

Adsorption Isotherm for the Heterogeneous Surface. (I)

Shōji UMEDA, Shiichirō TERANISHI and Kimio TARAMA*

(Kodama Laboratory)

Received June 15, 1954

Assuming that the distribution function presumed from the functional relation between the heat of adsorption and coverage reveals the heterogeneity of the surface itself, the isotherms for "uniform distribution", "rectilinear distribution," "exponential distribution" and "hyperbolic distribution" etc. have been derived respectively, and moreover the relations of the isosteric heat q and coverage θ have also been derived from some of these isotherms, and it has been shown that six experimental results are sufficiently representable by these isotherms by the use of physically reasonable values of constant parameters.

INTRODUCTION

Recently, relative to the activity of the solid catalyst, interest has been turned to the study on the adsorption of gas on the heterogeneous surface. The heterogeneity of the solid surface has been experimentally manifested in many cases,¹⁾ and some fundamental ideas as to theoretical derivation of isotherms²⁾⁻¹⁰⁾ or velocities^{3),11),12)} of gas adsorption on the heterogeneous surfaces have already been proposed by several researchers. The practical applications of these ideas, however, are restricted to a few special cases and some of these contain physically incorrect treatment.

We have studied on this subject from the more general and practical standpoint¹³⁾, and in this paper derivation of the isotherms for several heterogeneous surfaces and application of these to some experimental results are reported.

I. Determination of the Distribution Function

The heterogeneity of surface for adsorption is shown by the fact that the adsorption potential, ε^{**} , of gas on site of surface varies from site to site. Of course, there are cases where variation of ε is resulted even on the homogeneous surface from interaction between adsorbates or from induced variation of the work function of the adsorbent with the proceeding of the adsorption, but in the present report, the case where the surface itself is originally heterogeneous is treated. Accordingly, the distribution function, that is, the functional correlation between the adsorption potential and the number of sites in the surface on which gases are adsorbed with the equal adsorption potential, reveals heterogeneity of the surface itself.

* 梅田昭司, 寺西士一郎, 多羅間公雄

** ε is an absolute value of adsorption potential.

Now, the first problem of this work is the determination of the distribution function for the surface of the adsorbent from the experimental results.

For this, mainly two methods are available, the one from an analysis of the adsorption isotherm which was adopted by Roginsky⁹⁾ and Sips⁷⁾, and the other from the relation between isosteric heat of adsorption and the fraction of the surface covered by the adsorbates which was followed by Roginsky⁹⁾ et al¹⁰⁾.

The former method is restricted to a few special type isotherms owing to the mathematical difficulties, so we adopt the latter way, which is relatively easy for the practical application.

In a strict sense, the isosteric differential heat of adsorption, $q,^*$ is not equal to adsorption potential, ϵ , for q corresponds to the average of ϵ in some range. Nevertheless, under a certain condition, it may be assumed that the change of q with θ shows qualitatively the state of distribution of ϵ on the surface.

If so, from the functional relation between q and θ , such as $\theta=f(q)$, the distribution function $Z(\epsilon)$ can be presumed to be approximately

$$Z(\epsilon) \doteq cf'(q),$$

where c is the coefficient which is determined mainly by the surface area of adsorbent, and $f'(q)$ stands for the first differentiation of $f(q)$ with q .

Some examples of the experimentally observed relations between q and θ are given schematically in Fig. 1.

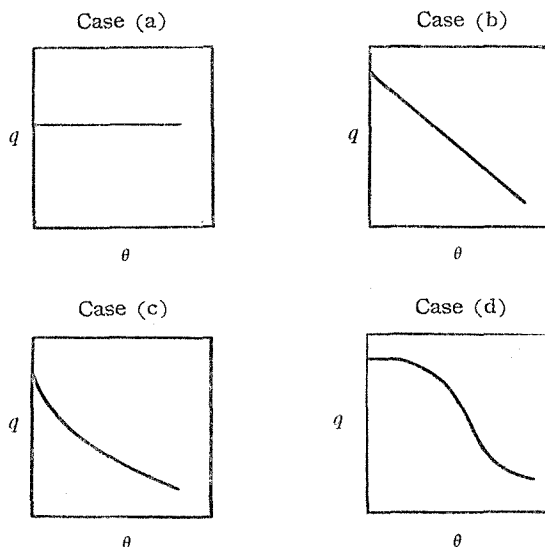


Fig. 1. Schematical representation of some relations between q and θ .

Case (a) in Fig. 1 is that for the homogeneous surface and ϵ is naturally cons-

* q is an absolute value of adsorption heat.

tant, and in case (b), q changes linearly with θ , as

$$\theta = c + b'q,$$

then the distribution function $Z(\epsilon)$ is constant

$$Z(\epsilon) = b. \quad (1.1)$$

This case is designated as "uniform distribution".

Next, in cases where a relation between q and θ is quadratic as in case (c)

$$\theta = c + b'q + a'q^2,$$

then $Z(\epsilon)$ is a linear function of ϵ as follows:

$$Z(\epsilon) = b + a\epsilon, \quad (1.2)$$

so this is designated as "rectilinear distribution".

Moreover, in cases where $f(q)$ is exponential or hyperbolic with q , $Z(\epsilon)$ becomes

$$Z(\epsilon) = ae^{-b\epsilon} \quad (1.3)$$

or

$$Z(\epsilon) = a/\epsilon^2, \quad (1.4)$$

and these cases are designated as "exponential distribution" and "hyperbolic distribution" respectively.

More generally, when the relation of q and θ is complex, for example, as in case (d) in Fig. 1, the surface is partially homogeneous, and the other part is heterogeneous, in which $Z(\epsilon)$ is given by the appropriate combination of some distribution functions mentioned above.

Now, the values of some constants in these equations (1.1), (1.2), (1.3) and (1.4) are to be calculated respectively from the following equation

$$S_0 = \int_{\epsilon_l}^{\epsilon_m} Z(\epsilon) d\epsilon, \quad (1.5)$$

where ϵ_m and ϵ_l are respectively the upper and lower limits of adsorption potentials in the range where $Z(\epsilon)$ is continuous for ϵ , and S_0 is the surface area represented by adsorption amount, and these are to be estimated from the experimental data.

II. Derivation of the Isotherms for the Heterogeneous Surfaces

Under the assumption that Langmuir isotherm may be available for the adsorption on the sites of which the adsorption potential is in the range from ϵ to $\epsilon + d\epsilon$, the number of occupied sites, that is, the amount of adsorbates on these, $N(\epsilon)$, is given by the following equation in the case of the nondissociative adsorption of one molecule on one site

$$N(\epsilon) = \frac{Z(\epsilon)d\epsilon}{1 + \frac{1}{p} e^{-\Delta S/R} e^{-\epsilon/RT}}, \quad (2.1)$$

p : equilibrium pressure, ΔS : entropy change due to adsorption,
 R : gas constant.

Then the total amount of the adsorbates on the surface, N is given by

$$N = \int_{\varepsilon_l}^{\varepsilon_m} \frac{Z(\varepsilon)d\varepsilon}{1 + \frac{1}{p} e^{-\Delta S/R} e^{-\varepsilon/RT}} \quad (2.2)$$

If a functional relation between ΔS and ε is known, the isotherms for various surfaces are obtainable by integration of eq. (2.2), but because this relation has not been theoretically derived as yet, the rectilinear relation between them is adopted in this paper as well as in Halsey's report²⁾ as follows,

$$\Delta S = \Delta S_0 - r\varepsilon \quad (2.3)$$

and the coefficient r is estimated from²⁾

$$r = 2R/\bar{\varepsilon} \quad (2.3')$$

in which $\bar{\varepsilon}$ is the mean value of ε .

From eq. (2.2) and (2.3) we have

$$N = \int_{\varepsilon_l}^{\varepsilon_m} \frac{Z(\varepsilon)d\varepsilon}{1 + fe^{-g\varepsilon}}, \quad (2.4)$$

where

$$f = \frac{A}{P} = \frac{1}{P} e^{-\Delta S_0/R}, \quad g = \frac{1}{R} \left(\frac{1}{T} - r \right). \quad (2.4')$$

In the case of the dissociative adsorption of diatomic molecule, f and g in the above equation should be revised as follows :

$$f = \sqrt{\frac{A}{P}} = \frac{1}{\sqrt{P}} e^{-\Delta S_0/2R}, \quad g = \frac{1}{2R} \left(\frac{1}{T} - r \right). \quad (2.4'')$$

(A) Rectilinear distribution $Z(\varepsilon) = a\varepsilon + b$. (1.2)

In this case, from eq. (2.4) the isotherm becomes

$$\begin{aligned} N = & b(\varepsilon_m - \varepsilon_l) + \frac{a}{2}(\varepsilon_m^2 - \varepsilon_l^2) + \left(\frac{b}{g} + \frac{a}{g^2} \ln f \right) \ln \left(\frac{1 + fe^{-g\varepsilon_m}}{1 + fe^{-g\varepsilon_l}} \right) \\ & - \frac{a}{g^2} \int_{1 + fe^{-g\varepsilon_l}}^{1 + fe^{-g\varepsilon_m}} \frac{\ln(x-1)}{x} dx, \quad (2.5) \\ & x = 1 + fe^{-g\varepsilon}. \end{aligned}$$

The last term in this equation is numerically integrated by the following equation with fairly good exactness.

$$\begin{aligned} - \int_{1 + fe^{-g\varepsilon_l}}^{1 + fe^{-g\varepsilon_m}} \frac{\ln(x-1)}{x} dx = & \int_{1 + fe^{-g\varepsilon_m}}^{1.8} \frac{\ln(x-1)}{x} dx \\ & + \int_{1.8}^{1 + fe^{-g\varepsilon_l}} \frac{\ln(x-1)}{x} dx, \quad (2.5') \end{aligned}$$

Adsorption Isotherm for the Heterogeneous Surface. (I)

where

$$\int_{1+fe^{-g\varepsilon_m}}^{1.8} \frac{\ln(x-1)}{x} dx = \left[\ln x \ln(x-1) \right]_{1+fe^{-g\varepsilon_m}}^{1.8} + \left[\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^2} x^n \right]_{fe^{-g\varepsilon_m}}^{0.8},$$

$$\int_{1.8}^{1+fe^{-g\varepsilon_l}} \frac{\ln(x-1)}{x} dx = \left[\frac{(\ln x)^2}{2} \right]_{1.8}^{1+fe^{-g\varepsilon_l}} + \left[\sum_{n=1}^{\infty} \frac{x^{-n}}{n^2} \right]_{1.8}^{1+fe^{-g\varepsilon_l}}.$$

When $1+fe^{-g\varepsilon_m} \doteq 1$ and $1+fe^{-g\varepsilon_l} \doteq fe^{-g\varepsilon_l}$, eq. (2.5) becomes

$$N = S_0 + \varepsilon_l \left(b + \frac{a}{2} \varepsilon_l \right) - bq - \frac{a}{2} q^2, \quad (2.6)$$

q : isosteric differential heat of adsorption from Clausius-Clapeyron's equation.

Differentiating the above equation with q , the rectilinear distribution function such as eq. (1.2) is derivable.

Moreover, within the same precision, $A = e^{-\Delta S_0/R}$ is determined by the next equation,

$$\ln A = \ln p - \frac{g}{a} \left\{ b \pm \sqrt{b^2 + 2a \left(S_0 + b\varepsilon_l + \frac{a}{2} \varepsilon_l^2 - N - \frac{a\pi^2}{6g^2} \right)} \right\} \quad (2.6')$$

$$(B) \text{ Unifrom distribution } Z(\varepsilon) = b. \quad (1.1)$$

Substituting $a=0$ in eq. (2.5), the isotherm for this surface is easily obtained,

$$N = b(\varepsilon_m - \varepsilon_l) + \frac{b}{g} \ln \left(\frac{1 + fe^{-g\varepsilon_m}}{1 + fe^{-g\varepsilon_l}} \right) \quad (2.7)$$

This isotherm is the same one already derived from the kinetical standpoint by Brunauer³⁾.

From this equation, the isosteric heat q is exactly derived:

$$q = -R \left(\frac{\partial \ln p}{\partial \frac{1}{T}} \right)_N$$

$$= \frac{(\varepsilon_m - \varepsilon_l)(1-\theta)}{1 - e^{-g(\varepsilon_m - \varepsilon_l)(1-\theta)}} + \frac{\varepsilon_l e^{-g\varepsilon_l} - \left\{ \varepsilon_m \theta + \varepsilon_l (1-\theta) e^{-g\varepsilon_l(1-\theta) - g\varepsilon_m \theta} \right\}}{e^{-g\varepsilon_l} - e^{-g\varepsilon_l(1-\theta) - g\varepsilon_m \theta}}$$

$$\theta = \frac{N}{S_0}, \quad (2.8)$$

and q varies linearly with θ in an appropriate range of θ as shown by the calculation for an example in the next section.

(C) Combined homogeneous surface.

The isotherm for the homogeneous part of the surface is naturally

$$N_i = \frac{Z_i}{1 + fe^{-g\epsilon_i}},$$

ϵ_i : adsorption potential for this part of the surface,

Z_i : number of sites in this part.

Accordingly, the isotherm on the surface which is composed of two homogeneous surfaces with adsorption potential ϵ_1 and ϵ_2 respectively, becomes

$$N = \frac{aS_0}{1 + fe^{-g\epsilon_1}} + \frac{(1-a)S_0}{1 + fe^{-g\epsilon_2}}, \quad (2.9)$$

where a is the fraction of the sites with the adsorption potential ϵ_1 to the whole sites S_0 .

The isosteric heat for this isotherm from the Clausius-Clapeyron's equation is found as follows :

$$q = \frac{1}{-\delta + \sqrt{\delta^2 + 4\beta}} \left\{ -\gamma + \frac{\delta\gamma + 2\beta(\epsilon_1 + \epsilon_2)}{\sqrt{\delta^2 + 4\beta}} \right\}, \quad (2.10)$$

$$\beta = A'B'\theta(1-\theta), \quad \gamma = B'\epsilon_2(a-\theta) + A'\epsilon_1(1-a-\theta),$$

$$\delta = B'(a-\theta) + A'(1-a-\theta),$$

$$A' = Ae^{-\epsilon_1/RT}, \quad B' = Ae^{-\epsilon_2/RT}.$$

(D) Exponential distribution $Z(\epsilon) = ae^{-b\epsilon}$. (1.3)

The isotherm for this distribution is given by the following equation :

$$N = \int_{\epsilon_l}^{\epsilon_m} \frac{ae^{-b\epsilon} d\epsilon}{\epsilon_l (1 + fe^{-g\epsilon})}, \quad (2.11)$$

which Halsey²⁾ had already suggested and integrated in the range of $\epsilon_m = \infty$ and $\epsilon_l = -\infty$. His integration range is, however, physically meaningless, for the total number of the adsorption sites becomes infinit by the adoption of this range as was pointed out by Hill⁸⁾.

When ϵ_m and ϵ_l are finite values respectively, integration of this equation is difficult, except by the numerical or graphycal method.

However, if $fe^{-g\epsilon} < 1$ in the range of $\epsilon_m \geq \epsilon \geq \epsilon_l$, this is expanded as follows :

$$N = -a \sum_{n=0}^{\infty} \frac{(-1)^n}{(ng+b)} f^n \left\{ e^{-\epsilon_m(ng+b)} - e^{-\epsilon_l(ng+b)} \right\} \quad (2.11')$$

and reversely if $fe^{-g\epsilon} > 1$ in the same range, eq. (2.11) becomes

$$N = -a \sum_{n=0}^{\infty} \frac{(-1)^n}{(b-g-ng)} f^{-(n+1)} \left\{ e^{-\epsilon_m(b-g-ng)} - e^{-\epsilon_l(b-g-ng)} \right\}. \quad (2.11'')$$

$$b < g$$

(E) Hyperbolic distribution $Z(\varepsilon) = a/\varepsilon^2$ (1.4)

As in the previous case (D), when $fe^{-\sigma\varepsilon} < 1$, the isotherm becomes

$$N = a \left[\left(\frac{1}{\varepsilon_l} - \frac{1}{\varepsilon_m} \right) + \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{ng} f^n \right. \\ \left. \left\{ \frac{e^{-ng\varepsilon_m}}{\varepsilon_m^2} \sum_{n'=0}^{\infty} \frac{(n'+1)!}{(-ng\varepsilon_m)^{n'}} - \frac{e^{-ng\varepsilon_l}}{\varepsilon_l^2} \sum_{n'=0}^{\infty} \frac{(n'+1)!}{(-ng\varepsilon_l)^{n'}} \right\} \right]; \quad (2.12)$$

when $fe^{-\sigma\varepsilon} > 1$, this becomes

$$N = a \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)g} f^{-(n+1)} \left\{ \frac{e^{(n+1)g\varepsilon_m}}{\varepsilon_m^2} \sum_{n'=0}^{\infty} \frac{(n'+1)!}{\{(n+1)g\varepsilon_m\}^{n'}} \right. \\ \left. - \frac{e^{(n+1)g\varepsilon_l}}{\varepsilon_l^2} \sum_{n'=0}^{\infty} \frac{(n'+1)!}{\{(n+1)g\varepsilon_l\}^{n'}} \right\}. \quad (2.12')$$

(F) More complex surface.

If the distribution function is represented by combining some of the distribution functions mentioned above, the isotherm for this surface is also given by the combination of isotherms for respective distributions as follows.

$$N = \sum_i N_i. \quad (2.13)$$

III. Application to Some Experimental Results.

(1) Adsorption of A on KCl studied by Young.¹⁴⁾

In this experiment, the isosteric heat q decreases almost linearly from 2.6 Kcal to about 1.9 Kcal with the increase of amount of adsorbates as shown in Fig. 2, so it can be considered that this is a good example of "uniform distribution".

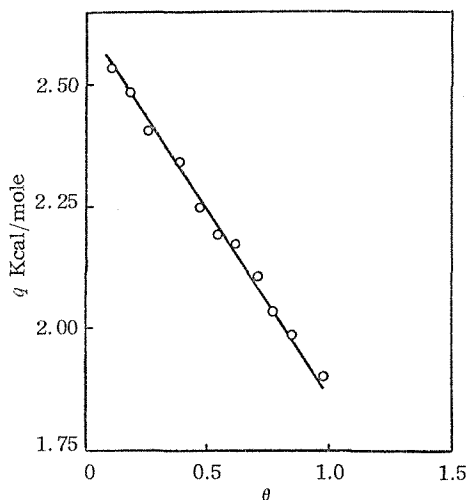


Fig. 2. q - θ relation for A on KCl.

○, Exp. Value

—, Calc. Value

Table 1. Constants used for the calculation of the isotherms.

No. of Example	Kind of adsorption	Heterogeneity of surface	Ratio of mix.	S_0	$\frac{\epsilon_m}{\text{Kcal mole}}$	$\frac{\epsilon_l}{\text{Kcal mole}}$	$\frac{r}{\text{degree}}$	$\frac{a}{\text{mole}^2 \cdot \text{cc cal}^2 \cdot \text{g}}$	$\frac{b}{\text{mole} \cdot \text{cc cal} \cdot \text{g}}$	A mmHg
(1)	A on KCl	“uniform”	1.0	$4.57 \times 10^{-7} \frac{\text{mole}}{\text{g}}$	2.6	1.86	1.78×10^{-3}	—	3.19×10^{-5}	6×10^5
(2)	H ₂ on Ni	homogeneous	0.225	$5.28 \frac{\text{cc}}{\text{NiOg}}$	26	0	3.06×10^{-4}	—	4.68×10^{-4}	1.6×10^7
		“uniform”	0.560		26					
		homogeneous	0.215		0					
(3)	H ₂ on Co	“uniform”	0.425	$2.92 \frac{\text{cc}}{\text{CoOg}}$	17	0	4.68×10^{-4}	—	7.3×10^{-5}	1×10^6
		homogeneous	0.575		0					
(4)	A on TiO ₂	“rectilinear”	1.0	$19.3 \frac{\text{cc}}{\text{g}}$	3.5	0	2.27×10^{-3}	-3.20×10^{-7}	3.29×10^{-3}	1×10^4
(5)	H ₂ on Fe	“rectilinear”	0.183	$0.446 \frac{\text{cc}}{\text{Fe}_3\text{O}_4\text{g}}$	19	0	4.18×10^{-1}	-2.46×10^{-10}	6.45×10^{-6}	1.06×10^6
		homogeneous	0.817		0					
(6)	H ₂ on W	“exponential”	1.0	$1 \times 10^{-5} \frac{\text{mole}}{\text{g}}$	34	0	2.34×10^{-4}	$3.47 \times 10^{-7*})$	$0.01^{**})$	6.4×10^7

*) $\frac{\text{mole} \cdot \text{mole}}{\text{Kcal} \cdot \text{g}}$ **) $\frac{\text{mole}}{\text{Kcal}}$

Adsorption Isotherm for the Heterogeneous Surface. (I)

Estimating S_0 , ε_m and ε_i from these experimental data, b in eq. (1.2) is straightforwardly decided and r in eq. (2.3') is also calculated by using a mean value of ε_m and ε_i , and then by selection of an appropriate value of A , the isotherm can be calculated from eq. (2.7). Values of these constants used for the calculation are lumped in Table 1.

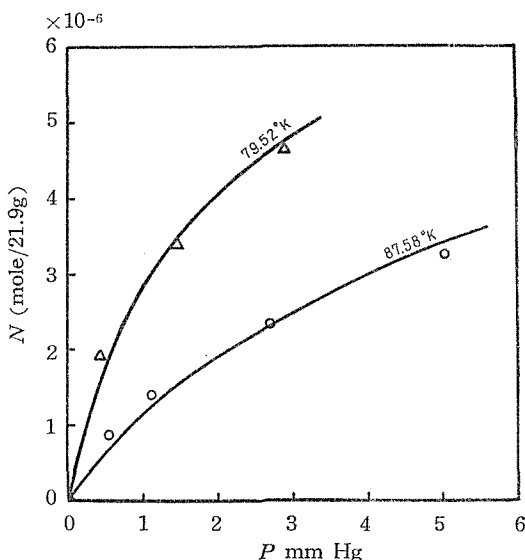


Fig. 3. Isotherm for A on KCl.

- △ , Exp. Value at 79.52°K
- , Exp. Value at 87.58°K
- , Calc. Value

As shown in Fig. 3 with full lines, the isotherms calculated at 79.52 and 87.58°K are in good agreement with experimental data in the range smaller than a half coverage, and moreover the relation between q and θ calculated by eq. (2.8) coincides very well with the experimental rectilinear relation, as in Fig. 2.

Young had tried to explain this relation of q and θ under the assumption that the surface of this octahedral KCl is mainly composed of homogeneous K^+ - and Cl^- - surfaces, but his trial had been unsuccessful even when the interaction between adsorbates was taken into consideration.

Accordingly it is clear that this experimental result is more successfully explainable from the standpoint of surface heterogeneity of "uniform distribution".

(2) Adsorption of H_2 on Ni by Kwan Izu¹⁵⁾.

Fig. 4 represents the relation of q and θ observed in the temperature range from 300 to 280°C in this experiment, that is, q is nearly constant of 26 Kcal in the smaller coverage than $\theta=0.2$, but from this coverage decreases rapidly in the rectilinear relation with θ .

Although values of q in the higher coverage have not been observed, we an-

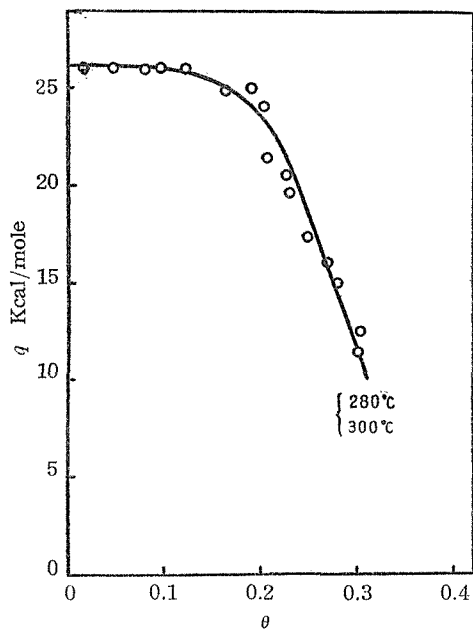


Fig. 4. q - θ relation for H_2 on Ni.

alysed this result under the assumption that the surface of this Ni was partially homogeneous and the remaining heterogeneous part was of "uniform distribution" and that the mixing ratios of these were as follows.

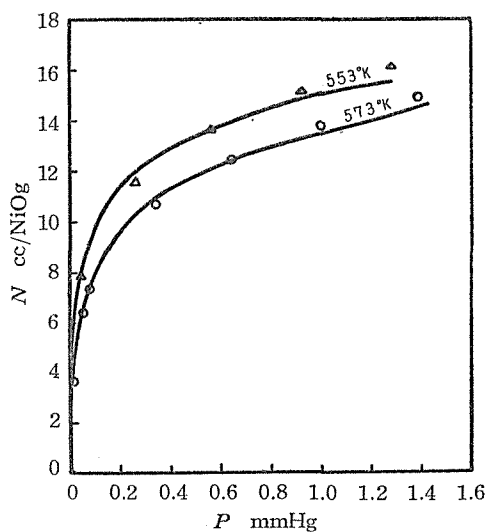


Fig. 5. Isotherm for H_2 on Ni.

- Δ , Exp. Value at 553°K
- \circ , Exp. Value at 573°K
- , Calc. Value

Adsorption Isotherm for the Heterogeneous Surface. (I)

Surface	q kcal	Fraction
Homogeneous	26	0.225
"Uniform dis."	26~0	0.560
Homogeneous	0	0.215

Determining respective constants which are tabulated in Table 1, in the same way as in the previous example, the isotherms for this dissociative adsorption of H_2 at 280 and 300°C were calculated respectively.

The results are in coincidence with the experimental data in smaller coverage than $\theta=0.3$, as shown in Fig. 5 with full lines.

(3) Adsorption of H_2 on Co by Kwan and Izu¹⁶⁾.

This result was also analyzed by nearly the same method as in the above example. The calculated isotherms at 375 and 423°K satisfy the experimental results as shown in Fig. 6. The constants used are lumped in Table 1.

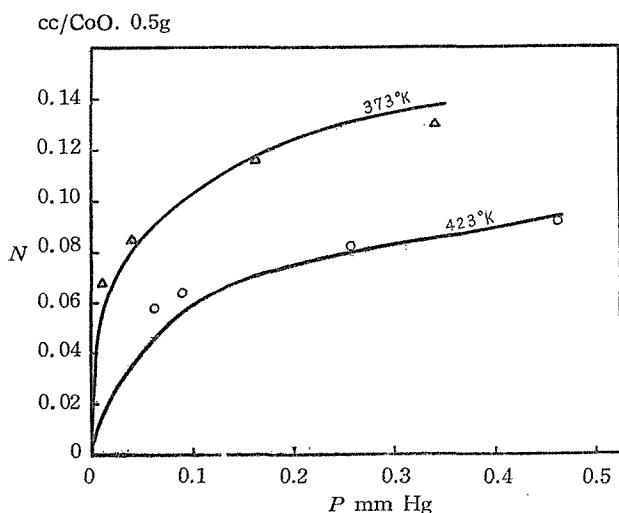


Fig. 6. Isotherm for H_2 on Co.

Δ, Exp. Value at 373°K
 ○, Exp. Value at 423°K
 —, Calc. Value

(4) Adsorption of A on TiO_2 by Drain and Morrison¹⁷⁾.

The relation between q and θ in this adsorption is relatively complex as in Fig. 7, but the quadratic relation can be considered when the change of q is ascribed to the interaction between adsorbates in the region of relatively higher coverage.

Accordingly we adopted this result as an example of "rectilinear distribution". One of the constants a and b in eq. (1.2) was decided by estimating reasonable values of S_0 , ϵ_m and ϵ_i from experimental data, and constant A and either of a and b were determined by trial and error method, and then a value of a was checked from the relation of q and θ at small coverage, and a value of A was compared with the

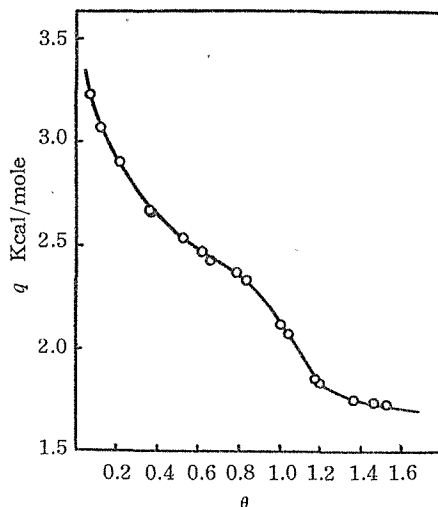


Fig. 7. q - θ relation for A on TiO_2 .

theoretical entropy change for adsorption as described afterwards.

The isotherm obtained by using the constants that are tabulated in Table 1, well coincides with the experimental data in the smaller coverage as in Fig. 8.

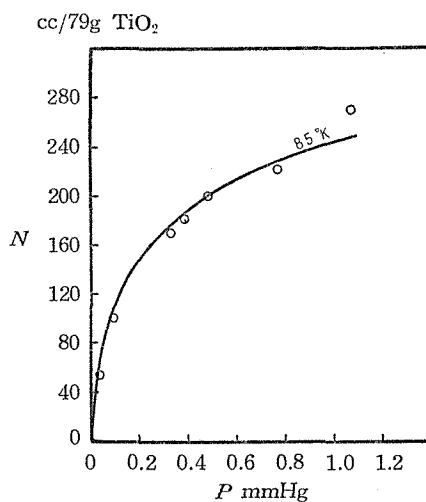


Fig. 8. Isotherm for A on TiO_2 .

O, Exp. Value
 —, Calc. Value

(5) Adsorption of H_2 on Fe by Kwan and Izu.¹⁸⁾

Kwan and his co-worker had studied on the adsorption of H_2 on pure Fe and Fe-catalyst for NH_3 -synthesis respectively and recognized the relation between q and θ in both cases such as in Fig. 9, and they had concluded that the surfaces of these were composed of two homogeneous surfaces as follows.

Adsorption Isotherm for the Heterogeneous Surface. (I)

	kcal	Fraction %	
		Pure Fe	Fe-cata.
First surface	17.5	1.4	7.0
Second surface	4.0	98.6	93.0

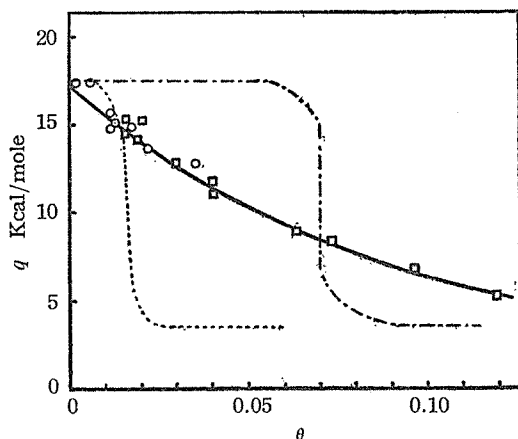


Fig. 9. q - θ relation for H_2 on Fe.

○, pure Fe
 □, Fe-cata
 , pure Fe } calc.
 - - - , Fe-cata }

However, calculating the relations of q and θ from eq (2.10) with the above data, the obtained results do not coincide with the experimental data as shown in Fig. 9.

So we presumed that the surface of this Fe was of "rectilinear distribution", and calculated the isotherm by the similar method as in the previous example, but in this case, the constants A , a and b which are given in Table 1, were simply decided by eq. (2.6) and (2.6'), since the approximations such as $1+fe^{-g\epsilon_m} \approx 1$ and $1+fe^{-g\epsilon_i} \approx fe^{-g\epsilon_i}$ were applicable.

The obtained isotherm at 25°C is comparable with the experimental one as shown in Fig. 10.

(6) Adsorption of H_2 on W by Frankenburg.¹⁰⁾

Halsey²⁾ had already analysed this experimental result by his isotherm for "exponential distribution", but as was mentioned above, his isotherm had been derived under erroneous assumptions, so we reanalysed this by more accurate equation derived in section II for "exponential distribution".

Estimating the values of S_0 , ϵ_m and ϵ_i from the experimental data, a and b in eq. (1.3) were determined by analysis of q - θ relation as in Fig. 11, and the values of these constants are lumped in Table 1.

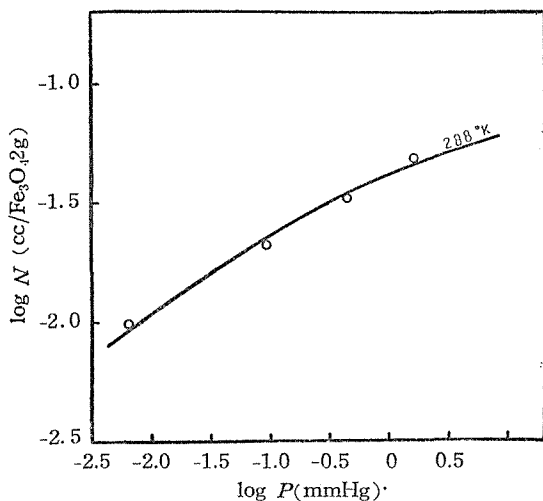


Fig. 10. Isotherm for H_2 in Fe.

○, Exp. Value
—, Calc. Value

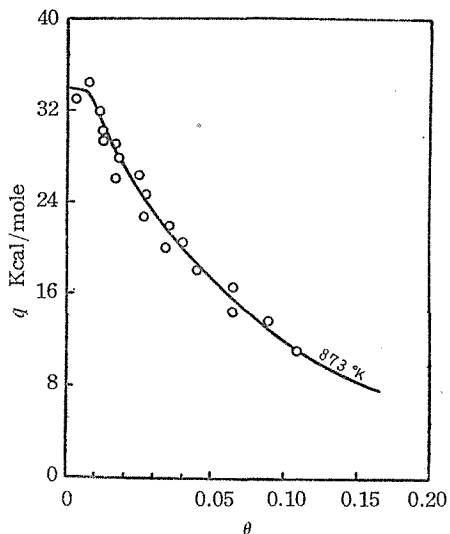


Fig. 11. q - θ relation for H_2 on W.

In this case, a condition such as $fe^{-\theta\varepsilon} > 1$ is satisfied in the whole range of ε under the lower pressure than 1 mmHg, so eq. (2.11) is available to calculate the isotherm and moreover in this equation the terms of expression higher than the fifth are negligible.

The calculated isotherm is sufficiently comparable with experimental data as shown in Fig. 12.

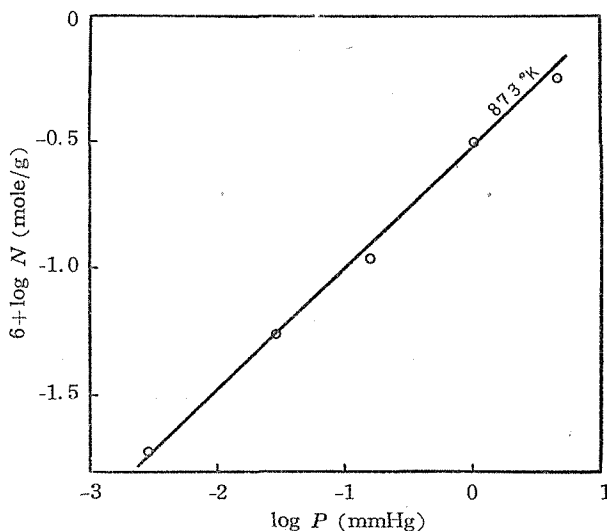


Fig. 12. Isotherm for H_2 on W.

○, Exp. Value
—, Calc. Value

(7) Examination about entropy term, A .

In all the above examples, calculations of the isotherms were performed by the use of appropriately assumed values of A respectively, so it must be examined whether these assumed values are adequate or not.

Now, an estimation of the theoretical value of entropy change for adsorption is difficult in general, but the following relation between entropy term and partition functions at some standard state is available for this examination:

$$e^{-\Delta S/R} = \frac{F_g \cdot F_s}{F_a}, \quad (3.1)$$

where F_g , F_a and F_s represent the partition functions of gas, adsorbate and adsorption site respectively.

When the state at $\theta=0$ is selected as standard, the entropy term $(e^{-\Delta S/R})_{\theta=0}$ is easily calculated from

$$A = e^{-\Delta S_0/R} \quad \text{and} \quad \Delta S = \Delta S_0 - r\varepsilon_m/n,$$

$n=1$ for nondissociative absorption,

$n=2$ for dissociative adsorption of diatomic molecule.

On the other hand, the right side of eq. (3.1) is estimated from the partition function F_g of gas under the following approximation:

$$\frac{F_g \cdot F_s}{F_a} \doteq F_g. \quad (3.2)$$

For example, in the case of the adsorption of H_2 at $T^\circ K$, eq. (3.1) becomes

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

where

(3.3)*

m : mass of H_2 -molecule,

I : moment of inertia in of H_2 -molecule,

ν : characteristic vibrational frequency of H_2 ,

k : Boltzmann's constant,

h : Planck's constant.

The entropy term from A used in calculation of the isotherm is approximately comparable with the theoretical one from the partition function in each example except for the case (5) as shown in Table 2, and even in the case (5), the effect of variation of A on the calculated result of the isotherm is relatively small, because square root of A is included in f .

Accordingly, it may be said that the values of A used in previous calculations are physically reasonable.

* Both sides of this equation are represented by pressure unit.

Table 2. Examination of Entropy terms.

No. of Example	Entropy term $e^{-\Delta S/R}$	
	from A	from part. func.
(1)	1.7×10^9	2.8×10^8
(2)	4.5×10^{10}	4.5×10^{10}
(3)	2.8×10^9	1.0×10^{10}
(4)	2.8×10^7	3.3×10^8
(5)	3.0×10^{11}	5.3×10^9
(6)	1.8×10^{11}	2.1×10^{11}

CONCLUSION

From the results obtained in previous section, it has been found that the experimentally observed isotherms are sufficiently representable by the isotherms derived theoretically for the various heterogeneous surfaces whose heterogeneity is approximately determined from the correlation between isosteric heat q and coverage θ , and that especially in the case of "uniform distribution", the experimental relation between q and θ is also explainable by the theoretical equation.

It is difficult, however, to conclude from these results only that the heterogeneity of the surface is completely given by the distribution function itself utilized in the calculation of the isotherm, because the effects of induced heterogeneity, interaction of adsorbates etc. are neglected in these calculations.

Precise examination about these effects on the adsorption isotherm will be reported in the succeeding papers²⁰.

REFERENCES

- (1) cf. P.H.Emmett, "Catalysis," Vol. 1, p.101 (1954) and W.G.Frankenburg, V.I. Komarevsky and E.K.Rideal "Advance in Catalysis," Vol. 1, p. 1 (1948).
- (2) G.D.Halsey and H.S.Taylor, *J.Chem. Phys.*, **15**, 624 (1947); G.D.Halsey, *ibid.*, **16**, 931 (1948); cf. "Advance in Catalysis," Vol. 4, p. 259 (1952).
- (3) S.Brunauer, K.S.Love and R.G.Keenan, *J.Am.Chem. Soc.*, **64**, 751 (1942).
- (4) S.Z.Roginsky, *Compt. rend. acad. sci. U.R.S.S.*, **45**, 61, 194 (1944); *Acta Physicochim.*, *U.R.S.S.*, **20**, 227 (1945); **22**, 61 (1947).
- (5) S.Z.Roginsky, *Compt. rend. acad. sci. U.R.S.S.*, **47**, 558 (1945); cf. "Advance in Catalysis," Vol. 5, p. 238 (1953).
- (6) J.Zeldowitch, *Acta Physicochim.*, *U.R.S.S.*, **1**, 961 (1935).
- (7) R.Sips, *J.Chem. Phys.*, **16**, 490 (1948), **18**, 1024 (1950).
- (8) T.L.Hill, *ibid.*, **17**, 762 (1949).
- (9) F.C.Tompkins, *J.Am. Chem. Soc.*, **64**, 751 (1942); *Trans. Faraday Soc.*, **46**, 569 (1950).
- (10) F.C.Tompkins, *ibid.*, **46**, 580 (1950).
- (11) G.D.Halsey, *J.Phys. and Colloid Chem.*, **55**, 21 (1951).
- (12) S.Z.Roginsky, *Acta. Physicochim.*, *U.R.S.S.*, **20**, 227 (1945).
- (13) K.Tarama, S.Teranishi and S.Umeda, read at the annual meeting of the Chemical Society of Japan in Kyoto on April 3, 1953.
- (14) D.M.Young, *Trans. Faraday Soc.*, **48**, 548 (1952).
- (15) T.Kwan and T.Izu, *Catalyst*, **4**, 28 (1948).

Adsorption Isotherm for the Heterogeneous Surface. (I)

- (16) T.Kwan and T.Izu, *ibid.*, 4, 44 (1948).
- (17) L.E.Drain and J.A.Morrison, *Trans. Faraday Soc.*, 48, 844 (1952).
- (18) T.Kwan and T.Izu, *Catalyst*, 6, 28 (1950).
- (19) W.G.Frankenburg, *J. Am. Chem. Soc.*, 66, 1827 (1944).
- (20) S.Umeda and K.Tarama, read at the meeting of the Chemical Society of Japan in Kyoto on May 29, 1954.