



HOKKAIDO UNIVERSITY

Title	THEORETICAL ISOTHERM OF HYDROGEN CHEMISORPTION BASED ON THE HOMOGENEOUS MODEL OF THE SURFACE OF ADSORBENT METAL
Author(s)	HORIUTI, Juro
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 9(2), 143-158
Issue Date	1961-10
Doc URL	https://hdl.handle.net/2115/24742
Type	departmental bulletin paper
File Information	9(2)_P143-158.pdf



THEORETICAL ISOTHERM OF HYDROGEN CHEMISORPTION BASED ON THE HOMOGENEOUS MODEL OF THE SURFACE OF ADSORBENT METAL

By

Juro HORIUTI^{*)}

(Received June 30, 1961)

Summary

Adsorption isotherm of hydrogen on nickel was calculated at 0°, 50°, 100°, 150°, 200°, 250° and 300°C with an approximation proved sufficiently accurate in a previous work²⁾. It was assumed²⁾ that hydrogen is chemisorbed as statistically independent adatoms each on one of the surface metal atoms of the (110)-lattice plane and that the adatoms exert repulsions against each other. Coverage θ was thus derived as a function $\theta(P)$ of hydrogen pressure P , which implied, as adjustable parameters, the repulsive potential and the heat of adsorption $\Delta\varepsilon$ at absolute zero temperature and at $\theta=0$. These parameters were adjusted so that the theoretical $\theta(P)$ ran proportional to the corresponding observed amount $v(P)$ of adsorption⁴⁾. The $\Delta\varepsilon$ thus adjusted led to the value 22 kcal of the differential heat of adsorption per mol of hydrogen at $\theta=0$ as compared with the observed value 26 kcal⁵⁾, whereas the appropriate proportionality factor $N=v/\theta$ yielded 1.1×10^{15} per unit BET-area in conformity with the crystallographic value of the number of the surface metal atoms.

The theoretical isotherm thus reproduced the observed value in the main, nevertheless v deviated beyond $N\theta$ the more, the higher the θ , and the deviation began to occur at the lower θ , the higher the temperature. The systematic deviation was qualitatively accounted for by allowing for an additional adsorption either of the same type as dealt with above on another lattice plane or of another type on the same lattice plane in accordance with the recent experimental conclusion¹¹⁾¹²⁾¹³⁾, which was theoretically established by TOYA⁹⁾¹⁰⁾ with close description both of the types.

Introduction

The present author and HIROTA¹⁾²⁾ have deduced isotherms of dissociative adsorption of hydrogen on nickel under the assumptions that hydrogen is chemisorbed to form statistically independent adatoms each on a physically identical site provided by a metal atom of (110)-lattice plane of f. c. c. nickel crystal

^{*)} Research Institute for Catalysis, Hokkaido University.

This model of adsorption led necessarily to an allowance for the repulsive interactions between each pair of adatoms, which was estimated as a function of distance by means of EYRING'S semi-empirical equation³⁾ of quantum-mechanical repulsive potential between non-bonded hydrogen atoms. The theoretical isotherm was derived in four different approximations, *i. e.* the first, second, third and "proportional" approximations. The first approximation took account of the repulsive potential only of the first nearest adatoms, the second that of the first and the second nearest ones, while the third one included that of the first and the second nearest ones, while the third one included that of the third nearest ones as well. In the "proportional" approximation the repulsive potential each of adatoms was assumed to be proportional to the covered fraction. The covered fraction θ is thus derived²⁾ as a function, particular to each approximation, of the ratio γ of the probability of a particular site to be occupied to that unoccupied for the limiting case $\theta \rightarrow 0$, which is expressed as²⁾

$$\gamma = \left\{ \frac{(2\pi m kT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} \right\}^{-1/2} \prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \\ \times \left(\frac{1.360 \times 980.5 P}{kT} \right)^{1/2} \exp\left(\frac{\Delta\epsilon}{kT}\right), \quad (1)$$

where m or I is the mass or the moment of inertia of hydrogen molecule in gas, k or h the BOLTZMANN or PLANCK constant, T the absolute temperature, ν_j the j -th normal vibrational frequency of adatom, P the pressure of hydrogen gas in mmHg and $\Delta\epsilon$ the heat of adsorption at absolute zero temperature and at $\theta=0$, *i. e.* the excess of energy of a hydrogen atom in gaseous molecule at the ground state over the ground state energy of adatom at $\theta=0$.

Isotherms of different approximations were thus numerically worked out at 50°C and compared with each other and observed ones with the following results²⁾. (I) The $\theta(\gamma)$ at 50°C of the second and the third approximation were almost congruent with each other, whereas those of the first and the "proportional" approximation deviated considerably from those for the former two. (II) The $\Delta\epsilon$ in (1) was adjusted to secure $\theta(\gamma)$ of the third approximation proportional to the observed amount $v(P)$ of adsorption⁴⁾, where γ and P correspond to each other according to (1); the ratio v/θ thus fixed yielded the crystallographic value $1.1 \times 10^{15} \text{ cm}^{-2}$ of the number of lattice points, whereas the adjusted value of $\Delta\epsilon$ reproduced the observed limiting value⁵⁾ 26 kcal of the differential heat of adsorption per mol hydrogen at $\theta=0$.

The present paper is concerned with the extension of the above calculation to other temperatures than 50°C for a further verification of the present model of adsorption. On the ground of the above conclusion (I), the second approxi-

mation was adopted for the practical calculation as a sufficiently accurate substitute for the extremely laborious third approximation. The $\theta(\bar{r})$ was thus deduced with reference to the (110)-lattice plane of nickel at 0° , 50° , 100° , 150° , 200° , 250° , and 300° , and collectively adjusted to the observations, by varying $\Delta\varepsilon$ and the magnitude of the repulsive potentials, for its proportionality to the observed $v(P)$.

It was thus found that the theory accounts well, in the main, for the experimental results as in the preceding work but associated with a systematic deviation that the observed v exceeds the theoretical value at higher value of θ and the deviation occurs at the lower θ , the higher the temperature.

The (110)-lattice plane was premised as the seat of adsorption in the present as well as in the preceding calculation²⁾ on the ground of the lowest energy of adatom at $\theta=0$ as deduced in a previous paper⁶⁾ from the least exchange repulsions exerted by the surface metal atoms other than that to which the adatom is bonded. This is in conformity with the conclusion arrived at recently by TOYA⁷⁾, that $\Delta\varepsilon$ is in general the greatest on the least dense lattice plane.

The adsorbed states of lower $\Delta\varepsilon$ may however come into play at higher θ of the (110)-lattice plane to cause the deviation observed. The deviation was qualitatively accounted for as shown below by allowing for a few cases of the additional adsorbed state of lower $\Delta\varepsilon$.

§ 1. Method of Calculation

The function $\theta(\bar{r})$ is calculated for the second approximation with reference to a set Σ of sites consisting of any one σ_0 of the physically identical sites on (110)-lattice plane, two first nearest sites σ_1 and σ_2 to σ_0 and two second nearest ones σ_3 and σ_4 as shown in Fig. 1. Let C be the whole macroscopic system consisting of definite amounts respectively of adsorbent and adsorbate hydrogen in adsorption equilibrium at constant temperature and constant total volume, and $\mathcal{Q}C_{\Sigma(0)}$ be the partition function of C at a particular state, where all constituent sites fo Σ are unoccupied. The second approximation leads, by Eqs. (26. a), (26. b), (26. c) and (26. d) of the preceding paper²⁾, to the factors

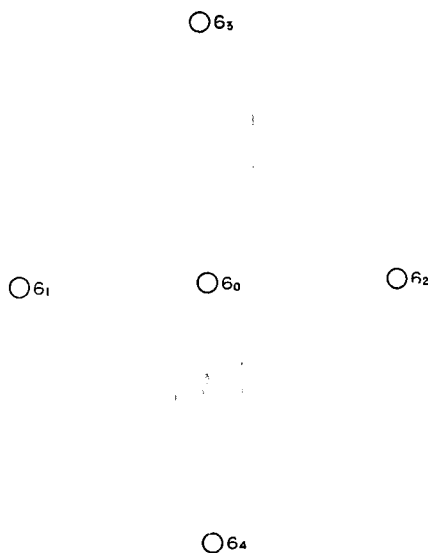


Fig. 1. Set Σ of sites on (110)-lattice plane.

$\varphi_{\sigma_0(\text{H})}$ and $\varphi_{\sigma_i(\text{O})}$ with which $\mathfrak{Q}C_{\Sigma(\text{O})}$ is multiplied to give the partition functions of C at the particular state, where σ_0 is occupied by an adsorbed hydrogen atom or σ_i ($i=0, 1, 2, 3, 4$) is unoccupied respectively with certainty, as

$$\varphi_{\sigma_0(\text{H})} = \gamma(1 + \gamma\eta_1\xi_1)^2(1 + \gamma\eta_{\text{II}}\xi_{\text{II}})^2 \quad (2. a)$$

$$\varphi_{\sigma_0(\text{O})} = (1 + \gamma\eta_1)^2(1 + \gamma\eta_{\text{II}})^2 \quad (2. b)$$

$$\varphi_{\sigma_1(\text{O})} = \varphi_{\sigma_2(\text{O})} = (1 + \gamma\eta_1)(1 + \gamma\eta_{\text{II}})^2 + \gamma(1 + \gamma\eta_1\xi_1)(1 + \gamma\eta_{\text{II}}\xi_{\text{II}})^2 \quad (2. c)$$

and

$$\varphi_{\sigma_3(\text{O})} = \varphi_{\sigma_4(\text{O})} = (1 + \gamma\eta_1)^2(1 + \gamma\eta_{\text{II}}) + \gamma(1 + \gamma\eta_1\xi_1)^2(1 + \gamma\eta_{\text{II}}\xi_{\text{II}}), \quad (2. d)$$

ξ_1 or ξ_{II} is the BOLTZMANN factor of the repulsive potential R_1 or R_{II} of an adatom due to another situated on the first or the second nearest site respectively, η_1 the factor which allows for the repulsive interactions of an adatom situated on σ_1 or σ_2 with other adatoms outside Σ and η_{II} the factor similar to η_1 of an adatom situated on σ_3 or σ_4 . Both η_1 and η_{II} were assumed to be functions solely of θ *) at a constant temperature, which are determined by the equation

$$\varphi_{\sigma_0(\text{O})} = \varphi_{\sigma_1(\text{O})} = \varphi_{\sigma_2(\text{O})} \quad (3)$$

in accordance with the BETHE-PEIERLS' method⁹⁾ from the known value of ξ_1 and ξ_{II} for any assigned value of γ . The factors $\varphi_{\sigma_0(\text{H})}$ and $\varphi_{\sigma_0(\text{O})}$ are now evaluated by (2. a) and (2. b), which give θ as a function of γ by the equation**)

$$\theta/(1-\theta) = \varphi_{\sigma_0(\text{H})}/\varphi_{\sigma_0(\text{O})}. \quad (4)$$

Eq. (4) states that the ratio $\theta/(1-\theta)$ of the probability θ of a site being occupied to that $1-\theta$ unoccupied equals the ratio of the partition function of the former state to that of the latter or the right-hand side of the above equation according to the definition of $\varphi_{\sigma_0(\text{H})}$ and $\varphi_{\sigma_0(\text{O})}$.

The values of the repulsive potentials in the present calculation were those used in the preceding work²⁾, *i. e.*

$$R_1 = 0.1068 \text{ e. V.}, \quad R_{\text{II}} = 0.01405 \text{ e. V.}$$

or the latters multiplied by a common factor ρ , which varied from 0.5 to 2.0.

§ 2. Results

The function $\theta(\gamma)$ were calculated according to § 1 for different values of

*) The arrangement of adatoms outside Σ , hence the repulsive interactions in question depend, besides on θ , on the particular arrangement of adatoms inside Σ at constant temperature. It is in consequence an approximation to assume η_1 or η_{II} a sole function of θ .

**) Cf. Eq. (6) of Ref. 2.

Theoretical Isotherm of Hydrogen Chemisorption Based on the Homogeneous Model

ρ and the result was fitted to the experimental results of $v(P)$ as described in §1 for different values of $\Delta\varepsilon$. Factors ρ thus tried were 0.5, 1.0 and 1.2 for temperatures 0°, 50°, 100°, 150°, 200°, 250° and 300°C, besides 0.6, 1.5 and 2.0 particularly for 150°C. The values of $\Delta\varepsilon$ examined were 10.3, 10.8, 11.3, 12.3 and 13.3 kcal/mol adatom. The best fit was obtained in the case, where $\rho=1.0$ and $\Delta\varepsilon=10.3$ kcal/mol adatom throughout these trials. Table 1 shows $\theta(\tau)$ in the latter case together with the associated values of η_1 , η_{11} and $\lambda=\theta/(1-\theta)\tau$, and Fig. 2 the plot of $\theta(\tau)$ in accordance with Table 1 against $v(P)$ at the corresponding P according to (1).

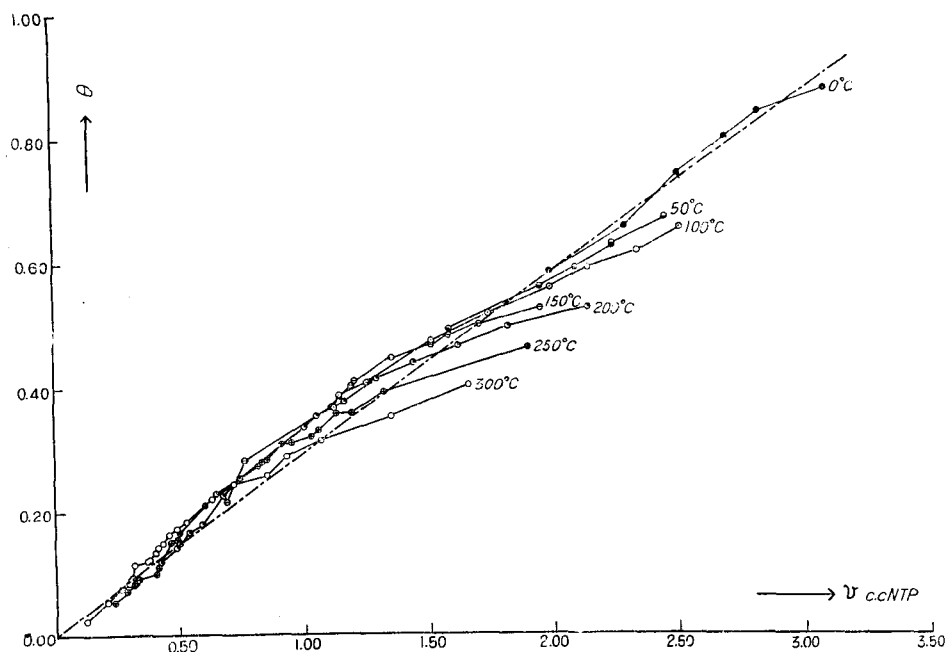


Fig. 2. Proportionality of observed amount v of adsorption to theoretical coverage θ of r -type adsorption; second approximation.
 $\Delta\varepsilon=10.3$ kcal/mol adatom, $R_I=0.1068$ e. V., $R_{II}=0.01405$ e. V.

It follows from the above value of $\Delta\varepsilon$ for the best fit that the limiting value at $\theta=0$ at 300°C of the differential heat of adsorption $RT^2(\partial \ln P/\partial T)_v$ per mol of H_2 is 22 kcal according to Eq. (30) of the preceding paper²⁾, which is somewhat lower than the observed value 26 kcal⁵⁾. Nevertheless, the proportionality constant 3.40 cc NTP of v to θ leads to the numbers of sites 1.1×10^{15} cm⁻² of (110)-lattice plane on the base of the BET surface area⁵⁾ 1.7×10^{15} cm⁻² per gm of NiO used for the preparation of the adsorbent by reduction. This value

TABLE 1. θ , η_I , η_{II} and $\lambda \equiv \theta/(1-\theta)r_r$ of Theoretical
 $R_I = 0.1068$ e. V.,

Temp. °C	0				50			
ξ_I	0.01070				0.02159			
ξ_{II}	0.5505				0.6038			
$\eta_I, \eta_{II}, \theta, \lambda$	η_I	η_{II}	θ	λ	η_I	η_{II}	θ	λ
$\log r_r$								
-1	0.8599	0.8205	0.07343	0.7926	0.8672	0.8243	0.07403	0.7995
0	0.5093	0.3880	0.2533	0.3393	0.5240	0.3913	0.2580	0.3478
1	0.2076	8.728×10^{-2}	0.4083	6.899×10^{-2}	0.2183	8.819×10^{-2}	0.4180	7.182×10^{-2}
2	7.291×10^{-2}	1.266×10^{-2}	0.4867	9.480×10^{-3}	7.877×10^{-2}	1.344×10^{-2}	0.5095	1.039×10^{-2}
3	2.503×10^{-2}	1.700×10^{-3}	0.5494	1.219×10^{-3}	2.892×10^{-2}	2.154×10^{-3}	0.6112	1.572×10^{-3}
4	9.328×10^{-3}	2.980×10^{-4}	0.6641	1.977×10^{-4}	1.285×10^{-2}	5.657×10^{-4}	0.7896	3.753×10^{-4}
5	4.516×10^{-3}	9.830×10^{-5}	0.8534	5.820×10^{-5}	8.643×10^{-3}	3.196×10^{-4}	0.9517	1.969×10^{-4}
6	3.411×10^{-3}	6.729×10^{-5}	0.9740	3.749×10^{-5}	7.977×10^{-3}	2.869×10^{-4}	0.9943	1.737×10^{-4}

Temp. °C	200				250			
ξ_I	0.07284				0.09356			
ξ_{II}	0.7085				0.7322			
$\eta_I, \eta_{II}, \theta, \lambda$	η_I	η_{II}	θ	λ	η_I	η_{II}	θ	λ
$\log r_r$								
-1	0.8836	0.8359	0.07554	0.8171	0.8880	0.8398	0.07598	0.8224
0	0.5595	0.4077	0.2719	0.3734	0.5698	0.4149	0.2766	0.3823
1	0.2482	9.839×10^{-2}	0.4570	8.417×10^{-2}	0.2584	0.10367	0.4724	8.954×10^{-2}
2	0.1015	1.964×10^{-2}	0.6130	1.584×10^{-2}	0.1113	2.303×10^{-2}	0.6519	1.873×10^{-2}
3	5.091×10^{-2}	6.163×10^{-3}	0.8220	4.618×10^{-3}	6.223×10^{-2}	8.841×10^{-3}	0.8704	6.715×10^{-3}
4	3.852×10^{-2}	4.051×10^{-3}	0.9667	2.898×10^{-3}	5.165×10^{-2}	6.688×10^{-3}	0.9801	4.924×10^{-3}
5	3.677×10^{-2}	3.789×10^{-3}	0.9963	2.688×10^{-3}	5.032×10^{-2}	6.438×10^{-3}	0.9979	4.717×10^{-3}
6	3.658×10^{-2}	3.762×10^{-3}	0.9996	2.666×10^{-3}	5.018×10^{-2}	6.413×10^{-3}	0.9998	4.696×10^{-3}

Theoretical Isotherm of Hydrogen Chemisorption Based on the Homogeneous Model

Isotherms of r -type Adsorption; Second Approximation

$R_{II} = 0.01405$ e. V.

100				150			
0.03610				0.05345			
0.6460				0.6802			
η_1	η_{11}	θ	λ	η_1	η_{11}	θ	λ
0.8733	0.8281	0.07469	0.8072	0.8787	0.8320	0.07506	0.8115
0.5368	0.3958	0.2626	0.3561	0.5485	0.4014	0.2672	0.3646
0.2282	9.047×10^{-2}	0.4294	7.526×10^{-2}	0.2381	9.394×10^{-2}	0.4426	7.939×10^{-2}
8.531×10^{-2}	1.485×10^{-2}	0.5393	1.171×10^{-2}	9.288×10^{-2}	1.691×10^{-2}	0.5746	1.351×10^{-2}
3.430×10^{-2}	2.957×10^{-3}	0.6850	2.175×10^{-3}	4.158×10^{-2}	4.245×10^{-3}	0.7589	3.147×10^{-3}
1.875×10^{-2}	1.146×10^{-3}	0.8854	7.726×10^{-4}	2.739×10^{-2}	2.246×10^{-3}	0.9397	1.558×10^{-3}
1.551×10^{-2}	8.765×10^{-4}	0.9828	5.697×10^{-4}	2.503×10^{-2}	1.976×10^{-3}	0.9926	1.347×10^{-3}
1.551×10^{-2}	8.454×10^{-4}	0.9982	5.465×10^{-4}	2.476×10^{-2}	1.947×10^{-3}	0.9993	1.324×10^{-3}

300			
0.1150			
0.7524			
η_1	η_{11}	θ	λ
0.8921	0.8438	0.07643	0.8275
0.5796	0.4225	0.2813	0.3914
0.2690	0.1096	0.4884	9.545×10^{-2}
0.1221	2.714×10^{-2}	0.6897	2.223×10^{-2}
7.526×10^{-2}	1.236×10^{-2}	0.9051	9.532×10^{-3}
6.631×10^{-2}	1.023×10^{-2}	0.9872	7.716×10^{-3}
6.525×10^{-2}	9.985×10^{-3}	0.9987	7.515×10^{-3}
6.514×10^{-2}	9.960×10^{-3}	0.9999	7.494×10^{-3}

of the number of sites is in agreement with the crystallographic value 1.1×10^{15} cm^{-2} of (110)-lattice plane of nickel assumed exclusively to constitute the BET-surface observed.

§ 3. Additional State of Adsorption

It is seen in Fig. 2 that (E_1) the observed v deviates beyond the theoretical value at higher P at every constant temperature and that (E_2) the deviation begins to occur at the lower θ , the higher the temperature. This effect may be attributed to an additional state of adsorption of lower $\Delta\varepsilon$ than that of the adsorption on the (110)-lattice plane so far dealt with.

TOYA⁹⁾¹⁰⁾ has shown quantum-mechanically that there exist two types, *i. e.* r -type and s -type, as called by him, of adsorption on the same lattice plane. The r -type adsorption is the chemisorption of the usual sense, *i. e.* that of adatom bonded to a metal atom from outside the electronic surface, whereas the s -type one is a sort of dissolution, where the appropriate sites of adsorption are situated immediately inside the electronic surface, each corresponding exclusively to a metal atom on the surface. The r -type adatoms exert repulsive interactions on each other, whereas s -type ones neither on each other nor on r -type ones¹⁰⁾. In the case of nickel in particular¹⁰⁾ r -adatoms are associated with a fairly larger value of $\Delta\varepsilon$ than s -adatoms are, but the energy of the formers increases or their $\Delta\varepsilon$ decreases appreciably with increase of the coverage due to the repulsive interactions, while that of s -adatoms remains practically constant independent of any sort of coverage. These theoretical conclusions are in conformity with the experimental one unequivocally arrived at by SUHRMANN *et al.*¹¹⁾, SACHTLER *et al.*¹²⁾ and ZWIETERING *et al.*¹³⁾, that there exist two different states of adsorption.

There may be two cases of s -type adsorption on the (110)-lattice plane associated with the r -type one on the same lattice plane, *i. e.* (A_1) a s -type adsorption site and a r -type one both pertaining to a surface metal atom are so coupled that only one of them is occupied at the same time and (A_2) both the types of adsorption take place independent of each other on the same lattice plane, so that a s -type adsorption site and a r -type one both pertaining to a metal atom may be occupied simultaneously without interference between them. Another possible case is that (B) an additional r -type adsorption takes place on a lattice plane other than (110).

We will deal with each of the three cases (A_1), (A_2) and (B) as the possible cause of the deviation mentioned above, after having reviewed a few general points of the theory of adsorption in the next sections.

§ 4. Adsorption Isotherm in General

We have for any case of localized adsorption of hydrogen atom^{1)2)6)*)}

$$\theta/\theta_0 = q^H/p^H, \quad (5)$$

where θ is the probability of a site being occupied by a hydrogen atom, which is identified with the appropriate coverage, θ_0 the probability of the site being unoccupied free to accept an adatom, q^H the BOLTZMANN factor of the increment w of the free energy of the whole system, caused by adding an adatom from outside the system to a definite, unoccupied site and p^H is the BOLTZMANN factor of the chemical potential of the adatom, which equals, in adsorption equilibrium, the chemical potential of hydrogen atom in gas or half the chemical potential of hydrogen molecule. If the site is exclusively occupied by a single sort of adatoms, θ_0 equals $1-\theta$. The w is either constant independent of θ or increases with increase of θ respectively in the absence or presence of interaction among adatoms at constant temperature and constant hydrogen pressure. We have, in the former case¹⁾²⁾

$$\theta/\theta_0 = \gamma, \quad (6. \theta)$$

where

$$\gamma = q_0^H/p^H \quad (6. \gamma)$$

and q_0^H is the particular value of q^H in the absence of the interactions. The value of q_0^H , hence that of γ depends on the lattice plane, on which the adatom is situated and on the type of adsorption. Eq. (6. γ) is developed²⁾ as (1) in accordance with the definition of q_0^H and p^H . Eq. (5) is written, with reference to (6), as

$$\theta/\theta_0 = \lambda\gamma, \quad (7. \theta)$$

where

$$\lambda = q^H/q_0^H \quad (7. \lambda)$$

is, according to the definition of q^H and q_0^H , the BOLTZMANN factor of the additional increase, due to the interactions, of free energy caused by the above process associate with q^H . The additional increase being positive in the present case of repulsive interaction, λ is less than unity and decreases with increase of θ or of γ , although $\lambda\gamma$ increases with γ , as seen in Table 1.

*) Cf. Eq. (19) of Ref. (2).

§ 5. γ -values

The γ depends, as mentioned above, on the type of adsorption as well as on the relevant lattice plane, because of the appropriate difference of $\Delta\varepsilon$ and ν_j 's in (1). The second factor of (1) is of the order of magnitude of unity for the values of ν_j 's compatible with the present picture of localized adsorption¹⁰. A considerable difference is effected, if at all, by that of $\Delta\varepsilon$. It follows that γ varies as \sqrt{P} in every case and that γ of r -adatom on (110) is greater than that of s -adatom on (110) or r -adatom on the other lattice plane on the ground of the greatest value of the relevant $\Delta\varepsilon$ as mentioned in the introduction and §3.

We will denote the particular value of γ for r - or s -type adsorption on the (110)-lattice plane respectively by γ_s and γ_r , and Eqs. from (2) to (7) will be read in what follows with γ there transcribed into γ_r .

The ratio of γ_r to γ_s is written as

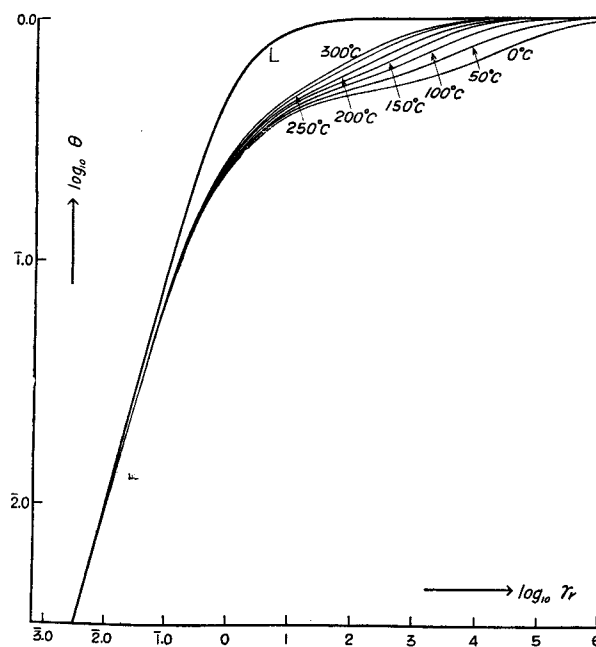


Fig. 3. Coverage θ of r -type adsorption.

L: Langmuir adsorption isotherm; other curves: theoretical isotherms of second approximation.

$\Delta\varepsilon = 10.3$ kcal/mol adatom, $R_I = 0.1068$ e.V., $R_{II} = 0.01405$ e.V.

$$\gamma_r/\gamma_s = \exp\left(\frac{\Delta\varepsilon_r - \Delta\varepsilon_s}{kT}\right) \quad (8)$$

according to (1), ignoring the difference of the second factor of (1) and denoting the value of $\Delta\varepsilon$ respectively appropriate to γ_r and γ_s by $\Delta\varepsilon_r$ and $\Delta\varepsilon_s$.

§ 6. Variation of θ with γ_r

Fig. 3 shows $\log_{10} \theta$ plotted against $\log_{10} \gamma_r$ at different temperatures according to the results of Table 1. The curve signified by L is the similar plot according to (6. θ) with θ_0 equated to $1-\theta$ *i. e.* the Langmuir adsorption isotherm, which is invariant of temperature.

We see in Fig. 3 that the curves at different temperatures inclusive of L run almost congruently with each other up to $\log \gamma_r = -1$, beyond which they more or less differentiate.

§ 7. Adsorption Isotherm in Case (A_i)

Notation σ_i will signify in this case the i -th adsorption site of r -adatom illustrated in Fig. 1 together with that of s -adatom coupled with it. Site σ_i will be termed occupied or unoccupied according as either or neither of the relevant coupled sites is occupied.

Adsorption isotherm in this case is derived in Appendix with the second approximation of the repulsive interactions among r -adatoms with each other, as

$$\frac{\theta_r}{1-\theta_r-\theta_s} = \frac{\bar{\varphi}_{\sigma_0(\text{H}_r)}}{\bar{\varphi}_{\sigma_0(\text{O})}}, \quad \frac{\theta_s}{1-\theta_r-\theta_s} = \gamma_s, \quad (9. r), (9. s)$$

where θ_r or θ_s is the coverage of r - or s -adatoms,

$$\bar{\varphi}_{\sigma_0(\text{H}_r)} = \gamma_r (1 + \gamma_{r(s)} \eta_{\text{I}} \hat{\xi}_{\text{I}})^2 (1 + \gamma_{r(s)} \eta_{\text{II}} \hat{\xi}_{\text{II}})^2, \quad (10. \text{H})$$

$$\bar{\varphi}_{\sigma_0(\text{O})} = (1 + \gamma_{r(s)} \eta_{\text{I}})^2 (1 + \gamma_{r(s)} \eta_{\text{II}})^2 \quad (10. \text{O})$$

and

$$\gamma_{r(s)} = \gamma_r / (1 + \gamma_s); \quad (11)$$

θ without suffix will be reserved to denote the coverage of the same lattice plane in the particular case, where $\gamma_s = 0$, hence $\theta_s = 0$ by (9. s). The θ is given by (7. θ), as

$$\theta/(1-\theta) = \lambda \gamma_r, \quad (12)$$

since $\theta_0 = 1-\theta$ in this case. $\bar{\varphi}_{\sigma_0(\text{H}_r)}$ or $\bar{\varphi}_{\sigma_0(\text{O})}$ is the factor, as shown in Appendix, by which $\mathfrak{Q}C_{\Sigma(\text{O})} (1 + \gamma_s)^4$ is multiplied to give the partition function of the whole system at the particular state, where σ_0 is occupied by a r -adatom or unoccupied

respectively; η_I , η_{II} , ξ_I and ξ_{II} are respectively of the same meanings as previously defined²⁾.

The η_I and η_{II} are determined by the equation

$$\bar{\varphi}_{\sigma_0(s)} = \bar{\varphi}_{\sigma_1(s)} = \bar{\varphi}_{\sigma_3(s)}, \quad (13)$$

where $\bar{\varphi}_{\sigma_1(s)}$ or $\bar{\varphi}_{\sigma_3(s)}$ is the factor for σ_1 or σ_3 similar to $\bar{\varphi}_{\sigma_0(s)}$ for σ_0 and expressed as shown in Appendix as

$$\bar{\varphi}_{\sigma_1(s)} = (1 + \gamma_{r(s)}\eta_I)(1 + \gamma_{r(s)}\eta_{II})^2 + \gamma_{r(s)}(1 + \gamma_{r(s)}\eta_I\xi_I)(1 + \gamma_{r(s)}\eta_{II}\xi_{II})^2, \quad (14. a)$$

$$\bar{\varphi}_{\sigma_3(s)} = (1 + \gamma_{r(s)}\eta_I)^2(1 + \gamma_{r(s)}\eta_{II}) + \gamma_{r(s)}(1 + \gamma_{r(s)}\eta_I\xi_I)^2(1 + \gamma_{r(s)}\eta_{II}\xi_{II}). \quad (14. b)$$

We see from (10), (13) and (14) that $\bar{\varphi}_{\sigma_0(H_r)}/\bar{\varphi}_{\sigma_0(s)}\gamma_r$ is the identical function of γ_r , with that

$$F(\gamma_r) \equiv \varphi_{\sigma_0(H_r)}/\varphi_{\sigma_0(s)}\gamma_r \quad (15)$$

of γ_r , which is deduced from (2) and (3) without allowance for s-type adsorption;

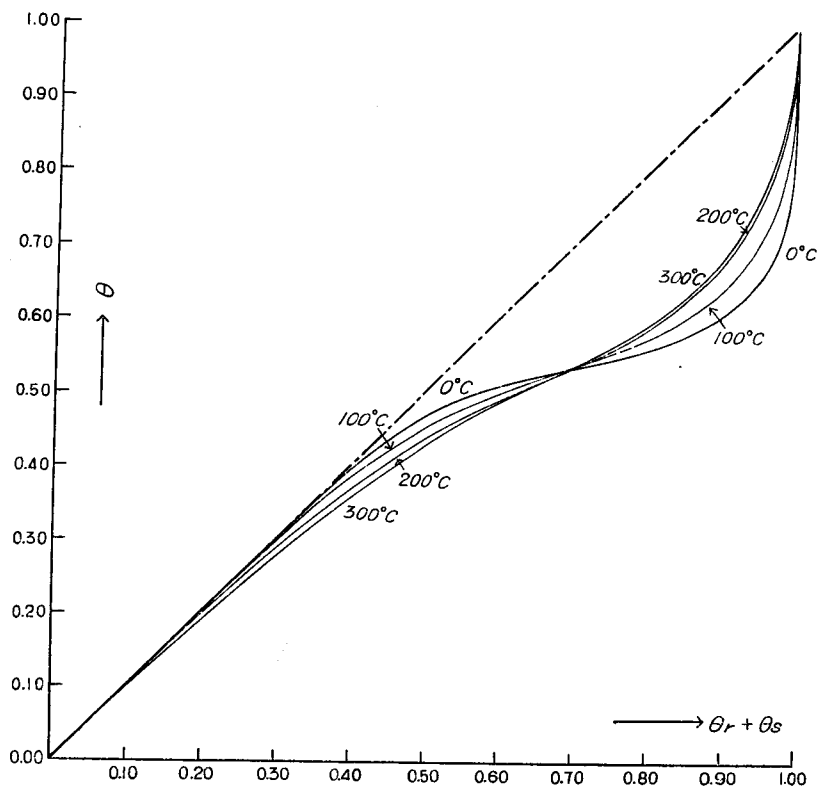


Fig. 4. Deviation of $\theta_r + \theta_s$ from θ in Case (A₁).

we have hence

$$\bar{\varphi}_{\theta_0(H_r)}/\bar{\varphi}_{\theta_0(O)}\gamma_r = F(\gamma_{r(s)}) \quad (16)$$

or according to (9)

$$\frac{\theta_r + \theta_s}{1 - \theta_r - \theta_s} = F(\gamma_{r(s)})\gamma_r + \gamma_s. \quad (17)$$

Fig. 4 shows $\theta(\gamma_r)$ plotted against $\theta_r + \theta_s$, which is calculated by (8), (11) and (17) with the constant $\Delta\epsilon_r - \Delta\epsilon_s$ fitted arbitrarily to the value $\gamma_r/\gamma_s = 10^3$ at 0°C. We see in Fig. 4 that the observed deviation (E_1) and (E_2), §3 is qualitatively reproduced by those of $\theta_r + \theta_s$ from θ .

§ 8. Cases (A₂) and (B)

The amount of adsorption v in Case (A₂) is given as

$$v = N(\theta + \theta_s), \quad (18. v)$$

where N is the adsorbed amount on the (110)-lattice plane at full coverage either of r - or s -type adsorption alone. The θ_s is given according to (6. θ)^{*}, owing to the absence of interactions mentioned in §3, simply as

$$\theta_s/(1 - \theta_s) = \gamma_s. \quad (18. \theta)$$

The θ_s is hence given as a function of γ_s by curve L in Fig. 3 with θ and γ_r there replaced by θ_s and γ_s respectively, whereas θ in (18. v) by other curve of the relevant temperature in the Figure. Both γ_r and γ_s increase now proportional to \sqrt{P} according to §5 at constant ratio γ_r/γ_s at constant temperature. It follows from Fig. 3 with reference to (18), that θ_s increases relative to θ , rapidly with increase of P at constant temperature, *i.e.* that the deviation of v from $N\theta$ increases with increase of P in accordance with (E_1), §3.

The ratio γ_r/γ_s decreases now rapidly with increase of temperature as mentioned in the preceding section. As seen in Fig. 3, however, θ increases at constant γ_r with increase of temperature, whereas decreases at constant temperature with decrease of γ_r . It follows that at a certain γ_s , say 0.1, where θ_s causes a definite amount of perceptible deviation of v from $N\theta$ according to (18), the appropriate value of θ decreases with increase of temperature in accordance with (E_2), §3, provided that the decrease of θ with the decrease of γ_r overcompensates its increase with temperature mentioned above.

In Case (B), v is given as

^{*}) The θ_0 in (6. θ) equals $1 - \theta_s$ in this case, since the occupation of the site of r -type adatom does not affect θ_0 according to the premise.

$$v = N\theta + N'\theta', \quad (19. v)$$

where N or N' is the adsorbed amount at full coverage of r -atoms respectively of the (110) or the other lattice plane in question. We consider the case first, where N' is approximately of the same magnitude as N . The θ' is expressed by an equation similar to (12), *i. e.*

$$\theta'/(1-\theta') = \lambda'\gamma', \quad (19. \theta)$$

where γ' is the γ of r -atom on the other lattice plane and λ' is the factor allowing for the repulsive interaction, similar to λ in (12). The curve of $\log_{10} \theta'$ versus γ' is in general different from L or other curves in Fig. 3, because of the factor λ' being particular to the lattice plane. We might admit however that the curve of $\log_{10} \theta'$ versus γ' is approximately reproduced around $\gamma' = 0.1$, where θ' begins to cause a perceptible deviation of v from $N\theta$ according to (19. v), by the curves of $\log_{10} \theta$ versus $\log_{10} \gamma_r$ in Fig. 3, which is not very much different thereabout even from L. The γ_r/γ' is now constant at constant temperature, very large compared with unity according to §5 and decreases rapidly with increase of temperature similar to γ_r/γ_s dealt with in §7.

Let P be so far increased as γ' attains *ca.* 0.1, where θ' begins to cause a perceptible deviation of v from $N\theta$ according to (19. v). Since θ increases much slower than θ' does with increase of P for $\gamma' \simeq 0.1$ and $\gamma_r \gg \gamma'$ as seen in Fig. 3, the relative deviation increases with increase of P in accordance with the experimental result (E_1), §3. The value of γ_r for $\gamma' \simeq 0.1$ decreases now rapidly with increase of temperature, so that the appropriate θ may decrease with increase of temperature in accordance with (E_2), §3, as in the previous cases.

If $N' \gg N$, a perceptible deviation of v occurs at much lower γ' than in the case of $N' = N$, the foregoing arguments being then similarly valid. On the other hand no deviation should occur practically, if $N' \ll N$.

§ 9. Conclusion

The observed isotherms at different temperatures were accounted for in the main as that of r -type adsorption on (110)-lattice plane in extension of the previous work at 50°C²⁾.

It was observed that the adsorbed amount v exceeds the above theoretical value at higher θ and the value of θ , where v begins to deviate perceptibly from the theoretical value, is reduced with rise of temperature.

The deviation was qualitatively accounted for by attributing it to additional s -type adsorptions on the same lattice plane or such r -type adsorption on some other lattice plane.

It appears, however, that we are not so far at the present stage to decide any of these possibilities as responsible for the actual deviation by quantitative comparison of the experimental results with the theoretical conclusions.

The present author wishes to thank Professor T. TOYA for his kind interest in the present work and his valuable advices and Mr. Y. ODA for his sincere assistance.

Appendix

Adsorption Isotherm of Case (A₁)

Eqs. (9), (10), (11), (13) and (14), which define the adsorption isotherm in this case, are derived as follows.

Let $\varphi_{\sigma_0(\sigma_0)}$ be the factor by which $\mathfrak{Q}C_{\Sigma(\sigma_0)}$ is multiplied to give the partition function of the whole system at the particular state, where σ_0 is unoccupied. The $\varphi_{\sigma_0(\sigma_0)}$ is given as the sum of the factors relevant to all the adsorbed states of Σ compatible with the condition that σ_0 is unoccupied. These states are classified into four groups, where sites of Σ other than σ_0 , *i. e.* σ_1 , σ_2 , σ_3 and σ_4 are occupied respectively by none, one, two, three and four adatoms, each being either *s*-or *r*-type one.

The factor for none of adatom is simply unity and that for one adatom is $4\gamma_s + 2\gamma_r\eta_1 + 2\gamma_r\eta_{11}$, where the first term corresponds to the occupation any of the four sites, *i. e.* σ_1 , σ_2 , σ_3 and σ_4 , by a *s*-adatom, the second term to the occupation of σ_1 or σ_2 by a *r*-adatom and the last one to the occupation of σ_3 or σ_4 by a *r*-adatom.

The factor for the two adatoms on the four sites is given as $6\gamma_s^2 + 6\gamma_s\gamma_r\eta_1 + 6\gamma_s\gamma_r\eta_{11} + \gamma_r^2(\eta_1^2 + \eta_{11}^2 + 4\eta_1\eta_{11})$; the first term is the factor for two *s*-adatoms, the second and third terms those for one *s*-adatom and one *r*-adatom and the fourth term that for two *r*-adatoms respectively arrayed on the four sites; the second or the third term corresponds respectively to six cases in all of the *r*-adatom occupying one of the two first or the second nearest sites to σ_0 and the *s*-adatom occupying one of the three remaining sites.

The factor for the three adatoms is given similarly as

$$4\gamma_s^3 + 6\gamma_s^2\gamma_r(\eta_1 + \eta_{11}) + 2\gamma_s\gamma_r^2(\eta_1^2 + \eta_{11}^2 + 4\eta_1\eta_{11}) + 2\gamma_r^3\eta_1\eta_{11}(\eta_1 + \eta_{11}).$$

The first, second, third and fourth terms correspond respectively to the cases, where three, two, one and none of the three adatoms are *s*-type ones and the rests are *r*-adatoms.

The factor for four adatoms occupying the four sites is given similarly as

$$\gamma_s^4 + 2\gamma_s^3\gamma_r(\eta_1 + \eta_{11}) + \gamma_s^2\gamma_r^2(\eta_1^2 + 4\eta_1\eta_{11} + \eta_{11}^2) + 2\gamma_s\gamma_r^3\eta_1\eta_{11}(\eta_1 + \eta_{11}) + \gamma_r^4\eta_1^2\eta_{11}^2.$$

The factor $\varphi_{\sigma_0(o)}$ is now the sum of all the factors given above, which is factored as

$$\varphi_{\sigma_0(o)} = (1 + \gamma_s + \gamma_r \gamma_{II})^2 (1 + \gamma_s + \gamma_r \gamma_I)^2$$

or with reference to (11) as

$$\varphi_{\sigma_0(o)} = (1 + \gamma_s)^4 (1 + \gamma_{r(s)} \gamma_{II})^2 (1 + \gamma_{r(s)} \gamma_{II})^2.$$

We have now the factor $\bar{\varphi}_{\sigma_0(o)}$, by which $\mathfrak{Q}C_{\Sigma(o)}(1 + \gamma_s)^4$ is multiplied to give the partition function of the whole system at the particular state, where σ_0 is unoccupied, as given by (10.0).

The factors $\bar{\varphi}_{\sigma_0(H_r)}$, $\bar{\varphi}_{\sigma_1(o)}$, and $\bar{\varphi}_{\sigma_s(o)}$ are similarly derived.

The left-hand side of (9.r) or (9.s) is now the ratio of the probability θ_r or θ_s of a definite site being occupied respectively by a r - or s -type adatom to that $\theta_0 = 1 - \theta_r - \theta_s$ of the same site being unoccupied, which ratio is equated to that of the appropriate partition functions on the right-hand side; the latter ratio is $\bar{\varphi}_{\sigma_0(H_r)}/\bar{\varphi}_{\sigma_0(o)}$ for r -adatom, whereas simply γ_s for s -adatom because of absence of interactions similarly to the case of (6).

References

- 1) J. HORIUTI, This Journal, **1**, 8 (1948-51).
- 2) J. HORIUTI and K. HIROTA, This Journal, **8**, 51 (1960).
- 3) H. EYRING, J. Am. Chem. Soc., **53**, 2537 (1931).
- 4) T. KINUYAMA and T. KWAN, This Journal, **4**, 199 (1956-7).
- 5) T. KWAN, This Journal, **1**, 81 (1948-51).
- 6) G. OKAMOTO, J. HORIUTI and K. HIROTA, Sci. Papers Inst. Phys. Chem. Research, Tokyo, **29**, 223 (1936).
- 7) T. TOYA, to be printed in this volume.
- 8) H. A. BETHE, Proc. Roy. Soc. London, **A 150**, 552 (1935).
R. E. PEIERLS, Proc. Cambridge Phil. Soc., **32**, 471 (1936).
- 9) T. TOYA, This Journal, **6**, 308 (1958).
- 10) T. TOYA, This Journal, **8**, 209 (1960).
- 11) R. SUHRMANN, Y. MIZUSHIMA, A. HERMANN and G. WEDLER, Z. phys. Chem. N. F., **20**, 332 (1959).
R. SUHRMANN, G. WEDLER and H. GENTSCH, *ibid.*, **17**, 350 (1958).
R. SUHRMANN, C. WEDLER and D. SCHLIEPHAKE, *ibid.*, **12**, 128 (1957).
Y. MIZUSHIMA, J. Phys. Soc. Japan, **15**, 1614 (1960).
- 12) W. M. H. SACTLER and G. J. H. DORGELO, Bull. Soc. Chim. Belg. **67**, 465 (1958);
Z. phys. Chem. N. F., **25**, 69 (1960).
- 13) P. ZWIETERING, H. L. T. KOKS and C. VAN HEERDEN, J. Phys. Chem. Solids, **11**, 18 (1959).
- 14) J. HORIUTI, This volume, p. 108.