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NOTE ON THE DIFFERENTIAL ISOTOPIC METHOD FOR DECIDING HETEROGENEITY OR HOMOGENEITY OF CATALYST'S SURFACE

By

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Introduction

It is a general finding that the differential heat of adsorption on catalyst's surface decreases with increase of coverage θ. This decrease has been interpreted on the basis of the two contrasting models of catalyst's surface, *i.e.*, the homogeneous and the heterogeneous models[1]. It is assumed with the latter model that sites provide different energies of adsorption and those with lower energies are occupied earlier resulting in the decrease of the differential heat of adsorption with increase of coverage. On the other hand, sites of adsorption are physically identical with each other as assumed with the former model, whereas the repulsive interaction between adsorbates gives rise to the decrease of heat of adsorption.

ROGINSKY[2)3)] and KEIER[3)] have developed recently the differential isotopic method (abbreviated hereafter as D.I.M.) experimentally to decide between the two models. The principle of the method is as follows. Fig. 1 (a) shows the energy of sites which differs from each other in accordance with the heterogeneous model[2)3)]. An amount of adsorbate A, when adsorbed first, occupies the sites with lower energies as mentioned above (see Fig. 1 (b)). Isotope B of A subsequently adsorbed occupies now the sites of higher energies (see Fig. 1 (c)). Let θ_A or θ_B be the coverage of A and B thus results. If we now pump out to reduce the total coverage θ from $\theta=\theta_A+\theta_B$ to $\theta=\theta_A$, the adsorbate B introduced later will be desorbed preferentially, provided that the migration is negligible. In the case of homogeneous model, on the other hand, the energies of adsorbates are as shown by Fig. 2 (a), (b) and (c) at the respective stages corresponding to those of Fig. 1 (a), (b) and (c), if the energies of adsorbates are raised uniformly by repulsive potential between adsorbates in proportion to the coverage as assumed by the latter authors[2)3)] (the relevent

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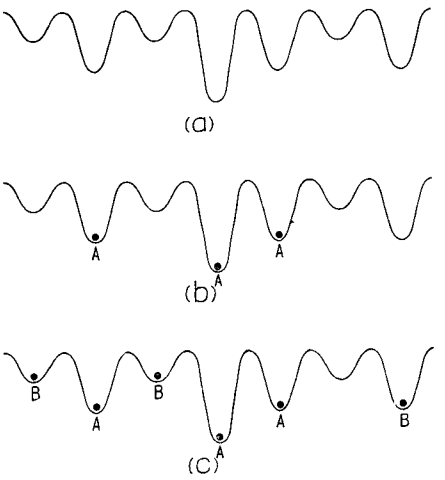

Fig. 1. Energy of adsorbate according to the heterogeneous model.

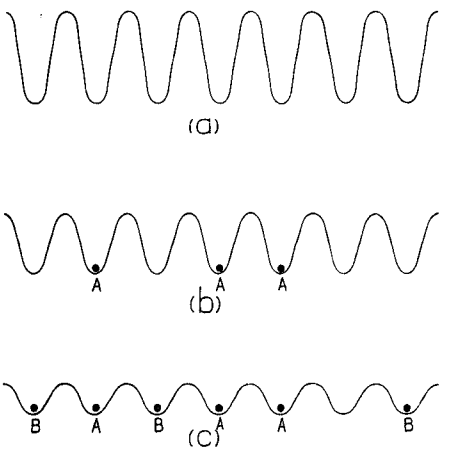

Fig. 2. Energy of adsorbate according to the homogeneous model ("proportional approximation").

approximation is termed the "proportional" one hereafter). The ratio of the amounts of A and B desorbed is then simply $\theta_A : \theta_B$, *i.e.*, that without any preference, admitted that the isotopic effects are negligible.

It is shown in this note that the conclusion deduced from the homogeneous model by a closer approximation differs essentially in this regard from the above one reached by the "proportional" approximation. The energies of adsorbates introduced earlier are lower generally than those adsorbed later according to the "closer" approximation indicating that the "proportional" approximation is short on deciding between homogeneity and heterogeneity on the basis of D.I.M. observation.

In accordance with the homogeneous model there will be worked out in § 1 the adsorption energies of adsorbates and the energies with which unoccupied sites would accomodate adsorbates with special reference to the adsorption of hydrogen atom on (110)-plane of nickel crystal, and, on the basis of the results, in § 2, the ratio of the amounts of A and B to be desorbed. The energy with which an unoccupied site would accomodate an adatom, *i.e.* the energy of it supposed to be situated in the unoccupied site, will simply be termed the energy of the unoccupied site.

§ 1. Distribution of adsorption energies as a function of θ

Fig. 3 shows the (110)-plane of f.c.c. nickel crystal. Two first nearest sites to that σ_0 of interest are denoted by σ_1 and σ_2, and two second nearest

ones by σ_3 and σ_4. We will take only the repulsive potential between adatoms on the first nearest sites into account. The relevant repulsive potential r_0 is taken as $r_0 = 0.1209 \times 23.06$ kcal/mol according to HORIUTI *et al.*[4].

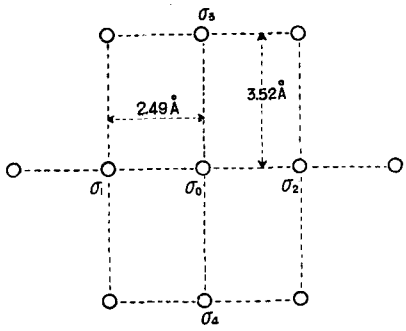

Fig. 3. The (110)-plane of Ni crystal.

Let now $\sum$ be a group of sites consisting of a particular site σ_0 of interest and its two first nearest sites σ_1 and σ_2. There are in all eight possible states of $\sum$ with regard to its occupation by hydrogen atoms, *i.e.*, (○ ● ○), (● ● ○), (○ ● ●), (● ● ●), (○ ○ ○), (● ○ ○), (○ ○ ●) and (● ○ ●), where solid or open circle denotes occupied or unoccupied site respectively; the first four patterns show the states with σ_0 occupied and the last four those with σ_0 unoccupied.

The statistical-mechanical probabilities $P(\sum)$ of these patterns are given, according to the extension of BETHE and PEIERS' theory by HORIUTI and HIROTA[4], as

$$\begin{aligned}
&P(\circ\bullet\circ) = N\gamma\,,\\
&P(\bullet\bullet\circ) = P(\circ\bullet\bullet) = N\gamma^2\xi\eta\,,\\
&P(\bullet\bullet\bullet) = N\gamma^3\xi^2\eta^2\,,\\
&P(\circ\circ\circ) = N\,,\\
&P(\bullet\circ\circ) = P(\circ\circ\bullet) = N\gamma\eta\,,\\
&P(\bullet\circ\bullet) = N\gamma^2\eta^2\,,
\end{aligned} \tag{1.1}$$

where N is the normalization factor which makes the sum of $P(\sum)$ over the eight states of $\sum$ equal unity as

$$N = \left\{\gamma(1+\gamma\xi\eta)^2 + (1+\gamma\eta)^2\right\}^{-1}, \tag{1.2}$$

ξ the BOLTZMANN factor $\exp(-r_0/RT)$ of the repulsive potential r_0 between nearest adatoms, and

$$\gamma = Q^{H}/P^{H}\,, \tag{1.3}$$

where P^{H} is the BOLTZMANN factor of the chemical potential μ^{H}, and

$$Q^{H} = \exp(-w/RT)\,, \tag{1.4}$$

is the BOLTZMANN factor of the increment w of the free energy of the whole system*) caused by addition of a hydrogen atom to unoccupied σ_0, keeping

*) The closed macroscopic system consisting of the adsorbent and the adsorbate at constant volume and temperature.

σ_1 and σ_2 empty. The η is the BOLTZMANN factor $\exp(-\varepsilon/RT)$ of the additional increment ε of the free energy*) due to the repulsion from outside $\sum$, which is approximated as a sole function of θ.

The coverage θ is given by (1.1) with special reference to σ_0, as

$$\theta = \mathrm{P}(\circ\bullet\circ)+\mathrm{P}(\bullet\bullet\circ)+\mathrm{P}(\circ\bullet\bullet)+\mathrm{P}(\bullet\bullet\bullet), \tag{1.5}$$

and the η is determined by the condition that σ_1 as well as σ_0 is occupied with the same probability, *i.e.*,

$$\begin{aligned}&\mathrm{P}(\bullet\circ\circ)+\mathrm{P}(\bullet\circ\bullet)+\mathrm{P}(\bullet\bullet\circ)+\mathrm{P}(\bullet\bullet\bullet)\\ &=\mathrm{P}(\circ\bullet\circ)+\mathrm{P}(\bullet\bullet\circ)+\mathrm{P}(\circ\bullet\bullet)+\mathrm{P}(\bullet\bullet\bullet).\end{aligned} \tag{1.6}$$

We have from (1.1), (1.2) and (1.5)

$$\theta = \gamma(1+\gamma\xi\eta)^2\Big/\left\{\gamma(1+\gamma\xi\eta)^2+(1+\gamma\eta)^2\right\}, \tag{1.7}$$

and from (1.6)

$$\begin{aligned}&N(\gamma\eta+\gamma^2\eta^2+\gamma^2\xi\eta+\gamma^3\xi^2\eta^2)\\ &=N\gamma(1+\gamma\xi\eta)^2,\end{aligned}$$

hence,

$$\eta = \left\{(\gamma\xi-1)+\sqrt{(\gamma\xi-1)^2+4\gamma}\right\}\Big/2\gamma. \tag{1.8}$$

The energy of adatom adsorbed on σ_0 is w for $(\circ\bullet\circ)$, $w+r_0$ for $(\circ\bullet\bullet)$ and $(\bullet\bullet\circ)$, and $w+2r_0$ for $(\bullet\bullet\bullet)$, respectively. The numbers $\mathrm{n_a}(w)$, $\mathrm{n_a}(w+r_0)$ and $\mathrm{n_a}(w+2r_0)$ of adatoms with energies w, $w+r_0$ and $w+2r_0$ are respectively $\mathrm{P}(\circ\bullet\circ)$, $\mathrm{P}(\circ\bullet\bullet)+\mathrm{P}(\bullet\bullet\circ)$, and $\mathrm{P}(\bullet\bullet\bullet)$ each multiplied by the total number of sites. Similarly, the numbers $\mathrm{n_s}(w)$, $\mathrm{n_s}(w+r_0)$ and $\mathrm{n}\,(w+2r_0)$ of unoccupied sites of energies w, $w+r_0$ and $w+2\mathrm{r}_0$ are respectively $\mathrm{P}(\circ\circ\circ)$, $\mathrm{P}(\circ\circ\bullet)+\mathrm{P}(\bullet\circ\circ)$ and $\mathrm{P}(\bullet\circ\bullet)$ each multiplied by the total number of sites.

Table I shows $\gamma\eta$, $\gamma\xi\eta$, $\mathrm{n_a}(w)$ *etc.*, and $\mathrm{n_s}(w)$ *etc.* for $\gamma=10^2$, 2.10^2 and 3.10^2 at 50°C, and for the total number of sites being 1,000. The pressure p mm Hg of hydrogen gas is related with γ as[4] $\gamma=1.887\sqrt{p}$ at 50°C.

§ 2. The ratio of amounts of A and B desorbed

Consider that A is first adsorbed up to $\theta_\mathrm{A}=0.542$ and then isotope B of A adsorbed from $\theta=\theta_\mathrm{A}=0.542$ to $\theta=\theta_\mathrm{A}+\theta_\mathrm{B}=0.663$, hence $\theta_\mathrm{B}=0.121$, without migration of A during the adsorption of B at 50°C. Distribution of A adatoms over different energies before the admission of B is given by $\mathrm{n_a}(w)$, $\mathrm{n_a}(w+r_0)$

*) This will be called simply the energy of the adatom in what follows in accordance with the usual terminology.

TABLE I.

$r_0 = 0.1209 \times 23.06$ kcal/mol. $\xi = 0.01301$.

The total number of sites: 1,000.

γ	10	$2 \cdot 10^2$	$3 \cdot 10^2$
$\gamma\eta$	10.01	14.96	18.85
$\gamma\xi\eta$	0.130	0.195	0.245
θ	0.512	0.528	0.542
$n_a(w)$	400	370	350
$n_a(w+r_0)$	104	144	172
$n_a(w+2r_0)$	8	14	20
$n_s(w)$	4	2	1
$n_s(w+r_0)$	84	56	42
$n_s(w+2r_0)$	400	414	415

and $n_a(w+2r_0)$ for $\gamma = 3 \cdot 10^2$ in Table I. The ratio of the amount to be desorbed of A to that of B is now calculated in what follows.

Adatoms of A are changed in their energy by admission of B due to the interactions, whereas the energy of each adatom of B depends upon how the adjacent sites to that on which it is adsorbed are occupied by adatoms of A. The energy change of A adatoms and the energy of B adatoms are first deduced as below from the different possible pattern of occupation of nearest five sites on a line with the site σ_0 to be occupied by a B atom at the middle; the probability of any of the other four sites to be occupied by another B atom is neglected, which is exactly valid when $\theta_B \ll 1-\theta_A$.

Fig. 4 (a), (b) and (c) show the cases, where the two nearest pair of sites to σ_0 are occupied by A atoms and Fig. 4 (d) and (e) the cases, where only one of the nearest sites is occupied. Those, where both the two nearest pair of sites are unoccupied are neglected in accordance with the negligibly small amount of $n(w)$ shown in Table I.

Let x_1, x_2 and x_3 be the numbers of cases (a), (b) and (c) to occur respectivaly. The energy of A atoms adjacent to B atom is raised by r_0 due to the interaction. In case of (a), $2x_1$ adatoms of A are thus raised in energy from w to $w+r_0$; in (b), x_2 ones of A are raised from the energy w to $w+r_0$ and the same number of A from $w+r_0$ to $w+2r_0$; in (c) the energy of $2x_3$ adatoms of A are raised from $w+r_0$ to $w+2r_0$. In these, $x_1+x_2+x_3$ of B atoms occupy the sites with energy of $w+2r_0$, while the algebraic increase in number of A atoms with energies w, $w+r_0$ and $w+2r_0$ are respectively $-2x_1-x_2$, $2x_1-2x_3$ and

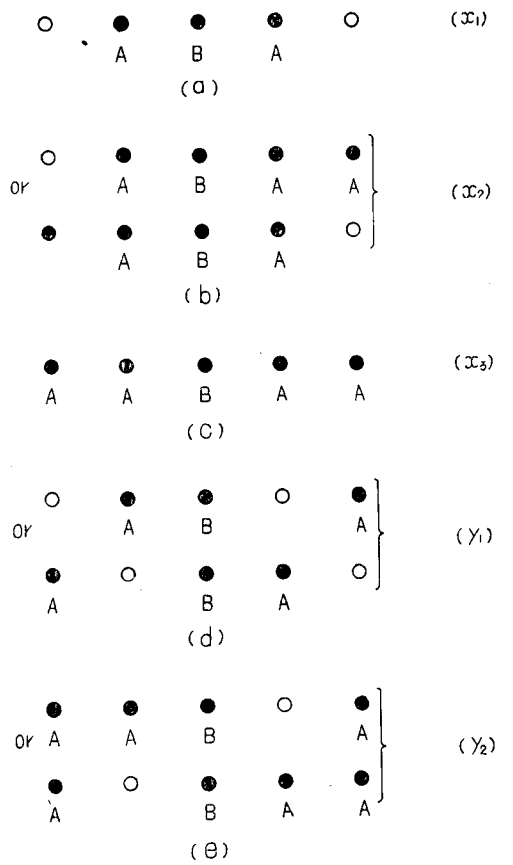

Fig. 4. The x_1, x_2, x_3, y_1 and y_2 are the numbers of cases (a), (b), (c), (d) and (e) respectively.

x_2+2x_3 in accordance with the above discussions.

Let y_1 and y_2 be the numbers of the cases of (d) and (e). The resultant increase in number of A adatoms with energies w, $w+r_0$ and $w+2r_0$ are $-y_1$, y_1-y_2 and y_2 respectively and B adatoms with energy $w+r_0$ are formed by y_1+y_2.

The above results of the admission of B adatoms are summarized below.

(i) The total number of B adatoms is

$$(x_1+x_2+x_3)+(y_1+y_2),$$

$(x_1+x_2+x_3)$ being the number of those with energy $w+2r_0$ and (y_1+y_2) that of those with energy $w+r_0$.

(ii) A adatoms with energy w increases by

$-2x_1-x_2-y_1$.

(iii) A adatoms with energy $w+r_0$ increases by

$2x_1-2x_3+y_1-y_2$.

(iv) A adatoms with energy $w+2r_0$ increases by

$x_2+2x_3+y_2$.

The increase of unoccupied sites of different energies is similarly deduced as below.

(v) The increase of unoccupied sites of the energy $w+r_0$ is

$-2(y_1+y_2)$.

(vi) The increase of those of energy $w+2r_0$ is

$-(x_1+x_2+x_3)+(y_1+y_2)$.

Approximately $n_a^{(B)}(w+r_0)\equiv y_1+y_2$ atoms of B are adsorbed first on the sites of the lower energy $w+r_0$ (the sites of energy w are practically negligible for $\theta\approx 0.5$ as mentioned above), and then $n_a^{(B)}(w+2r_0)\equiv x_1+x_2+x_3$ atoms of B occupy the sites with the higher energy $w+2r_0$ in accordance with (i).

The $n_a^{(B)}(w+r_0)$ equals $n_s(w+r_0)/2$, since two unoccupied sites of energy $w+r_0$ disappear for every adatom occupying σ_0 according to (v), *i.e.*,

$$n_a^{(B)}(w+r_0)=n_s(w+r_0)/2 . \qquad (2.1\,a)$$

We have, besides, $y_1:y_2=1:\gamma\xi\eta$ in accordance with the preceding section, hence

$$y_1=\frac{n_s(w+r_0)}{2}\frac{1}{(1+\gamma\xi\eta)} , \qquad (2.1.b)$$

and

$$y_2=\frac{n_s(w+r_0)}{2}\frac{\gamma\xi\eta}{(1+\eta\xi\eta)} . \qquad (2.1.c)$$

The $n_a^{(B)}(w+2r_0)\equiv x_1+x_2+x_3$ is given as

$$n_a^{(B)}(w+2r_0)=10^3\cdot\theta_B-n_a^{(B)}(w+r_0) , \qquad (2.2)$$

where the coefficient 10^3 of θ_B is the total number of sites under consideration.

The number $n_a^{(A)}(w+2r_0)$ of A adatoms with energy $w+2r_0$ after the adsorption of B is given, on the other hand, in terms of that $n_a(w+2r_0)$ before according to (iv), as

$$n_a^{(A)}(w+2r_0)=n_a(w+2r_0)+x_2+2x_3+y_2 , \qquad (2.3)$$

where y_2 is given by (2.1.c) and x_2 and x_3 are readily determined by the relations

$$x_1 : x_2 : x_3 = 1 : 2\gamma\xi\eta : (\gamma\xi\eta)^2 \tag{2.4}$$

and $x_1+x_2+x_3 \equiv n_a^{(B)}(w+2r_0)$, as

$$x_2 = n_a^{(B)}(w+2r_0)\cdot 2\gamma\xi\eta/(1+\gamma\xi\eta)^2 , \tag{2.5.a}$$

and

$$x_3 \equiv n_a^{(B)}(w+2r_0)\ (\gamma\xi\eta)^2/(1+\gamma\xi\eta)^2 . \tag{2.5.b}$$

Consider now that the adsorbate is pumped out immediately after the introduction of B; the ratio of the amount of A to that of B first desorbed respectively should equal that of $n_a^{(A)}(w+2r_0)$ to $n_a^{(B)}(w+2r_0)$, which is developed by (2.3), (2.1.c), (2.5.a) and (2.5.b), as

$$n_a(w+2r_0) + \left\{n_a^{(B)}(w+2r_0)+n_s(w+r_0)/4\right\}\left\{2\gamma\xi\eta/(1+\gamma\xi\eta)\right\} : n_a^{(B)}(w+2r_0) . \tag{2.6}$$

We have hence for $\theta_A=0.542$, $\theta_B=0.121$ and $T=50°C$, approximately,

$$n_a^{(A)}(w+2r_0) : n_a^{(B)}(w+2r_0) = 63 : 100 \tag{2.7}$$

by (2.2) and (2.1.a) on the base of $n_a(w+2r_0)=20$, $n_s(w+r_0)=42$ and $\gamma\xi\eta=0.245$ for $\gamma=3\cdot10^2$ according to Table I.

This ratio is calculated, on the other hand, by the "proportional" approximation at

$$\theta_A : \theta_B = 0.542 : 0.121 \approx 54 : 12 . \tag{2.8}$$

It is concluded by the comparison of (2.7) and (2.8) that the "proportional" approximation is incapable of accounting for the predominant desorption of B in contrast to the present approximation.

The above conclusion is valid even if we take account of the dissociative adsorption of hydrogen molecule. OKAMOTO, HORIUTI and HIROTA[5] concluded that hydrogen molecule is adsorbed on the pair of sites similar to those consisting of σ_0 and σ_3, or σ_0 and σ_4 in Fig. 3. The ratio of desorption of isotopes A and B is in consequence given identically by (2.6), insofar as we take account only of the repulsions between first nearest sites, *i.e.*, the correlation among adatoms on each line parallel to that through σ_1, σ_0 and σ_2.

Conclusion

ROGINSKY and KEIER[3] have concluded that nickel surface is heterogeneous

from the experimental results on the preferential desorption of hydrogen isotope adsorbed later. It was now shown that the experimental result is equally accounted for, at least qualitatively, on the basis of the homogeneous model, hence not an exclusive evidence for the heterogeneity.

The present approximation gives, as readily seen, the identical results with that from the "proportional" approximation, when $\theta_A+\theta_B=1$, so that one might think that D.I.M. would then decide between heterogeneity and homogeneity. However, another difficulty is encountered in that case. Recently, the existence of two types of adsorption of hydrogen atom on Ni surface is concluded experimentally by SACHTLER *et al.*[6], SUHRMANN *et al.*[7] and ZWITERING *et al.*[8], on the one hand and theoretically deduced by the present author[9] on the other hand. The one type of adsorption occurs at the initial stage of adsorption with larger heat of adsorption and the other type does at later stage with smaller heat of adsorption. It follows that the isotope adsorbed later may be pumped out first even then inspite of the homogeneity of surface.

A more detailed analysis of the results of D.I.M. would be required in order to elucidate the physical nature of catalyst's surface.

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