

Adsorption Isotherm for Heterogeneous Surface. (II)

The Effects of Induced Heterogeneity and of Interaction Energy between the Adsorbed Particles on the Decrease of the Heat of Adsorption¹⁾.

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In the previous paper, the authors have analyzed the several adsorption isotherms by assuming that the functional relationship between the heat of adsorption and the coverage indicates a *priori* heterogeneity of the surface, and that the changes of the adsorption heats with increasing coverage are dependent on the interaction between the adsorbed particles and the so-called "induced heterogeneity" as in the case of the change of the work function of the absorbent with adsorption.

In this paper, effects of the latter two factors have been checked with the results that the lateral interaction could not satisfactorily account for the decrease of the heat of adsorption which is more than 10 Kcal/mol in the case of chemisorption or the small heat decrease in the case of physical adsorption either. The "induced heterogeneity" can account for the adsorption isotherm reasonably, so far as the heat of adsorption ΔH of particles adsorbed already changes uniformly and simultaneously all over the surface layer whenever a particle is adsorbed, and the linear relationship between ΔS and ΔH is accepted. But in the case of induced heterogeneity, it is not yet clear what mechanism is involved in the heat decrease of adsorption accompanying with increasing coverage and, therefore, it is impossible to assume the physical model for the surface state.

INTRODUCTION

In the previous paper of the authors²⁾, it has been found that the isotherms obtained experimentally are in line with the theoretical ones for the various heterogeneous surfaces. The heterogeneity of the surface was determined from the correlation between the isosteric heat of adsorption and coverage of the surface.

Roberts³⁾, Miller⁴⁾ and Wang⁵⁾ have explained statistically the variation of the adsorption heat with increasing coverage due to the lateral interaction of the adsorbate. Horiuti *et al*⁶⁾ have calculated the repulsive potential between adatoms of hydrogen by means of Morse potential. Recently, Vol'kenstein⁷⁾ has estimated the interaction function between adsorbed particles, $\phi(r)$, and distribution function of surface sites, $\rho(Q)$, for some representative adsorption isotherms, and illustrated the relationships between $\phi(r)$ and $\rho(Q)$.

Induced heterogeneity have been supported by Boudart, Weisz and others.⁸⁾ Boudart has emphasized the effect of a double layer on the heat of adsorption, and assumed that a double layer is set up on the surface and changes the work func-

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tion of the adsorbent when the adatoms cover the metal surface. Weisz has attempted to illustrate the effect of electronic charge transfer between adsorbate and adsorbent on chemisorption.

The purpose of this paper is to investigate to what extent will be tenable both of "repulsive force" and "induced heterogeneity" hypothesis in explaining the decrease of the heat which occurs when the surface of the catalyst is assumed not to be necessarily heterogeneous.

(1) **Contribution to the Heat Decrease of Adsorption from "Induced Heterogeneity"**

It might be presumed that the surface is *a priori* homogeneous and that the differential heat of adsorption of adatoms occupying the surface sites changes uniformly and simultaneously all over the surface layer, when each gas particle is adsorbed on the surface. This phenomenon is considered to be due to the "heterogeneity" induced by a adsorbed particle, as, for instance, in the change of the work function of the adsorbent with the amount of the gas adsorbed. Under this circumstance, the isotherm of the Langmuir type is applicable so far as the interaction between the adsorbates is negligible. The equilibrium constant of adsorption K in this isotherm, however, changes as a function of the coverage.

Then, we can express the isotherm by the following equations :

$$\frac{\theta}{1-\theta} = K(\theta)p = p \exp(-\Delta H(\theta)/RT) \exp(\Delta S(\theta)/R) \quad (1)$$

$$\Delta S(\theta) = R \left\{ \ln \frac{\theta}{p(1-\theta)} + \frac{\Delta H(\theta)}{RT} \right\} \dots \dots \text{for non-dissociative ads.} \quad (2)$$

$$\text{or } 2R \left\{ \ln \frac{\theta}{p^{1/2}(1-\theta)} + \frac{\Delta H(\theta)}{2RT} \right\} \dots \dots \text{for dissociative ads. of} \quad (3)$$

diatomic molecule

where θ is the coverage of the surface, p is the equilibrium pressure and ΔH is the enthalpy change. The equations (2) and (3) represent the non-configurational entropy change ΔS when each molecule or atom occupies one lattice point on the surface respectively. If the functional relationship between ΔH and ΔS was estimated, amount of adsorption would have been calculated at any equilibrium pressure and temperature. But in fact, these functional relationship is hardly obtained from the theoretical standpoint. In this case ΔS values and the relationship between ΔS and ΔH are obtained by introducing the relationship obtained experimentally between the heat of adsorption ΔH and coverage θ at the pressure p in the Langmuir type equation. These are plotted in Fig. 1 to Fig. 4. It can be seen that there is linearity between ΔH and ΔS , which have been used in derivation of isotherm^{2,9)} on the heterogeneous surface. Although no theoretical basis for this linear relationship has yet been clearly understood, so far as that is acceptable, the adsorption isotherm is satisfactorily obtained for any pressure by introducing the relationship between ΔS and ΔH into the isotherm. To ascertain the equations (2) and (3) to be reasonable as the Langmuir isotherm, the value of ΔS at $\theta=0$ was compared with the theoretical one calculated from the partition function under the corresponding condition. The calculated entropy term for the homonuclear diatomic molecule is given as follows.

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$$(\exp(-\Delta S/R))_{\theta=0} \doteq kT \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} (1 - \exp(-h\nu/kT))^{-1} e^{7/2} \quad (4)$$

The calculated entropy values are nearly in agreement with the observed ones except the case of hydrogen adsorption on iron, as shown in Table 1. Therefore, it

Table 1. The calculated and observed entropy factors when the gas particles were adsorbed on the bare surface.

Adsorption System	Adsorption Temperature °K	$e^{-\Delta S/R}$ or $e^{-\Delta S/2R}$	
		Observed value	Calculated value
Ar-KCl	80	7.450×10^8	2.813×10^8
Ar-TiO ₂	85	1.793×10^8	3.279×10^8
H ₂ -Ni	563	1.570×10^5	2.127×10^5
H ₂ -Co	373	2.249×10^5	1.035×10^5
H ₂ -Fe	306	1.288×10^7	7.297×10^4
H ₂ -W	873	6.005×10^5	4.584×10^5
N ₂ -W	873	1.555×10^7	1.886×10^7

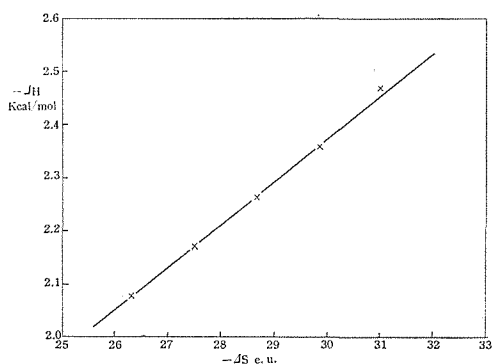


Fig. 1. The functional relation between ΔH and ΔS when Argon adsorbed on the KCl surface.

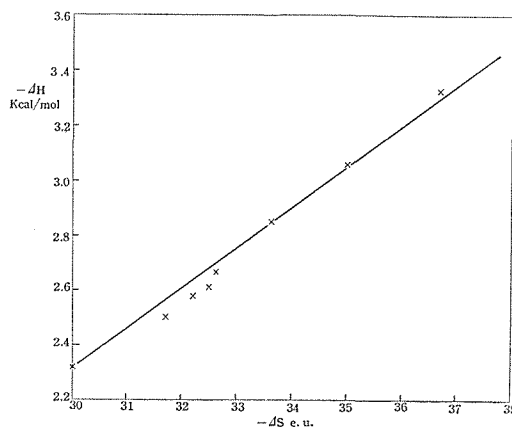


Fig. 2. The functional relation between ΔH and ΔS when Argon adsorbed on the TiO₂ surface.

will be concluded that the adsorption can be evaluated reasonably for any equilibrium pressure using the Langmuir isotherm, in which the linear relationships must be established between the entropy and enthalpy as shown in Fig. 1 to Fig. 4, when we consider that the heat of adsorption should decrease uniformly all over the surface layer as a result of adsorption of each particle, even if the surface is *a priori* homogeneous.

(2) Contribution to the Heat Decrease of Adsorption from the Interaction between the Adsorbed Particles

The effects of repulsive forces between the adatoms or molecules on the heat

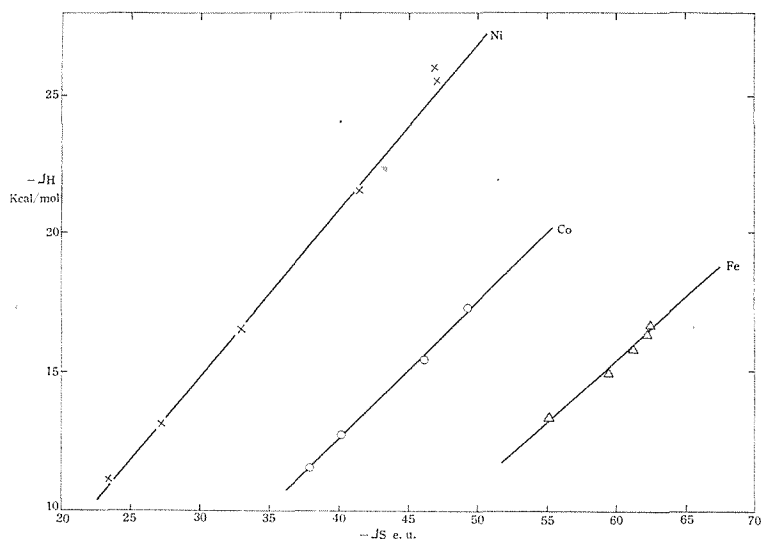


Fig. 3. The functional relations between ΔH and ΔS when H_2 adsorbed on the Ni, Co and Fe surfaces.

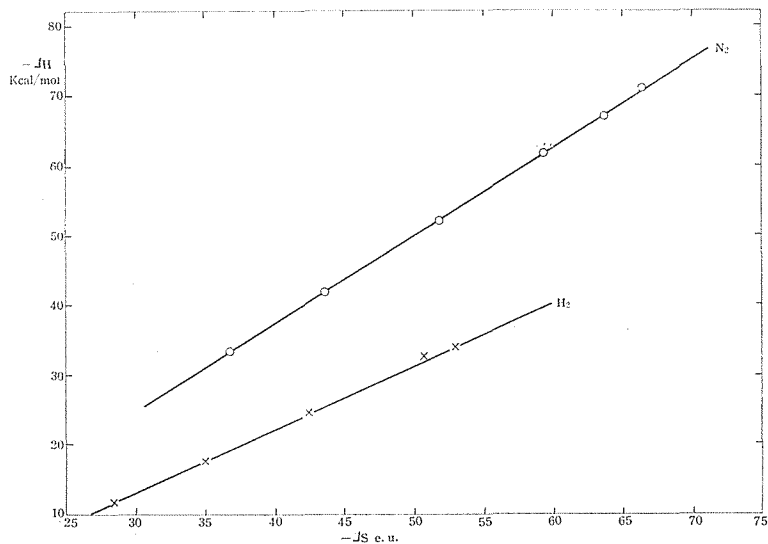


Fig. 4. The functional relations between ΔH and ΔS when H_2 and N_2 adsorbed on the W surface.

of adsorption have been described, and calculated heat decreases over the range of the monolayer completed have always been compared with the experimentals. The functional relationship between the heat decrease and the increasing coverage will be left out of the scope of the present investigation.

A) **The interaction energy between the neutral particles.** The van der Waals' force between the neighboring molecules adsorbed can be calculated from the Lennard-Jone's equation¹⁰⁾

$$E(r) = \frac{1}{12}\lambda r^{-12} - \frac{1}{6}\mu r^{-6} \quad (5)$$

in which r is the distance between the molecules, λ and μ are the constants for the repulsion and attraction of the molecular species respectively.

The interaction energy between non-bonded hydrogen adatoms can be obtained by the following equation¹¹⁾,

$$E(H-H) = Q - \frac{J}{2} = 35[1 - \{1 - \exp(1.85(0.75 - r))\}^2] \text{Kcal/mol} \quad (6)$$

where Q and J are the Coulomb and Exchange Integrals respectively, and r is the distance between the two nuclei.

In the case of non-bonded nitrogen adatoms, the interaction energy between the electrons in the $2s$ and $2p$ orbitals can be calculated by the following equation, using Kotani's Table¹²⁾, on the same assumption as in the case of hydrogen.

The equation is given by

$$\begin{aligned} E(N-N) &= Q - \frac{1}{2}J \\ &= 4K_{ss} + 4K_{so} + 8K_{s\pi} + K_{oo} + 4K_{o\pi} + 2K_{\pi\pi} + 2K_{\pi\pi'} \\ &\quad - 2J_{ss} - 2J_{so} - 4J_{s\pi} - \frac{1}{2}J_{oo} - 2J_{o\pi} - J_{\pi\pi} - J_{\pi\pi'} \end{aligned} \quad (7)$$

where

$$\begin{aligned} K_{ss} &= \frac{1}{R} - 2K_{ss} + D_{ssss} & K_{oo} &= \frac{1}{R} - 2K_{oo} + D_{oooo} \\ K_{so} &= \frac{1}{R} - K_{ss} - K_{oo} + D_{soso} & K_{o\pi} &= \frac{1}{R} - K_{oo} - K_{\pi\pi} + D_{o\pi o\pi} \\ K_{s\pi} &= \frac{1}{R} - K_{ss} - K_{\pi\pi} + D_{s\pi s\pi} & K_{\pi\pi} &= \frac{1}{R} - 2K_{\pi\pi} + D_{\pi\pi\pi\pi} \\ J_{ss} &= \frac{S_{ss}^2}{R} - 2S_{ss}J_{ss} + C_{ssss} & K_{\pi\pi'} &= \frac{1}{R} - 2K_{\pi\pi} + D_{\pi\pi'\pi\pi'} \\ J_{so} &= \frac{S_{so}^2}{R} - 2S_{so}J_{so} + C_{soso} & J_{oo} &= \frac{S_{oo}^2}{R} - 2S_{oo}J_{oo} + C_{oooo} \\ J_{s\pi} &= C_{\pi s s \pi} & J_{o\pi} &= C_{o\pi o\pi} \\ J_{\pi\pi} &= \frac{S_{\pi\pi}^2}{R} - 2S_{\pi\pi}J_{\pi\pi} + C_{\pi\pi\pi\pi} \\ J_{\pi\pi'} &= C_{\pi\pi'\pi'\pi} \end{aligned}$$

and the integrals mentioned above are given as follows.

Overlap Integral

$$S_{\alpha\beta} = \int a_{\alpha}(1) * b_{\beta}(1) d\tau$$

Nuclear Attraction Integral

$$K_{\alpha\beta} = \int a_{\alpha}(1) * \left(\frac{1}{r_{\beta 1}} \right) a_{\beta}(1) d\tau$$

Resonance Integral

$$J_{\alpha\beta} = \int b_{\alpha}(1) * \left(\frac{1}{r_{\beta 1}} \right) a_{\beta}(1) d\tau$$

Coulomb Integral

$$D_{\alpha\beta\gamma\delta} = \int a_{\alpha}(1) * a_{\gamma}(1) \left(\frac{1}{r_{12}} \right) b_{\beta}(2) * b_{\delta}(2) d\tau_1 d\tau_2$$

Exchange Integral

$$C_{\alpha\beta\gamma\delta} = \int a_{\alpha}(1) * b_{\gamma}(1) \left(\frac{1}{r_{12}} \right) b_{\beta}(2) * a_{\delta}(2) d\tau_1 d\tau_2$$

where a and b represent the nuclei and α and β represent the orbitals and these values are obtained from Kotani's Table.

Recently, Vanderslice *et al*¹³⁾, have studied the interaction between ground-state nitrogen atoms independently. They have calculated potential energy curves for N-N interactions, assuming that only the $2p$ electrons on each atom can be paired together in various ways, when two nitrogen atoms approach.

The results calculated by the equations mentioned above are shown in Table 2.

i) Argon adsorption on (111) plane of KCl¹⁴⁾. The interaction energy, calculated by Young, is -0.90 Kcal/mol, that is the attractive force, when the monolayer is completed. But the observed decrease of the heat at $\theta=1$ has been shown as $\Delta q = +0.74$ Kcal/mol in Table 2. Therefore, the decrease of the heat with the advance of adsorption is not accounted for as due to the interaction between the adsorbed molecules.

Table. 2. The interaction energies between adsorbed particles. + and - signs represent the repulsive and attractive energies respectively.

Adsorption System	Interaction energy at $\theta=1$, Kcal/mol.			Observed heat fall, Δq Kcal/mol.	Equation used
	(100) plane	(110) plane	(111) plane		
Ar-KCl			-0.90	+0.74	Young
Ar-TiO ₂	Case-a: +4.77 Case-b: -0.57			+1.50	(5)
N ₂ -Ni	+6.37	+3.38		+16.0 at $\theta=0.3$	(6)
H ₂ -Co		+3.02		+7.0 at $\theta=0.1$	(6)
H ₂ -Fe	+3.12	+7.02	+0.48	+13.0 at $\theta=0.1$	(6)
H ₂ -W	+1.76	+3.56	+0.21	+22.0 at $\theta=0.1$	(6)
N ₂ -W		≈ -0.03		+50.0 at $\theta=0.7$	(7)

ii) Argon adsorption on (100) plane of Rutile¹⁵⁾. Fig. 5 shows the models of the adsorbed layers formed on a square lattice of Rutile. In Case-A, the repulsive energy calculated by eq. (5) is 4.77 *Kcal/mol* as shown in Table 2, which is larger than the adsorbate-adsorbent binding energy, *i. e.* the heat of adsorption at $\theta=0$, 3.5 *Kcal/mol*. So, the adsorption on the site 0 in Fig. 5 precludes adsorption of the particles on the nearest neighbour sites 1, 2, 3 and 4, but adsorption is permitted on the more remote sites 5, 6, 7, 8 and others. From the distribution of these particles the adsorbed volume should be reduced to one half of the experimental value when the monolayer is completed.

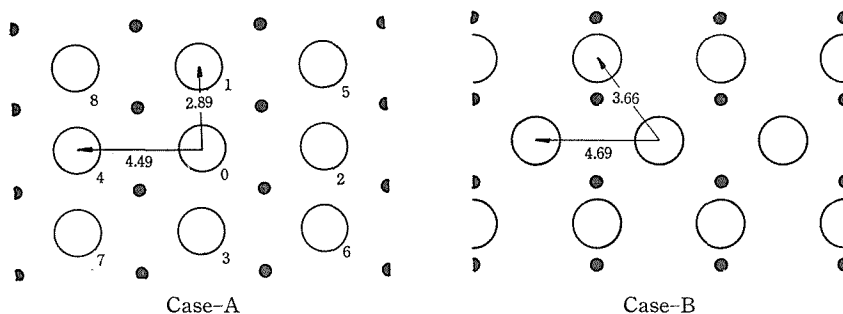


Fig. 5. Models of Argon adsorption on the (100) plane of TiO_2 .

○ adsorbed molecule ; ● Ti atom.

We have considered more reasonable configuration as shown in Case-B, in which the attractive force operates as in the former example.

It should be reasonable to consider the Argon adsorption as the physical one at so low temperatures as in the cases of i) and ii), and to estimate the energy of interaction between adsorbed molecules from the heat of vaporization to be -1.56 *Kcal/mol*, when the monolayer is completed.

Consequently, the decrease of the heat with increasing coverage is hardly accounted for in term of the effect of interaction between physically adsorbed molecules.

iii) Hydrogen adsorption on (100) and (110) planes of $\text{Ni}^{16)}$, (110) plane of $\text{Co}^{17)}$, (100), (110) and (111) planes of $\text{Fe}^{18)}$ and $\text{W}^{19)}$. The adsorption behaviors on these square metal lattices are shown in Fig. 6 to Fig. 9. Hydrogen adsorptions in these cases are dissociative chemisorptions. Each adatom occupies the respective lattice point. The calculated values of the interaction energy are summarized in Table 2, and they are all much lower than those of the experimental heat decreases. For Co catalyst, (100) and (111) planes may be also exposed on the surface. But, as the interaction energies between the adatoms on the lattice points of (110) plane must be the greatest in all the species of crystal surface, the energy value in Table 2 may indicate the upper limit of interactions on the surface of Co catalyst.

iv) Nitrogen adsorption on (110) plane of $\text{W}^{20)}$. The interaction energy, which is the value at a distance of 2.74 Å between the adatoms on (110) plane, has been calculated by equation (7). The calculated value at $\theta=1$ is very small negative one, -0.03 *Kcal/mol*. In the Kotani's Table, each integral value above $\delta R=7$ is

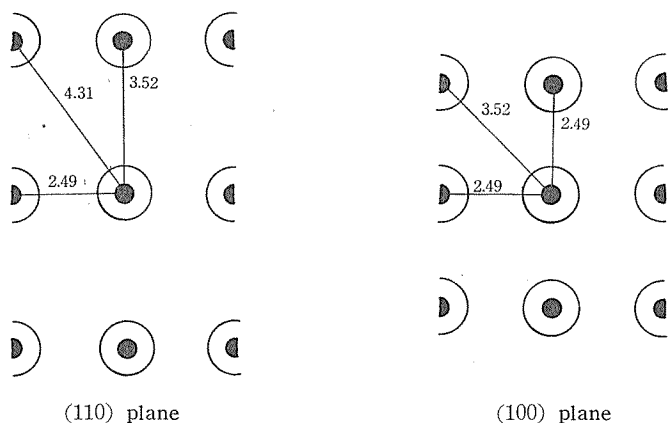


Fig. 6. Models of H_2 adsorption on the Ni surface.

○ adatom ; ● Ni atom.

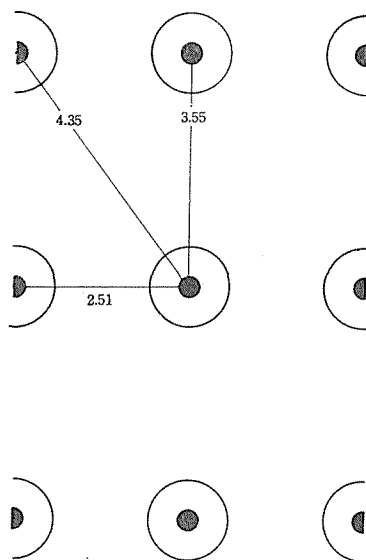


Fig. 7. Model of H_2 adsorption on the (110) plane of Co.

○ ad-atom ; ● Co atom.

not given. But in this calculation δR is 10.08, so the interaction energy has been estimated by a extrapolation. In this calculation, δ is a half of the effective charge of the nucleus and R , the lattice spacing, is represented by Bohr unit.

Interactions on (100) and (111) planes are not so remarkable as in the case of (110) plane, so the values in Table 2 represent the upper limit of the interaction energies as in the case of Co catalyst.

B) The interaction energy between ions or induced dipoles. The electrostatic interaction energy has been evaluated and compared with the experimental values, when the adatoms were ionized or the surface dipole was produced because of the electron transfer from adsorbate to metal or *vice versa*.

The interaction energy between ions will be given by the following equation,

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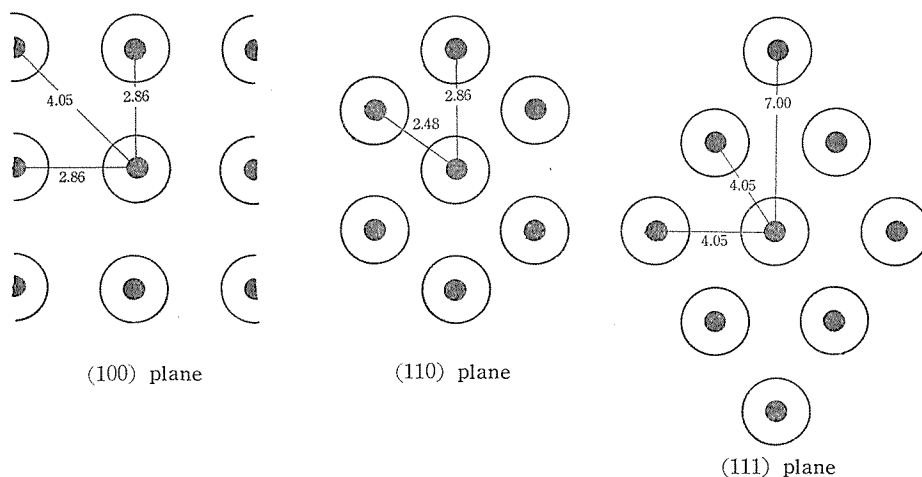


Fig. 8. Models of H₂ adsorption on the Fe surface.

○ ad-atom ; ● Fe atom.

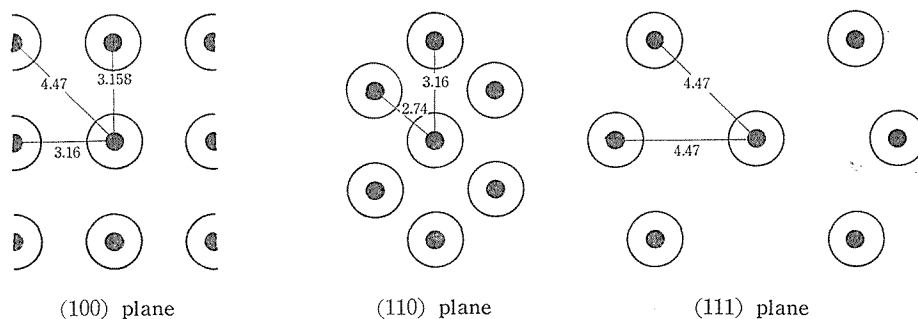


Fig. 9. Models of H₂ or N₂ adsorption on the W surface.

○ ad-atom ; ● W atom.

$$E(\text{ion-ion}) = e^2/r. \quad (8)$$

For example, hydrogen atoms occupying the lattice sites of Ni¹⁶⁾ may be assumed to be ionized all over the layer. In Fig. 10, the repulsive energy is more than 700 Kcal/mol when the interactions between the adatoms on the site 0 and the nearest neighbor sites from 1 to 8 are considered. So the adsorption on the site 0 precludes the adsorption on the nearest neighbor sites. Assuming that the particles are to be adsorbed on the sites where the repulsive energy less than the heat of adsorption at $\theta=0$ operates, it will be seen that adsorption is permitted only on the more remote site, that is, one site among a, b, c and d in Fig. 10. Under these circumstances, adsorption should be much less than experimental values¹⁶⁾ unless some neutral adatoms were accepted in addition to the ionized particles when the monolayer on the surface is completed. So long as the surface of catalyst is uniform, it is hardly be presumed that only a part of adsorbate is partially ionized and the other is neutral.

The interaction energy between the induced dipoles of Argon produced on (111) plane of KCl has been measured by Young¹⁴⁾ at $\theta=1$. The first electrostatic poten-

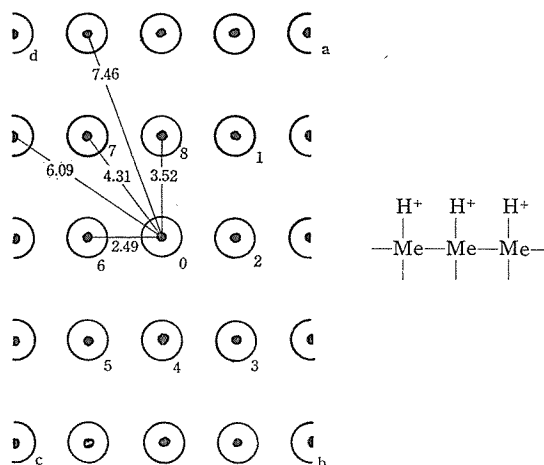


Fig. 10. Model of adsorption of hydrogen ions on the Ni surface.
 ○ adsorbed ion ; ● Ni atom.

tial was $+0.035 \text{ Kcal/mol}$ when Argon was polarized on K^+ ion of KCl crystal surface, and the second was $+0.010 \text{ Kcal/mol}$ when Argon occupied Cl^- lattice point on the surface. These are far from the heat decrease $\Delta q = 0.74 \text{ Kcal/mol}$ at $\theta = 1$.

CONCLUSION

To account for the decrease of the heat with gas adsorption, various factors have been analyzed, such as *a priori* surface heterogeneity²⁰, "induced heterogeneity" due to the adsorption of particles, and the interaction between the adatoms or the admolecules. There are cases when neither the analysis of the isotherms nor that of the heat of adsorption is adequate enough to determine whether the experimental result should be accounted for by *a priori* surface heterogeneity or by the "induced heterogeneity". In such cases, it is necessary that experimental analysis of each adsorption system must be conducted to confirm whether the catalyst surface is *a priori* heterogeneous or not²¹. But in this article, it becomes evident that the lateral interaction can not satisfactorily account for the decrease of the heat of adsorption which is more than 10 Kcal/mol in the case of chemisorption or the small heat decrease in the case of physical adsorption either. It is inferred that the "induced heterogeneity" will reasonably account for the adsorption isotherm so far as the heat of adsorption ΔH of particles adsorbed already changes uniformly and simultaneously all over the surface layer when each particle is adsorbed and the linear relationships between ΔS and ΔH are accepted.

But in the case of induced heterogeneity it is not yet clear what mechanism is involved in the heat decrease of adsorption accompanying with increasing coverage and, therefore, it is impossible to assume the physical model for the surface state.

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