concluded that the two types of adsorbed hydrogen on platinum are intrinsically the same with the r- and s-type adsorption on nickel. The complicated aspects for platinum are attributed to a less difference of *ca.* 0.4 kcal/mol between the heats of adsorption of both adatoms than that of *ca.* 10 kcal/mol in the case of nickel.

The broad and intensive band at  $4.86 \mu$  in the infrared absorption spectra is assigned to the s-adatom decreasing the work function and the resistance, whereas the other sharp band, at  $4.74 \mu$ , detectable at lower temperatures and higher pressures, to the r-adatom increasing the work function and the resistance. The contrasting band breadths are also discussed qualitatively.

## Introduction

It has been established both experimentally<sup>1-9)</sup> and theoretically<sup>10-13)</sup> that there exist two types of adsorption on nickel, one of them, called r-type adsorption, increases both the work function as well as the electric resistance of the evaporated clean nickel metal, while the other, called s-type one, decreases the work function as well as the resistance<sup>12)</sup>. The r-adatom is bonded to fixed metal atom and is vibrating around the equilibrium position. Hence, the contribution to the entropy of the whole system per adatom is rather small except that to the differential configuration entropy<sup>13)</sup>. The bond nature of s-adatom on metal surface is, on the other hand, a sort of dissolution of hydrogen atom into the metal, dissociating into a proton and an electron in the conduction

\*) Supported in part by the Grant in Aid of the Fundamental Research of the Ministry of Education.

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band, the equilibrium position being at a distance *ca.* 0.5 Å inside from the electronic surface<sup>12)</sup>. The s-atom is not bonded to any fixed metal atom, is conducting two dimensional translation in a plane parallel to the surface, vibrating normal to the surface and in consequence contributes *ca.* 10 e. u. per s-atom to the entropy<sup>13)</sup>.

Recently, MIGNOLET<sup>14)</sup>, SUHRMANN, WEDLER and GENTSCH<sup>15)</sup>, and SACHTLER and DORGELO<sup>16)</sup> have observed the effects of adsorbed hydrogen on the work function and the electric resistance of the evaporated platinum film. They concluded that there existed two types of adsorption of the effects similar to but more complicated than those in the case of nickel.

PLISKIN and EISCHEMS<sup>17)</sup> recently succeeded to observe the infrared absorption of the adsorbed hydrogen on platinum. They observed two bands, one broad and the other sharp, the latter being more intensive at lower temperatures, from which they concluded that there exist two types of hydrogen adatoms on platinum surface.

The present paper is concerned with elucidation of the above effects of hydrogen adsorption on platinum on the basis of the theory developed by HORIUTI and the present author<sup>11-13)</sup>. It is thus shown that the two types of adsorbed hydrogen on platinum is intrinsically the same with the r- and the s-type adsorptions on nickel, attributing the complicated aspects for platinum to a less difference between the heats of adsorption of both adatoms than that in the case of nickel.

It is, further, concluded that the broad band in the infrared spectra is due to the s-atom, and the sharp one due to the r-atom. The temperature behaviour of the respective band intensities as well as the half-breadths of the bands are interpreted theoretically in conformity with the observations.

### **§ 1. Infrared spectra of adsorbed hydrogen on platinum as observed by PLISKIN and EISCHEMS**

PLISKIN and EISCHEMS<sup>17)</sup> were the first to observe the infrared absorption bands of the adsorbed hydrogen on platinum, although not successful to find those on nickel despite many attempts to detect them<sup>18)</sup>. The alumina-supported platinum they prepared were of the average particle size of 15 to 20 Å, as estimated from the amount of adsorbed carbon monoxide.

The spectra of adsorbed hydrogen on alumina-supported platinum are shown in Fig. 1 and 2. Spectrum A in Fig. 1 was observed with a hydrogen pressure of 40 cmHg and at a sample temperature of 35°C. The intensity of the bands at 35°C was found to be a function of pressure up to about 40 cmHg. The intensity of the bands was not sensitive to further pressure increase up to

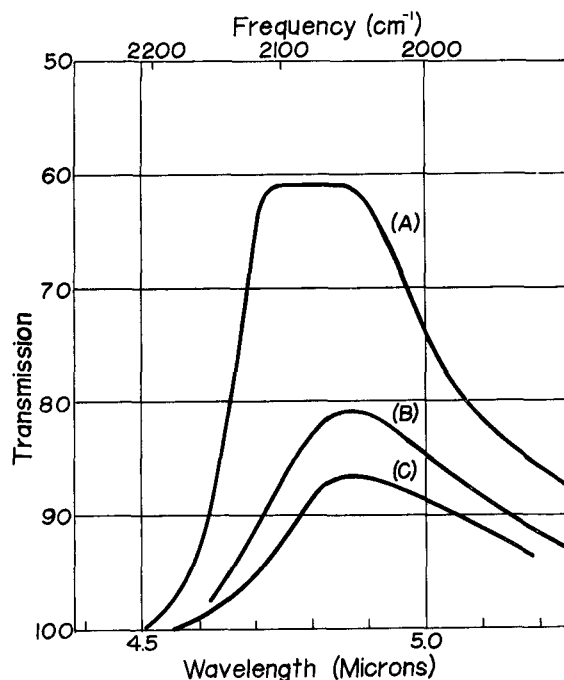


Fig. 1. Infrared spectra of hydrogen adsorbed on platinum.

- (A) at 35°C and 40 cmHg hydrogen pressure ;
- (B) hydrogen in the case of (A) evacuated and observed at 35°C ;
- (C) at 350°C and 40 cmHg hydrogen pressure (after PLISKIN and EISCHENS<sup>17)</sup>).

76 cmHg. The pressure was now reduced to 10 mmHg and after 10 minutes spectrum B was observed at 35°C. Spectrum C was then observed by raising the temperature to 350°C and hydrogen pressure to 40cmHg. Band at 4.86  $\mu$  was found in any cases of A, B and C, while A has besides another band at 4.74  $\mu$  with a smaller half-breadth of the band as compared with the band at 4.86  $\mu$ .

The band at 4.74  $\mu$  became much more distinguished at lower temperature, as seen in Fig. 2. Spectrum A in Fig. 2 was obtained on exposing a fresh alumina-supported platinum sample to hydrogen of 70 cmHg and at sample temperature 35°C, and after cooling the sample to -50°C spectrum B was observed. Spectrum B shows a significant intensity increase and some sharpening of the 4.74  $\mu$  band, whereas there was no significant intensity change of the shoulder at 4.86  $\mu$ . Evacuating now hydrogen at -50°C, the 4.74  $\mu$  band disappeared as seen in C in Fig. 2. The shape of the 4.86  $\mu$  band in spectrum C indicates the presence of only one broad band at this position.

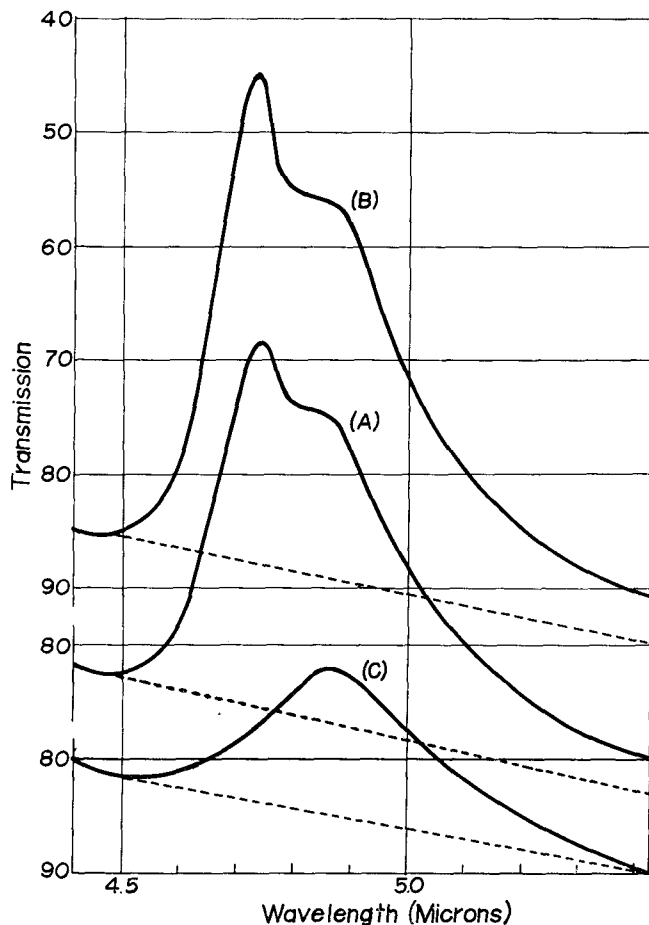


Fig. 2. Infrared spectra of hydrogen adsorbed on platinum.

- (A) at 35°C and 70 cmHg hydrogen pressure;
- (B) at -50°C and 70 cmHg hydrogen pressure;
- (C) hydrogen in the case of (B) evacuated at -50°C and observed at the same temperature (after PLISKIN and EISCHENS<sup>17</sup>).

PLISKIN and EISCHENS<sup>17</sup>) attributed the band at 4.86  $\mu$  to strongly bonded hydrogen adatoms and the band at 4.74  $\mu$  to weakly bonded ones, the nature of the strong and the weak bonds being assumed "basically" different.

Fig. 3 shows the spectrum of deuterium chemisorbed on the same sample as that of Fig. 1. Spectrum A in Fig. 3 was observed at 35°C and at 40 cmHg pressure of deuterium. Spectrum B was observed at 350°C and 40 cmHg deuterium pressure. The deuterium spectra show bands at 6.76  $\mu$  and 6.60  $\mu$

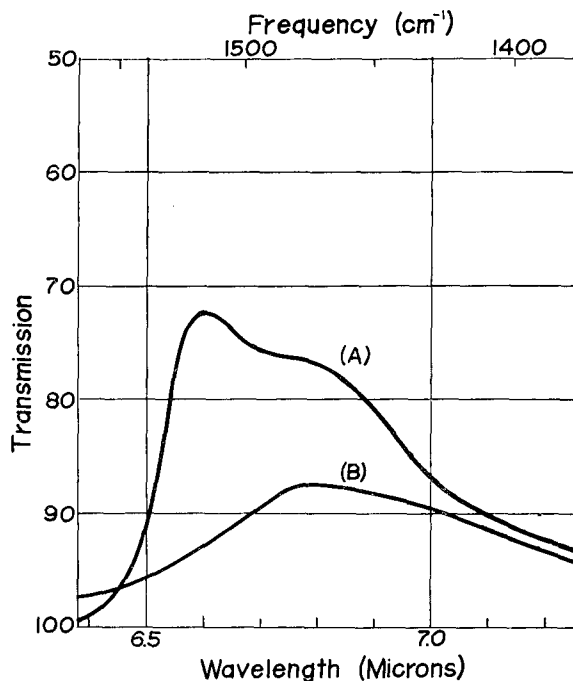


Fig 3. Infrared spectra of deuterium adsorbed on platinum.

- (A) at 35°C and 40 cmHg deuterium pressure ;
- (B) at 350°C and 40 cmHg deuterium pressure (after PLISKIN and EISCHEMS<sup>17)</sup>).

which were similarly attributed by PLISKIN and EISCHEMS to cases of the strongly and weakly bonded deuterium respectively. Isotopic shifts are 1.39 in the ratio of wave length both in the cases of the strong and the weak bonds.

The band positions of adsorbed hydrogen on silica-supported samples were found the same as those on alumina-supported platinum.

PLISKIN and EISCHEMS<sup>17)</sup> discussed different possibilities of accounting for the experimental facts. If adatoms have only one "basic" type of adsorption,

*e.g.*, Pt-H or Pt  $\begin{matrix} \text{H} \\ \diagdown \quad \diagup \\ \text{Pt} \quad \text{Pt} \end{matrix}$ , but two different bond strengths depending on different crystal faces, adatoms more weakly bonded must be readily removed and associated as well with the appropriate band position at lower wave length. This being not the case, the above possibility was excluded.

Another possibility considered<sup>17)</sup> was to assign the band at 4.74  $\mu$  which was more readily removable by evacuation to molecule-ion (H-H)<sup>+</sup> and the other at 4.86  $\mu$  Pt-H. To test this possibility the platinum sample was exposed to a 1 : 1 mixture of H<sub>2</sub> and D<sub>2</sub> at a total pressure of one atmosphere, which

was equilibrated to the mixture of 26.5% H<sub>2</sub>, 46.3% HD and 27.1% D<sub>2</sub> as observed by mass spectrometer analysis. There were observed as the result two bands in the 4.8  $\mu$  region as shown in Fig. 2 and other two in the 6.7  $\mu$  region as in Fig. 3 but no other band at all. The possibility that the band at 4.74  $\mu$  was due to (H-H)<sup>1</sup> was thus excluded, since if at all, there must be observed bands due to (H-D)<sup>†</sup> in the 5.4  $\mu$  region.

## § 2. Two types of adsorbed hydrogen on platinum

We have seen that the observation of the infrared spectra led to the conclusion that there exist two types of chemisorbed hydrogen, which are different in the nature of bond. It might be remarked below that the same conclusion is amplified by the experimental results on the effect of hydrogen adsorption on the work function and on the electric resistance of clean and thin platinum films.

MIGNOLET<sup>14)</sup> studied the adsorption of hydrogen on platinum by following the change in work function. He observed two types of chemisorbed hydrogen, one increased the work function and the other decreased it. The former type of adsorption appeared at low coverage of adsorption at  $-190^{\circ}\text{C}$ , while the latter predominates at the higher coverage of adsorption at  $-190^{\circ}\text{C}$  and at all coverage at  $20^{\circ}\text{C}$ .

SUHRMANN, WEDLER, and GENTSCH<sup>15)</sup> have also been led to conclude two types of adsorption on the platinum films by observation of the electric resistance and the photoelectric emission as a function of coverage. One type of adsorption decreased both the work function and the resistance, which predominated except at low temperatures below  $-183^{\circ}\text{C}$  and at low coverage below *ca.* 0.2, where the other type was detectable, which increased both the work function and the resistance.

SACHTLER and DORGELO<sup>16)</sup> observed that the resistance (1) decreased at  $0^{\circ}\text{C}$  by 0.7%, (2) either increased or decreased at  $-196^{\circ}\text{C}$  depending on the factors such as the thickness of films *etc.*, and (3) increased at  $-210^{\circ}\text{C}$  by 2.5% respectively by hydrogen adsorption. They have concluded thus that there exist two types of adsorption, one increases and the other decreases the resistance.

The result may be summarised as follows. There are two types of chemisorbed hydrogen on platinum. The one type decreases the work function and the resistance, and predominates at high temperatures. The other type of adsorption increases the work function and the resistance, and its effect is only detectable at very low temperatures and at low coverage<sup>\*)</sup>.

\*) At higher coverage, its effects is masked by the other effect. It does not necessary mean that this type of adsorption does not occur at higher coverage.

Two types of adsorption have been recognized also by observations of infrared absorption as reviewed in the foregoing section. The strongly bonded adsorption of the broad band at  $4.8 \mu$  may now reasonably be assigned to the one decreasing the resistance and the work function, which predominates at higher temperatures, whereas the other of the sharp band at  $4.74 \mu$ , detectable at lower temperatures, to the one increasing the resistance and the work function.

The validity of this assignment will be discussed further in the subsequent sections from the theoretical point of view, in order to elucidate the contrasting breadths of these two bands.

### § 3. The nature of adsorption bond

Hydrogen adsorption has two distinctly different effects, as reviewed in § 2, on the conductivity and the work function of evaporated platinum films, which two different bond types of hydrogen adatom have been respectively attributed to. The similar aspects of the effect of hydrogen adsorption have been observed with evaporated films of nickel<sup>3-8)</sup>, iron<sup>19)</sup>, and palladium<sup>20)</sup>.

The energy of the system of a hydrogen atom and metal with  $N$  conduction electrons has previously been investigated<sup>11,12)</sup>, starting from a linear combination of SLATER determinants of different configurations of  $N+1$  electrons, and determining the coefficients of the linear combination by the variation method or by the self-consistent field method. It has, thus, been concluded, that there exist in general two different types of adsorption, which are called the r-type adsorption and s-type adsorption, respectively<sup>12)</sup>. The two different bond types are now theoretically investigated in this section, with special reference to the effect of adatom on metal electrons, on which state the conductivity and the work function depend.

#### 3. 1. The bond of r-adatom on metal

The wave function  $\Psi_r$  of the  $N+1$  electrons may be formulated as

$$\begin{aligned} \Psi_r = & a_0 \varphi(\mathbf{k}_1, \dots, \mathbf{k}_N, 1s) + \sum a_{\alpha s, s\ell} \varphi(\mathbf{k}_1, \dots, \underset{(\ell)}{\mathbf{k}_\alpha}, \dots, \mathbf{k}_N, 1s) \\ & + \sum b_{\alpha s} \varphi(\mathbf{k}_1, \dots, \mathbf{k}_N, \mathbf{k}_\alpha) + \sum c_{s\ell} \varphi(\mathbf{k}_1, \dots, 1s, \dots, \underset{(\ell)}{\mathbf{k}_N}, 1s), \quad (1) \end{aligned}$$

provided that the characteristic of  $1s$  electron of the hydrogen atom is reserved to a good extent.  $\varphi(\mathbf{k}_1, \dots, \mathbf{k}_N, 1s)$  in Eq. (1) is the SLATER determinant constructed by  $N$  BLOCH wave functions with respective wave number vectors  $\mathbf{k}_1, \dots, \mathbf{k}_N$  and  $1s$ -wave function of hydrogen atom, appropriate to the ground state of the system. The second term  $\sum a_{\alpha s, s\ell} \varphi(\mathbf{k}_1, \dots, \underset{(\ell)}{\mathbf{k}_\alpha}, \dots, \mathbf{k}_N, 1s)$  corresponds similarly to the excited neutral states, the third one to the positively charged

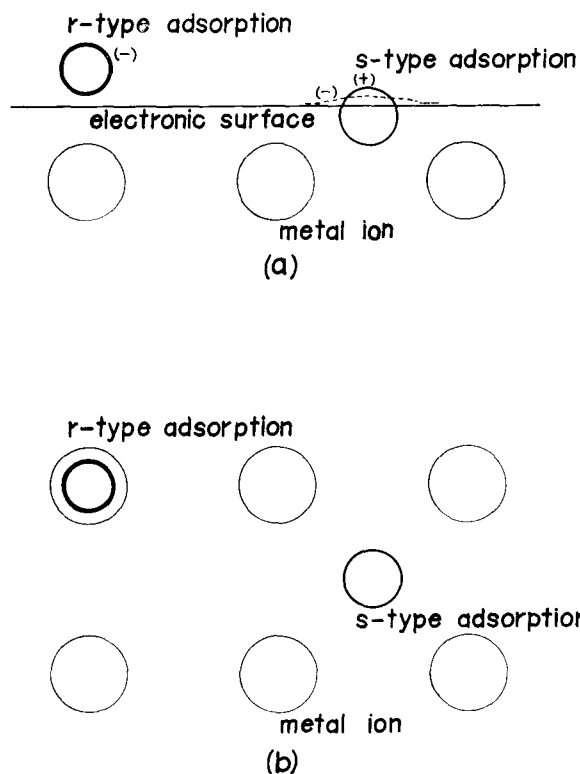
states of the adatom and the fourth one to its negatively charged state;  $1s$  or  $\mathbf{k}_\alpha$  denotes an electron in  $1s$  or  $\mathbf{k}_\alpha$  level transferred from  $\mathbf{k}_i$  level of metal, resulting in the excited state of the system, and the summations extend over the respective excited states;  $a_0$ ,  $a_{\alpha s, si}$ ,  $b_{\alpha s}$  and  $c_{si}$  are constant coefficients satisfying the normalization condition

$$a_0^2 + \sum |a_{\alpha s, si}|^2 + \sum |b_{\alpha s}|^2 + \sum |c_{si}|^2 = 1.$$

The energy of the ground state given by the first terms becomes higher, when hydrogen atom is brought near the metal surface, owing to the exchange repulsions between  $1s$ -electron and metal electrons<sup>21)</sup>. However, the energy appropriate to  $\Psi_r$ , has been found appreciably lower than that of the ground state alone at certain positions of hydrogen atom owing to the resonance between the ground state and the other states represented by the second, third and fourth terms on the right hand side of Eq. (1). The heat of adsorption has thus been evaluated for nickel at *ca.* 3.0 eV/adatom, and the equilibrium distance at *ca.* 1 Å outside the electronic surface, or at 2.5 Å from the surface metal atom layer. The present author called the adatom thus described the *r*-adatom. Since the nature of this bond is similar to the usual covalent bond in the molecular orbital theory, the equilibrium position of *r*-adatom is probably right above a metal atom but not in the interstitial one of the surface, and in consequence *r*-adatom is vibrating around the equilibrium position with one mode perpendicular and the other two modes parallel respectively to the surface.

The *r*-adatom is slightly negatively polarized, because the contribution from the fourth term on the right side of Eq. (1) representing the states ( $M^+ - H^-$ ) is greater than that from the third terms corresponding to the states ( $M^- - H^+$ ), the energies of the former being nearer to that of the ground state than that of the latter, while the matrix elements of the interactions between the ground state and respective states are practically the same<sup>11)</sup>. The negative polarization of *r*-adatom is *ca.* 0.02 in units of elementary charge, hence the *r*-type adsorption increases the work function of the metal so much.

That the resonance energy between the ground state ( $\mathbf{k}_1, \dots, \mathbf{k}_i, \dots, \mathbf{k}_N, 1s$ ) and a state ( $\mathbf{k}_1, \dots, 1s, \dots, \mathbf{k}_N, 1s$ ) or ( $\mathbf{k}_1, \dots, \mathbf{k}_i, \dots, \mathbf{k}_N, \mathbf{k}_\alpha$ ) *etc.* is so large as to give a stable *r*-adatom, implies that a metal electron  $\mathbf{k}_i$  impinging the *r*-adatom is readily trapped in  $1s$ -level and  $1s$ -electron of *r*-adatom is in turn readily emitted into the metal, thus participating in the bond formation on the one hand and increasing the electric resistance of the metal as shown in § 4. 1 on the other hand. The cross section of this sort of scattering have been evaluated<sup>12)</sup> at  $3 \sim 4\pi r_s^2$ , where  $r_s$  is the radius of the sphere with the volume of the



**Fig. 4.** Two types of adsorption. The r-type adatom is slightly negatively polarized, and its equilibrium position right above a metal ion at *ca.* 1 Å outside the electronic surface of the metal. The equilibrium position of s-type adsorption is interstitial and *ca.* 0.5 Å inside the electronic surface. The dotted line shows the smoothing effect inducing dipole moment.

atomic polyhedron of a metal atom.

The above mentioned effects of r-adatom on metal electrons are furthermore responsible for the pronounced repulsions between adatoms, as follows. Two r-adatoms compete for metal electrons as their cross sections overlap to weaken each other's bonds, hence resulting in a pronounced repulsive interaction between them.

### 3. 2. The bond of s-adatom on metal

The s-adatom is likened to dissolved atom in metal, dissociated into a proton and an electron in the conduction band, as reviewed in what follows.

If the proton in question is situated inside the metal, the energy of  $1s$  orbital is raised considerably and the electron of the orbital is now put in the conduction band of the metal. The appropriate wave function of  $N+1$

electrons has been expressed by the linear combination of SLATER determinants of  $N+1$  BLOCH wave functions, and the coefficients of the linear combination have been determined by the self-consistent field method<sup>(12)</sup>. The relevant extra electron density around the dissolved proton  $\delta\rho$  has thus been determined as

$$\delta\rho = \lambda^3/8 \pi \cdot \exp(-\lambda r), \quad (2)$$

and the heat of dissolution is given by  $-I + \varphi + \lambda e^2/4$ , where  $\lambda$  is a constant evaluated at  $1/0.30 \text{ \AA}$  for nickel and  $1/0.34 \text{ \AA}$  for platinum,  $I$  the ionization energy of hydrogen atom and  $\varphi$  the work function of the metal.

The equilibrium position and the appropriate energy of proton have been determined by an alternative simple treatment, resorting to the expression of kinetic energy of  $N+1$  electrons according to THOMAS, FERMI and WEIZSAECKER<sup>(12)</sup>. The heat of dissolution of hydrogen atom has thus been calculated as a function of the distance from the electronic surface, and the equilibrium position was found inside the electronic surface  $0.5 \text{ \AA}$  apart from it and interstitial of surface metal ions. The energy at the equilibrium position has been found larger than the heat of dissolution in the interior of metal by  $0.5\text{eV} \sim 1.0 \text{ eV}$ . This type of adsorption, described as the s-type adsorption by the present author, is thus a sort of dissolution of hydrogen atom dissociated into a proton inside the metal near the electronic surface and an electron in the conduction band of the metal.

It is readily seen as follows how the energy of dissolved proton lowers, as the proton is brought to the surface from the interior of the metal. The sum of kinetic energies of  $N+1$  electrons are given by the THOMAS-FERMI expression as

$$\frac{4\pi h^2}{5m} \left(\frac{3}{8\pi}\right)^{5/3} \int (\rho + \delta\rho)^{5/3} d\tau,$$

where  $m$  is the mass of an electron,  $h$  the PLANCK constant,  $d\tau$  the volume element,  $\rho$  the electron density of the metal without any perturbation, and  $\delta\rho$  is that given by Eq. (2). Since

$$\int (\rho + \delta\rho) d\tau = N+1$$

irrespective of the position of the proton, so that the integral  $\int (\rho + \delta\rho)^{5/3} d\tau$  is the smaller, the evener the distribution of  $\rho + \delta\rho$ . The integral, hence, is reduced by bringing the peak of extra density  $\delta\rho$  around the proton along with it from the interior of the metal toward the electronic surface, where  $\rho$  decays outward.

The s-type adsorption is always associated with dipole moment of the order

of  $0.06 \times 10^{-18}$  DEBYE<sup>12)</sup> as the result of the smoothing effect of the part of the electron cloud  $\delta\rho$  around the proton protruded from the electronic surface, as shown by dotted line in Fig. 4 (a), which decreases the work function of the metal.

The resistance of the metal is decreased by s-atom, as the number of conduction electrons is increased<sup>12)</sup>. The cross section of scattering metal electrons by s-atom has been evaluated<sup>12)</sup> at  $0.3\pi r_s^2$ , hence its scattering effect on the resistance is not so important in contrast with r-atom, as detailed in § 4.

The s-type adsorption likened as above to dissolution implies that s-atom is not bound to any fixed metal atom, but conducts two dimensional translations in a plane parallel to the surface and vibrates normal to the surface in the interstitial surface position. Actually the dissolved proton is not bonded to any fixed metal atom<sup>22)</sup> and conducting three dimensional translations, as demonstrated by the NMR<sup>23)</sup>.

#### § 4. The change of electrical resistance by adsorption

We are now ready to discuss the change of resistance of evaporated metal film by adsorption in the light of the bond nature of hydrogen adsorption.

##### 4. 1. The general formalism

The specific electric conductivity  $\sigma$  of a metal film is theoretically derived by FUCHS<sup>21)</sup> and SONDHEIMER<sup>21)</sup> as a function of the thickness  $d$  of the film, the number  $n$  of conduction electrons per unit volume, the mean free path  $l$ , the mean velocity  $v$  of an electron at the FERMI surface, and the probability  $p$  of specular reflection of an electron at the surface of the film, as

$$\sigma = \sigma_0 \Phi_p(d/l)/(d/l), \quad (3)$$

where

$$\frac{x}{\Phi_p(x)} = 1 - \frac{3}{2x} (1-p) \int_0^\infty \left( \frac{1}{t^3} - \frac{1}{t^5} \right) \frac{1 - \exp(-xt)}{1 - p \cdot \exp(-xt)} dt \quad (4)$$

and

$$\sigma_0 = \frac{ne^2l}{mv} \quad (5)$$

is the specific conductivity of the bulk metal.

The resistance  $R$  of a thin film is proportional to  $1/(\sigma \cdot d)$ , the proportional constant  $c'$  depending on the conditions of the experiment. We have, hence, from (3) and (5),

$$R(d) = \frac{c'}{\sigma \cdot d} = \frac{c'}{d^2} \frac{mv}{ne^2} \left( \frac{d}{l} \right) \left\{ \Phi_p(d/l) / (d/l) \right\}^{-1} \quad (6)$$

or

$$cR(d) d^2 = (d/l)^2 / \Phi_p(d/l) \quad (7)$$

where

$$c = \frac{ne^2}{c' m v} \quad (8)$$

is another constant.

If an amount of hydrogen adsorbed increases the number of free electrons per unit volume by  $\delta n$ , the change in resistance,  $\delta R$ , is given by Eqs. (7) and (8), as

$$\frac{\delta R}{R} = - \frac{\delta n}{n} + \frac{\delta v}{v} = - \frac{2}{3} \frac{\delta n}{n}, \quad (9)$$

since

$$v \propto n^{1/3} \quad \text{and} \quad \delta v/v = (1/3)(\delta n/n).$$

It should be noted that the relative increase  $\delta R/R$  is independent of temperature.

If the probability  $p_0$  of specular reflection at the surface in the absence of adsorbate is reduced to  $p$  by hydrogen adsorption the increase  $\delta R$  of resistance is given by Eq. (7) as

$$c\delta R(d) d^2 = \left\{ (d/l)^2 / \Phi_p(d/l) - (d/l)^2 / \Phi_{p_0}(d/l) \right\} \quad (10)$$

The right hand side is approximately independent of  $(d/l)$  and is nearly equal\* to  $-\delta p/2$  for  $p \leq 0.3$  and  $\delta p \leq 0.3$ , where  $\delta p = p - p_0$ . Hence, we have

$$\delta R(d) = - \frac{\delta p}{2 c d^2}. \quad (11)$$

In this case, the increase  $\delta R$  is independent of temperature and inversely proportional to the square of thickness  $d$ , but the relative increase  $\delta R/R$  is not, provided that  $p_0$  and  $p$  are independent of the temperature.

It may now be taken practically established that the resistance on evaporated metal film is given as a function only of  $n$  and  $p$  according to Eqs. (9) and (11), on which basis the respective effects of the two types of adatoms on resistance are going to be discussed in what follows.

#### 4. 2. The change of resistance of evaporated nickel film

We summarise first the experimental and theoretical results<sup>12)</sup> of the changes

\*) See Table 1 in ref. (12).

of resistance of nickel films by hydrogen adsorption. MIZUSHIMA<sup>9)</sup> has observed the resistance of clean evaporated nickel films and their changes by hydrogen adsorption for  $d=30 \text{ \AA} \sim 500 \text{ \AA}$  and at  $T=273^\circ\text{K}$  and  $90^\circ\text{K}$ . His experimental results have been analysed on the basis of Eqs. (7), (9) and (11) as follows.

(1) The experimental curves of  $\log \{R(d) \cdot (d)^2\}$  vs.  $\log \{d\}$  for clean films and the theoretical ones of  $\log \{(d/l)^2 \Phi_{p_0}(d/l)\}$  vs.  $\log \{(d/l)\}$  are now adjusted to each other with reference to Eq. (7) by varying the three parameters, whose values at the best coincidence are

$$l = 150 \text{ \AA} \text{ at } T = 273^\circ\text{K}, \quad (12. a)$$

$$l = 270 \text{ \AA} \text{ at } T = 90^\circ\text{K}, \quad (12. b)$$

$$c = 3.6 \times 10^{-6} \Omega \text{ \AA}, \quad (12. c)$$

and  $p_0 = 0 \sim 0.3$ , (12. d)

for  $d \geq 100 \text{ \AA}$ .

For thinner films  $d < 100 \text{ \AA}$ , the experimental curves are no more adjustable to theoretical ones, indicating that the films has the structure containing many gaps.

(2) The scattering probability  $p_{irr}$  due to irregularities of the evaporated nickel films has been determined at  $v/330 \text{ \AA}$  from the mean free paths  $l_0$  of the nickel metal without any irregularity, *i. e.*<sup>26)</sup>,

$$l_0 = 270 \text{ \AA} \text{ at } T = 273^\circ\text{K}$$

or

$$l_0 = 2100 \text{ \AA} \text{ at } T = 90^\circ\text{K},$$

and from the above values of Eqs. (12. a) and (12. b). That  $p_{irr} = v/330 \text{ \AA}$  implies that the mean free path in the absence of thermal vibrations is  $330 \text{ \AA}$ <sup>\*)</sup>, which is of the same magnitude as that  $l_0 = 330 \text{ \AA}$  appropriate to the distortions caused by thermal vibrations at  $220^\circ\text{K}$ . It follows that the evaporated film is not so porous with gaps between crystal grains as usually conceived<sup>\*\*)</sup>.

\*) We have obtained this value by the equation

$$(1/150 - 1/270)^{-1} = 330 \text{ \AA} \text{ at } T = 273^\circ\text{K}$$

or  $(1/270 - 1/2100)^{-1} = 330 \text{ \AA} \text{ at } T = 90^\circ\text{K}.$

That the values at  $T=273^\circ\text{K}$  and  $90^\circ\text{K}$  are the same confirms the consistency of the present theory. This value implies that the specific resistance of evaporated nickel film with thermal treatment is approximately twice as that of single nickel crystal at room temperature, in good agreement with the experimental value by ANDERSON, BAKER and SANDERS<sup>27)</sup>.

\*\*\*) Cf. refs. (27) and (28).

(3) The number of conduction electrons of films is decreased by 0.02 per r-atom (see § 3.1), and the resultant increase of resistance of the  $n_i$  atomic layer film due to this effect is  $100 \times \frac{2}{3} \frac{0.02}{n_i} \%$  at full coverage according to Eq. (9). By s-type adsorption, the number of electrons is increased by unity per atom, hence the resistance of the film decreases by  $100 \times \frac{2}{3} \frac{1}{n_i} \%$  at full coverage.

On the other hand, the probability  $p_0$  of specular reflection of clean metal film is reduced to zero at the coverage  $\theta = \frac{1}{4} \sim \frac{1}{3}$  by the r-type adsorption with the scattering cross section of  $3 \sim 4 \pi r_s^2$ , thus resulting in the increase of resistance

$$\delta R(d) = \frac{p_0}{2cd^2} \quad (13)$$

as given by Eq. (11) where  $-\delta p = p_0$  in this case. By the s-type adsorption with the cross section  $0.3 \pi r_s^2$ , the value of  $p_0$  is reduced to  $0.7 p_0$  approximately at full coverage, hence the increase of resistance is  $\delta R = 0.3 p_0 / 2c \cdot d^2$  according to Eq. (11).

The resistance of nickel film is increased at the initial stage of adsorption, attains a maximum at the coverage  $\theta = 0.30 \sim 0.35$ , and decreases as far as  $\theta \simeq 0.7$ . The observed increase  $\delta R(d)$  obeys Eq. (13) with  $p_0 = 0.05^{**})$ , and is independent of temperature and inversely proportional to  $d^2$ . From  $\theta = 0.35$  to  $\theta = 0.7$  the relative decrease of the resistance by hydrogen adsorption is independent of temperature instead, and the increase in the number of conduction electrons is approximately 1 per atom, as estimated by Eq. (9)\*).

These results enables us unambiguously to attribute the initial increases of the resistance to the r-atom and the later decrease to the s-atom. It should be remarked that it is not necessary to take into account the resistance increase due to the reduction of  $p_0$  by the s-type adsorption, as  $p_0$  is exterminated by the preceding r-type adsorption.

(4) The above changes of resistance implies that the heat of r-type adsorption, is larger than that of s-type adsorption, which causes the r-type adsorption to precede. But the intense repulsions as remarked in § 3.1 reduces

\*) MIZUSHIMA omitted the factor  $2/3$  in Eq. (9), so that he attained  $\sim 0.6$  instead.

\*\*\*) It should be remarked that this value is obtained, assuming as if the adsorption occurred on both sides of the film. In consequence, the probability of an evaporated film is  $ca. 2 \times 0.05 = 0.1$  as estimated from the resistance increase.

the differential heat of r-atom steeply that the s-type adsorption prevails over r-type one beyond  $\theta \approx 0.35$ .

By the analysis of the isotherm of hydrogen adsorption on the model of r-type adsorption with intense repulsions and s-type adsorption without repulsions, we have obtained the following results<sup>29)</sup>, *i.e.* the heat of adsorption of r-atom is 12 kcal/g atom, that of s-atom 7 kcal/g atom, and the repulsive potential between r-adatoms at a distance of 2.49 Å is 0.12~0.15 eV.

### 4. 3. Change of resistance of evaporated platinum film

It has been experimentally concluded, as reviewed in § 2, that there exist two types of hydrogen adsorption on platinum; the one increases the electric resistance as well as the work function, revealing itself only at temperatures below 77°K and low coverage, and the other decreases both the resistance and the work function, which predominates at region of temperature and coverage outside that where the former type does.

We may, now, safely assign the former to the r-atom and the latter to the s-atom, and attribute the rather complex aspects of the effect of adsorption, in contrast to the case of nickel, to the smaller differences between the heats of adsorption of adatoms of the respective types, and to the large difference between their entropies, which is inherent in the natures of the respective adsorption bonds (§ 3. 1 and § 3. 2) as will be detailed in § 5. The r-atom thus prevails only at very low temperature and coverage on account of slightly higher heat of adsorption (of the order of magnitude 0.2 kcal/gram atom), but decays at higher coverage even at the very low temperature owing to the intense repulsions between r-adatoms; the s-atom prevails at higher temperatures, the small difference of adsorption heat being overcompensated by its large entropy.

(1) At temperatures as low as  $T = 63^\circ\text{K}$ , the resistance and the work function of platinum vary with coverage  $\theta$ , as mentioned in § 2, qualitatively similar to those of nickel dealt with in (3) of § 4. 2, as follows from the present theory, admitting a higher heat of r-atom. However, the coverage  $\theta_m$  at the maximum increase of resistance is expected to be smaller than that of nickel and the maximum there not as sharp as in the latter case, since s-adatoms of opposite effects would appear at the smaller coverage on account of the smaller excess of the heats of r-atom over that of s-atom.

The value of the probability  $p_0$  of specular reflection of clean evaporated platinum film is estimated at *ca.* 0.04 from the maximum value 2.5% of the relative increase of the resistance, as observed by SACHTLER and DORGELO<sup>16)</sup> at  $T = 63^\circ\text{K}$  as follows. The relative increase  $\delta R/R$  is given by Eqs. (7) and (11) as

$$\frac{\delta R}{R} = -\frac{\delta p}{2} \frac{\Phi_{p_0}(d/l)}{(d/l)^2}, \quad (14)$$

ignoring the effect of s-adatom. At the maximum observed of  $\delta R/R$ , the probability of specular reflection is assumed exterminated exclusively by r-adatom of  $3\sim 4 \pi r_s^2$  cross section. Hence, putting  $\delta p = -p_0$  in Eq. (14), and assuming  $d/l=0.4$  as is usually the case<sup>\*</sup>, we have  $p_0=0.04$  for  $(\delta R/R)_{\max}=2.5\%$  from Eq. (14) (see also Fig. 8 in ref. (12)). This value of  $p_0$  is its lower limit because of the neglect of the effect of s-adatom, which decrease  $\delta R/R$  by its opposite effect on the resistance.

(2) At temperatures above  $T=200^\circ\text{K}$ , the s-adatom predominates to decrease resistance by increasing the number of electrons according to Eq. (9). The thickness of the film is, for example,  $n_t=30$  atomic layers by order of magnitude in case of experiments of SUHRMANN, WEDLER and GENTSCH<sup>15)</sup>, when we have  $\delta R/R = -(2/3)(\delta n/n_t) = -2.2 \theta\%$ , since  $\delta n = \theta$  and  $n_t = 30$ ; *i.e.* the average number of s-adatom per surface metal atom is given by the coverage  $\theta$ , hence  $\delta n = \theta$ , admitting an electron is increased per an s-adatom; on the other hand, the number of conduction electrons is  $n_t$  per surface metal atom. The decrease  $\delta p$  of  $p_0$  by the s-adatom causes, on the other hand, the relative increase of resistance, which amounts approximately  $\theta \times 1\%$  on the base of  $p_0 = 0.04$ ,  $\delta p = -p_0(0.3 \pi r_s^2 / \pi r_s^2) \theta$  and  $d/l=0.4$  according to Eq. (14). Consequently,  $\delta R/R$  is  $-0.12\%$  for  $\theta=0.1$  as compared with the experimental value  $-0.11\%$  at  $\theta=0.1$  and  $T=295^\circ\text{K}$ . The effective increase of the number of conduction electrons is, on the other hand, approximately 0.55 ( $= (2.2-1.0)/2.2$ ) per s-adatom, which accounts for the experimental values of the effective increase less than unity, *e.g.* 0.52 at  $T=195^\circ\text{K}$  and  $\theta=0.06$ , and 0.20~0.28 at  $\theta=0\sim 0.4$  and  $T=295^\circ\text{K}$ , as observed by SUHRMANN, WEDLER and GENTSCH<sup>15)\*\*</sup>.

These authors have further observed at these temperatures that the effective increase of conduction electrons is diminished as the coverage is increased, and more markedly at lower temperatures. For example,  $\delta n_{\text{eff}}$  is approximately constant at 0.2~0.3 in the range of  $\theta=0.08\sim 0.4$ , and, as well, the work function remains more or less constant at  $295^\circ\text{K}$ , and  $\delta n_{\text{eff}}$  is decreased as  $\theta$  is increased beyond 0.4, whereas  $\delta n_{\text{eff}}$  is decreased at  $195^\circ\text{K}$  from 0.52 at  $\theta=0.06$  to 0.13 or less at  $\theta \geq 0.45$  and the work function increases slightly,

<sup>\*</sup>) See refs. 4)~8), 12) and 15). *Cf.* also § 4. 2.

<sup>\*\*</sup>) SUHRMANN, WEDLER and GENTSCH<sup>15)</sup> left out the factor 2/3 in Eq. (9) and assumed 0.6 for the number of electrons per Pt-atom. Hence, the resultant value for the effective increase of the number of electrons is more or less the same in the present discussion. The difference between  $\delta n_{\text{eff}}=0.52$  at  $195^\circ\text{K}$  and  $\delta n_{\text{eff}}=0.2\sim 0.3$  at  $295^\circ\text{K}$  may be due to the different initial values of  $f_0$ .

indicating that at  $T=295^\circ\text{K}$  the r-atom is practically absent at  $\theta=0\sim 0.4$ , but, at  $T=195^\circ\text{K}$  it begins to be adsorbed and is appreciably abundant at  $0.06<\theta<0.4$ , to increase the resistance or to diminish the effective increase of the number of the conduction electrons. The above results are summarised that the coverage of s-atom does not increase proportional to that of r-atom. These deviations from the proportionality are expected when the coverage of s-atom approximates unity, and, further they are expected even at lower coverages at lower temperatures, since the adsorption of s-atom accelerates that of r-atom with negative polarization by decreasing the work function and thus lowering its energy slightly.

(3) The effective change of the number of conduction electrons per adatom was found by SACHTLER and DORGELO<sup>16)</sup> fluctuating between positive and negative values at the temperatures intermediate between  $65^\circ\text{K}$  and  $195^\circ\text{K}$ . The r- and s-adatoms may be of comparable amounts at these temperatures. These sorts of adatoms are now of opposite effects on the resistance which are both sensitive to the thickness  $d$  of the film as well as to the probability  $p_0$  of specular reflection of the clean film. A small change in the latter quantities may in consequence give rise to the above observations.

### § 5. Entropy of adsorbed hydrogen

The study of entropy of adsorbed hydrogen would afford the admirable key to an assigning the adsorption state. An adatom at a definite site contributes an amount

$$\bar{S}_a = (\partial \underline{RT} \ln q / \partial T)_\theta, \quad (15)$$

to the entropy of the whole system, where  $\underline{R}$  is the gas constant and  $q$  is the partition function of an adatom. The  $\bar{S}_a$  thus defined is the partial molal entropy of adatom less the differential configurational entropy  $\underline{RT} \ln \frac{1-\theta}{\theta}$ .

The  $\bar{S}_a$  will be called the entropy of adatom in what follows.

The value  $q_r$  of  $q$  for r-atom is<sup>13)</sup>

$$q_r \equiv \prod_{j=1}^3 \left\{ 1 - \exp(-h\nu_j/kT) \right\}^{-1} \exp(-\varepsilon_0^r/kT), \quad (16)$$

where  $\varepsilon_0^r$  is the energy of the ground state of the r-atom; the frequency  $\nu_1$  of the stretching vibration is estimated for nickel at *ca.*  $2000 \text{ cm}^{-1}$ , and those  $\nu_2$  and  $\nu_3$  of bending vibrations at  $300\sim 400 \text{ cm}^{-1}$ .<sup>29,30)</sup> The appropriate value of  $\bar{S}_a$  is *ca.* 1 e.u. at room temperature.

The s-atom vibrates vertical to the surface, but translates two dimensionally

parallel to the surface, as discussed in § 3. 2. The value  $q_s$  of  $q$  for s-atom is given approximately as<sup>13)</sup>

$$q_s = \left\{ 1 - \exp(-h\nu/kT) \right\}^{-1} \cdot \frac{A \cdot 2\pi MkT}{h^2} \cdot \exp(-\varepsilon_0^s/kT), \quad (17)$$

where  $\varepsilon_0^s$  is the energy of the ground state of s-atom,  $\nu$  the perpendicular vibrational frequency,  $M$  the mass of proton, and  $A$  is *ca.* 10 Å area per s-atom. The value of  $\bar{S}_a$  is *ca.* 10 e.u. at room temperature for s-atom by Eq. (15).

The differential entropy  $S_i$  of the adsorbed layer at  $\theta$  is given by

$$S_i = \bar{S}_a - R \ln \frac{\theta}{1-\theta} \quad (\text{per gram atom}), \quad (18)$$

where the second term is the configurational entropy of the adsorbed layer. On the other hand, the differential entropy  $S_g$  of hydrogen in gas phase is expressed as

$$S_g = \bar{S}_g - R \ln p^{H_2}, \quad (19)$$

$$\bar{S}_g = \ln \frac{(2\pi M^{H_2} kT)^{3/2}}{h^3} \cdot \frac{4\pi^2 I^{H_2} kT}{h^2} \cdot \frac{kT}{1.36 \times 980} + \frac{7}{2} R, \quad (19. a)$$

where  $p^{H_2}$  is the pressure of the gas phase in mmHg,  $M^{H_2}$  or  $I^{H_2}$  is the mass or the moment of inertia of hydrogen molecule, and  $\bar{S}_g$  is the entropy of hydrogen gas at 1 mmHg. The difference of  $S_g/2$  and  $S_i$  is now  $Q/T$ , *i. e.*

$$S_g/2 - S_i = Q/T \quad (20)$$

where  $Q$  is the differential heat of adsorption per gram atom, given by

$$Q = -\frac{R}{2} \left( \frac{\partial \ln p^{H_2}}{\partial (1/T)} \right)_\theta. \quad (21)$$

Hence, we have from Eqs. (18), (19) and (20)

$$\bar{S}_a - R \ln \frac{\theta}{1-\theta} = \frac{\bar{S}_g}{2} - \frac{R}{2} \ln p^{H_2} - \frac{RT}{2} \left( \frac{\partial \ln p^{H_2}}{\partial T} \right)_\theta, \quad (22)$$

which enables us to determine the value of  $\bar{S}_a$  experimentally. Fig. 5 shows the  $\bar{S}_a$  side by side with  $2Q$ ,  $\delta R/R$  and the increment of work function  $\delta\phi$  respectively plotted against the coverage  $\theta$  for nickel. In the initial stage of adsorption, the r-atom predominates owing to its lower energy  $\varepsilon_0^r$  than that  $\varepsilon_0^s$  by 5 kcal/mol; in consequence the resistance and the work function are increased, while  $\bar{S}_a$  remains constant near zero. The energy of r-atoms are

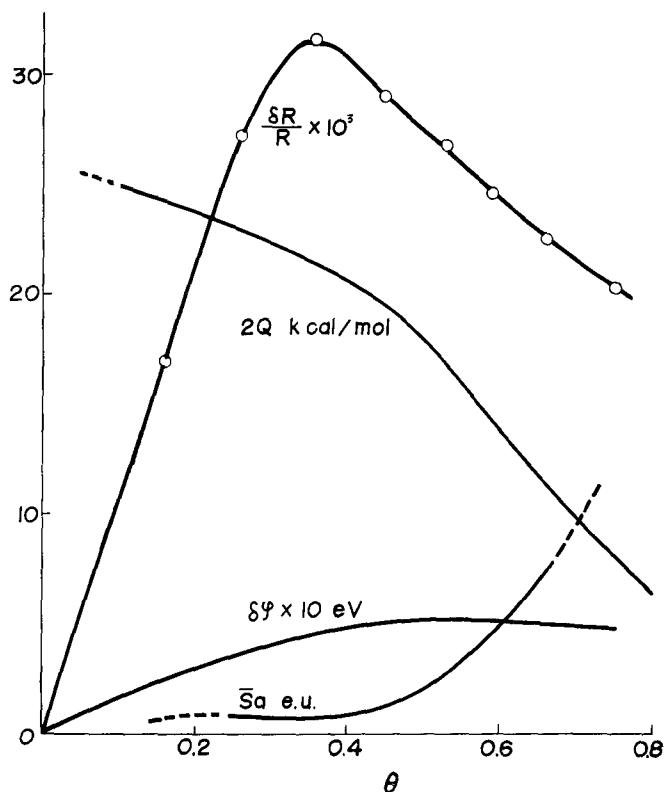


Fig. 5. Adsorption of hydrogen on nickel.

$\delta R/R$ : relative increment of resistance of  $0^\circ\text{C}$  after SUHRMANN, MIZUSHIMA, HERMANN and WEDLER<sup>5)</sup>.

$\delta\phi$ : increment of work function at  $20^\circ\text{C}$  after MIGNOLET<sup>3)</sup> and SUHRMANN *et al.*<sup>5)</sup>.

$\bar{S}_a$ : entropy of adatom at  $25^\circ\text{C}$  (partial molal entropy of adatom minus differential configurational entropy  $RT \ln(1-\theta/\theta)$  as evaluated by Eq. (22) from the data of RIDEAL and SWEETT<sup>31)</sup>, or  $\bar{S}_a = \bar{S}_s - RT \ln(1-\theta/\theta)$ , where  $\bar{S}_s$  is the "differential entropy" in the paper of RIDEAL and SWEETT<sup>31)</sup>.

$2Q$ : differential heat of adsorption per mol after RIDEAL and SWEETT<sup>31)</sup>.

raised as  $\theta$  is increased due to the intense repulsions between r-adatoms<sup>\*)</sup>, so that s-adatoms begins to be adsorbed around  $\theta \approx 0.3$ . In the region of  $\theta = 0.5 \sim 0.75$ , the s-adatom predominates instead and in consequence the resistance as well as the work function decreases, while  $\bar{S}_a$  increases steeply up to that of s-adatom, which is ten times as much as that of r-adatom. The behaviour of  $Q$  is interpreted similarly as follows;  $Q$  decrease with increase

\*) Repulsive potential amounts to 1.2~1.8 eV between a pair of r-adatoms adsorbed on nearest neighbouring metal atoms.

of  $\theta$  more and more steeply, because r-adatoms repulse each other increasingly with increase of  $\theta$  and in consequence are surpassed by s-adatoms in the rate of increase, which has lower differential heat of adsorption.

In the case of adsorption on platinum, the difference of the adsorption energy is small ( $\varepsilon_s^r - \varepsilon_s^s = -0.4$  kcal/mol), so that r-adatom predominates only at very low temperatures and low coverage. At higher temperatures, s-adatom preponderates on account of the larger differential entropy due to the two dimensional translation. The ratio of the partition function  $q_s/q_r$  is in consequence nearly 10 at room temperatures in this case. The lower limit of the value of  $\bar{S}_a$  as estimated by experiments<sup>15,32)</sup> is *ca.* 10 e.u. at 293°K on the base of  $p \cong 10^{-7}$  mmHg,  $\theta = 0.05$ ,  $2Q = 18$  kcal/mol, and  $\bar{S}_g = 22.3 R$ , which is in accord with the above theoretical conclusion that adatoms are practically in s-state for low coverage, contributing 10 e.u. per gram adatom as mentioned above.

## § 6. Discussions on the breadth of band in the infrared spectra produced by adsorbed hydrogen on platinum.

We are led, as seen in the subsequent sections § 6. 1 and § 6. 2, to the following two conclusions by the theoretical discussions in §§ 3, 4 and 5 on the natures of bonds of hydrogen adatom on metals, their effects on the electric resistance and the entropies of the two kind adatoms, with reference to the experimental results reviewed in §§ 1 and 2; (1) the broad band at  $4.86 \mu$  is due to the vibration of s-adatoms perpendicular to the surface and (2) the sharp band at  $4.74 \mu$  at higher pressures and lower temperatures originates from the stretching vibration of r-adatom perpendicular to the surface.

### 6. 1. General discussions on the breadth of band

We now discuss qualitatively the half-breadths  $\delta\nu$  of both the bands. The intensity of absorption band is proportional to<sup>33)</sup>

$$\frac{1}{2\pi} \frac{\Gamma}{(\nu - \nu_0)^2 + (\Gamma/2)^2}, \quad (23)$$

where  $\nu_0$  is the mean frequency of the band and  $\Gamma$  is the decay constant, or the reciprocal of the mean life of the excited state, half-breadth  $\delta\nu$  of the band being equal to  $\Gamma/2$ . The  $\delta\nu$  thus gives informations as to how the energies of the excited states are dissipated into other modes of vibrations through the perturbation of anharmonic terms of the potential<sup>\*)</sup>.

\*) The contribution to  $\Gamma$  from the interaction between the vibration of adatom and radiation is approximately  $2(\alpha e)^2 \nu / 3Mc^3 < 1 \text{ cm}^{-1}$ , where  $\alpha e \approx 0.1 e$  or  $M$  is effective charge or mass of an adatom, hence neglected in the present discussions.

The frequencies of the vibrations perpendicular to the surface of both r- and s-adatoms are approximately  $2000 \text{ cm}^{-1}$  as shown in § 1, which are more than ten times as much as the maximum frequency  $\nu_m = 150 \text{ cm}^{-1}$  of the metal, as estimated by the relation  $h\nu_m = k\theta_D$ , where  $k$  is the BOLTZMANN constant and  $\theta_D$  the DEBYE temperature of the metal. Hence, an excited state would transfer to the ground state simultaneously exciting, if at all, more than ten phonons through perturbation<sup>\*)</sup>

$$V_{st} = a_s \sum A(l, m, n, \dots) a_i^l a_j^m a_k^n \dots, \quad (24)$$

where  $a_s$  is the normal coordinate of the stretching vibration of r- or s-adatoms,  $A(l, m, n, \dots)$ 's are constant coefficients,  $a_i$  etc. normal coordinates of lattice vibrations; the sum of powers  $l, m, n, \dots$ , i. e.  $l+m+n+\dots$ , being larger than ten, the transition of this sort could hardly occur.

## 6. 2. The breadth of band due to r-adatom

The excited state of r-adatom may decay alternatively by exciting a few bending vibrations of adatoms of ca.  $400 \text{ cm}^{-1}$  and subsequently the energies of bending vibrations may further decay exciting two or three lattice vibrations of the maximum wave number  $150 \text{ cm}^{-1}$ , which is expected to occur much more readily than the direct one discussed in § 6. 1. The perturbation potential for r-adatom is<sup>\*\*)</sup>

$$V_{sb} = a_s \sum B(u, v) b_1^u b_2^v \quad (\text{with even } u \text{ and } v) \quad (25)$$

where  $B(u, v)$ 's are constant coefficients,  $b_1$  and  $b_2$  are normal coordinates of the two bending vibrations. Rectangular coordinate  $z$ ,  $x$  and  $y$  may be substituted for  $a_s$ ,  $b_1$  and  $b_2$ , where  $z$  is perpendicular and  $x$  or  $y$  parallel respectively to the surface plane and the origin is the equilibrium position of the r-adatom. Hence we have in place of Eq. (25),

$$V_{sb} = z \sum B(u, v) x^u y^v, \quad (26)$$

The above substitution is justified on the ground that the observed isotopic shift 1.39 is very near to the square root of the ratio of the mass of a deuteron to that of a proton, which indicates that metal atoms are practically fixed without participating in the localized vibrations of adatoms.

The r-adatom is, as reviewed in § 3. 1, situated on a metal atom, to which it is bonded, at a distance of ca.  $2.5 \text{ \AA}$  from the atom, or  $1 \text{ \AA}$  from the electronic surface, outside the surface. The distance between an r-adatom and

\*) The transition  $(n=1) \rightarrow (n=0)$ , now in question is caused by the linear term with respect to  $a_s$  according to the selection rule, hence its higher order terms are ignored.

\*\*\*) Odd number of  $u$  or  $v$  are excluded on the (100) or (110) plane because of symmetry.

a next nearest metal atom is *ca.* 3.5 Å for the smallest distance 2.5 Å between metal atoms. On the other hand, the amplitudes of the stretching vibration with  $\nu_1=2000\text{ cm}^{-1}$  are 0.1 Å or 0.2 Å for the ground or excited state, and those of the bending vibrations with  $\nu_2$  or  $\nu_3=400\text{ cm}^{-1}$  are 0.3 Å or 0.6 Å for the ground or doubly excited state. Hence, the r-atom is confined in a very small region around the equilibrium position, for apart from metal atoms, so that the perturbation with high powers  $u$  and  $v$  will be not appreciable in the region.

Similar situation is expected in the case of Zn-H or O-H group on the surface of zinc-oxide<sup>31)</sup>, or of O-H group of conventional compound<sup>35)</sup>, where the hydrogen is bonded to a definite atom, Zn or O, but situated remote from other atoms of the crystal or the molecule.

We are thus led to infer that the half-breadth of the band at 4.74  $\mu$  due to r-atom would be of the same order of magnitude with that of the band of Zn-H or O-H group, as is actually the case. The observed half-breadth is *ca.* 20  $\text{cm}^{-1}$ , or the mean life is *ca.*  $10^{-12}$  sec., which is twenty times as much as the period  $5 \times 10^{-14}$  sec. of the bending vibration in accordance with above inference.

### 6. 3. The breadth of band due to s-atom

An s-atom conducts two dimensional translation and has a large entropy as detailed in § 5, which implies that the potential is more or less constant in a plane parallel to the surface. The vibration normal to the surface is damped, on the other hand, only through the transfer of its energy to the translational motion, inasmuch as the transfer to the lattice vibration is hardly possible as discussed in § 6. 1. The potential is now steeply raised in the vicinity of a metal ion, owing to the screened COULOMB repulsion between a metal ion and a proton. Hence the higher order anharmonic terms of the expansion of perturbation potential such as

$$V_{st} = z \sum C(m, n) (x/x_0)^m (y/y_0)^n \quad (\text{with even } n \text{ and } m)^{*}) \quad (27)$$

will be appreciable there, where  $x$ ,  $y$  and  $z$  are rectangular coordinates,  $z$  is normal,  $x$  or  $y$  parallel to the surface plane, and the origin is at the midpoint of the equilibrium position of an s-atom in the interstitial surface site;  $2x_0$  and  $2y_0$  are distances between adjacent metal atoms in the  $x$  and  $y$  directions respectively, so that  $x = \pm x_0$ ,  $y = \pm y_0$  and  $z \approx 0.5\text{Å} - r_s$  <sup>\*\*)</sup> are coordinates of metal atoms, where the above series is divergent. The anharmonic terms of

\*) Odd numbers of  $n$  or  $m$  are excluded because of symmetry.

\*\*\*) Cf. § 3. 2.

Eq. (27) of appreciable amount near a metal ion may give rise to the broader band of s-adatom as compared with that of r-adatom. This effect on the band breadth is amplified by the condition of energy conservation within  $kT$  imposed upon the transition; the condition is only restrictedly fulfilled in the case of the energy dissipation of the excited stretching vibration of r-adatom on account of the far larger level distance of *ca.*  $400\text{ cm}^{-1}$  of bending vibration than  $kT$ , whereas the condition is readily satisfied in case of s-adatom because of the level distance of translational motion, which is even smaller than  $kT$ . In other words, the number of final states of the transition is more abundant in case of s-adatom, hence the stretching vibration of s-adatom is damped more rapidly than that of r-adatom to render the band further broader.

The half breadth of the band of s-adatom, or the reciprocal of mean life of its excited state might be estimated simply as below, assuming that s-adatom transfers from the excited vibrational state to the ground state, as it collides with the metal ion. The frequency of the collision<sup>\*)</sup> is approximately  $200\text{ cm}^{-1}$  in wave number units at  $0^\circ\text{C}$ , and in consequence the mean life  $1/\Gamma$  is *ca.*  $(200 \times 3 \cdot 10^{10})^{-1} = 0.15 \cdot 10^{-12}$  sec, which amounts to only one sixth of the mean life of the excited state of r-adatom mentioned in § 6. 2. Hence we have  $\delta\nu = 100\text{ cm}^{-1}$  according to the relation  $\delta\nu = \Gamma/2$ , which is of the same order of magnitude as the observed one,  $100\text{ cm}^{-1}$ .

### Conclusions

1. It has been shown that the two types of hydrogen adsorption on platinum as deduced from the experiments on the effects on the work function and electric resistance are intrinsically the same with the r- and s-type adsorptions theoretically concluded by the present author.

2. The complicated aspects of the effects on the work function and resistance for platinum have been attributed to a less difference between the heats of adsorption of both adatoms than that in the case of nickel.

3. The equilibrium position of r-adatom is right above a metal atom at surface and is vibrating around the equilibrium position with one mode perpendicular and the other two modes parallel to the surface. The s-adatom, likened to dissolution, is not bound to any fixed metal atom, but conducts two dimensional translations in a plane parallel to the surface and vibrates normal to the surface in the interstitial surface position. Hence, the contribution to the

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\*) The mean velocity of proton is  $(2kT/M)^{1/2}$ , hence mean time of collision is  $3.5\text{Å}/(2kT/M)^{1/2} = 1.5 \cdot 10^{-12}$  sec or  $200\text{ cm}^{-1}$  in wave number units. For deuteron, the half-breadth is  $1/\sqrt{2}$  of that for hydrogen.

entropy of the s-atom is larger than those of r-atom as actually observed.

4. The broad and intensive band at  $4.86\mu$  in the infrared absorption spectra of hydrogen adsorbed on platinum is assigned to the s-atom, and the sharp and weak band at  $4.74\mu$  to the r-atom. The band breadths are estimated by the above model (conclusion 3) in satisfactory agreement with observations.

### Acknowledgments

The present author wishes to express his sincere thanks to Prof. J. HORIUTI for his profound interest and stimulating discussions on the present work. He wishes also to express his hearty thanks to Dr. K. AZUMA, Dr. S. MATSUSHITA, Miss NAKADA and members of the group of "Kinetics on Electrode". He would like to acknowledge the contributions of Mrs. R. WAKE, Mr. T. NAGAYAMA and Miss T. KAWAI, who helped in preparing the manuscript.

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