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ON THE HETEROGENEOUS MODEL OF THE SURFACE OF ADSORBENTS

By

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Summary

Heterogeneous model of adsorbent's surface was examined by comparing the distribution functions[6] derived from adsorption isotherms at different temperatures observed with the same portion of adsorbent, which should be congruent with each other according to the model. Observed isotherms dealt with in the present work were those of hydrogen adsorbed on nickel[12] or tungsten[13] each at 0°, 100°, 200° and 300°C, which obeyed the FREUNDLICH's law.

Distribution function $F(E)$ was derived from the latter isotherms for each adsorbent postulating LANGMUIR type coverage $\theta(E, \mu)=[1+\exp\{(E-\mu)/RT\}]^{-1}$ of sites of adsorption energy E, where μ is the chemical potential of adsorbate.

$F(E)$ was deduced from Freundlich type isotherm by SIPS[17)19)] and TODES and BONDAREVA[18)] by means of LAPLACE or STIELTJES transform but with the result leading to infinite sites of adsorption on finite adsorbent. To elude the latter difficulty, SIPS[17)19)] proposed a few alternative isotherms, which are shown, however, to conflict with observations. Formally identical function $F(E)$ with that obtained by SIPS[17)19)], TODES and BONDAREVA[18)] was now shown to be derived from the observation by an extension of SOMMERFELD's integral method applied to the free electron theory of metals but with its range specified as relevant to the observation, hence there existed no reason to extrapolate the function beyond the range, where alone the observations are duly responsible for the function, to be confronted with the above difficulty.

The segments of $F(E)$ thus based respectively upon observed isotherms at different temperatures were found to deviate widely from each other in either adsorbent of Ni or W.

It was now shown statistical-mechanically that the ground state energy E_0 of adsorbate localized on a site differs from E, except at absolute zero temperature, according to the equation $E_0=E+RT\ln q_0$, where q_0 is the vibrational partition function of the adsorbate given in terms, besides of temperature, of normal vibrational frequencies of the localized adsorbate, hence that exactly the congruence of $F_0(E_0)$, rather than of $F(E)$, should be required by the heterogeneous model, where $F_0(E_0)$ is the distribution function $F(E)$ expressed as a function of E_0. The vibrational frequencies were now inversely worked out for the congruence of $F_0(E_0)$. In the case of atomic adsorption in particular, where statistically independent hydrogen atoms are formed by dissociative adsorption of hydrogen, the three normal vibrations were assumed to consist of one stiff vibration of valence bond and two soft lateral vibrations of equal

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frequency ν. The ν was thus found as small as $6\sim30\,cm^{-1}$ in wave number, *i.e.* that of microwave or far infrared in order for the distribution functions $F_0(E_0)$ to be congruent. These "microwave" frequencies were now shown to conflict with the localized adsorption premised in the distribution function method of the heterogeneous model.

An alternative assumption of molecular adsorption, in which the two constituent atoms of hydrogen molecule in gas are bound to each other to some extent when adsorbed, was shown to afford no relief to the above contradiction.

The heterogeneous model associated with the distribution function method was thus disproved.

Introduction

Two contrasting models of the surface of adsorbent or catalyst are assumed at present to comprehend the experimental results of adsorption and contact catalysis; one is the homogeneous model and the other the heterogeneous one, respectively originating from LANGMUIR[1] and H. S. TAYLOR[2]. The theory based on the homogeneous model have developed into the crystal plane theory[3][4], which attributes to each lattice point an equal function of composing a site of adsorption or a seat of elementary reaction, taking account of the repulsive interactions among adsorbed chemical species inclusive of the activated complex of the elementary reaction situated on the surface[4]. A recent extension of the theory based on this model[5] has shown that the two adjustable parameters comprized in the theoretical adsorption isotherm of hydrogen on nickel, when fitted to the observed isotherm, reproduced, in confirmation of the underlying model, the crystallographic value $10^{15}\,cm^{-2}$ of the number of sites and the observed limiting value 26 kcal/mol of the heat of adsorption at low coverage.

The theory based on the heterogeneous model has developed, on the other hand, into the distribution function method[6], which presupposes the distribution of sites as a function of adsorption energy without counting upon the interactions among adsorbates*).

DOLIN and ERSCHLER[7] observed that both the models led to an identical result with special reference to the rate of hydrogen electrode reaction, and Keii[8][9] demonstrated and exemplified the identity with adsorption isotherm, adsorption rates and electrode reaction rates. TOYA[10] has besides arrived at a remarkable conclusion, that the experimental results of the differential isotopic method[11] is not an exclusive evidence for the heterogeneous model as generally accepted to be but is as well accounted for on the basis of the homogeneous model.

*) It is accepted in either case of the model that a site is exclusively occupied by an adsorbate at the same time, which is not included in what is called interactions here.

The present paper is concerned with a test to the heterogeneous model of comparing distribution functions derived from isotherms observed at different temperatures, which should be congruent with each other for the latter model to be valid.

§ 1. Outline of the method

We consider the case of hydrogen adsorption, where each molecule is adsorbed as a pair of hydrogen atoms more or less bound to each other or to dissociate into completely statistically independent atoms adsorbed; the former or the latter adsorption will be termed molecular or atomic adsorption and the respective adsorbate simply adsorbed atom or molecule respectively. Let μ be the chemical potential of adsorbate, E its energy and $F(E)dE$ the number of sites providing the energy of adsorbate lying between E and $E+dE$ in accordance with the distribution function method, where $F(E)$ is the distribution function of E. The total amount of hydrogen adsorbed is now

$$v = \int_{-\infty}^{+\infty} \theta(E, \mu) F(E)\, dE\,, \tag{1}$$

where θ is the covered fraction of sites of energy E and given as a LANGMUIR type function of E and chemical potential μ of the adsorbate, *i.e.*,

$$\theta = \left\{1 + \exp\left(\frac{E-\mu}{RT}\right)\right\}^{-1}. \tag{2}$$

The μ equals, in equilibrium of molecular or atomic adsorption, the chemical potential μ_G of hydrogen gas or a half of μ_G respectively; μ_G is expressed as

$$\mu_G = \mu_1 + RT \ln P\,, \tag{3}$$

where P is the hydrogen pressure and μ_1 is the value of μ_G at $P=1$ mmHg.

The left-hand side v of (1) is now known to obey the FREUNDLICH'S law in the case of hydrogen adsorption on nickel[12] or tungsten[13][14] except at very low P, as

$$v = v_1 P^c\,, \tag{4}$$

where v_1 and c are constant at constant temperature.

The energy of adsorbate on a site is not sharply defined but distributed thermally over different quantum states. On this ground the E in conformity with (2) is not the energy itself except at absolute zero temperature but essentially the free energy *i.e.* the increment of free energy of whole system caused by bringing an adsorbate from outside the system onto a definite, unoccupied site. This point was previously taken into account in the analysis of adsorption and heterogeneous reaction by the present author *et al.*[4][15] and recently by MATSUDA[16] in the analysis of electric capacity of hydrogen electrodes. Population of a

quantum state by FERMI gas is given by θ of (2) analogously but as a function of sharply defined eigenvalue in distinction from the present case.

E will be given in terms of the energy E_0 of the ground state of the adsorbate and temperature in the next section, hence the distribution function $F_0(E_0)$ relevant to the heterogeneous model determined in later sections.

SIPS[17] and TODES and BONDAREVA[18] have applied the theory of LAPLACE or STIELTJES transform for the determination of $F(E)$ of (1) from know function v of μ, as exemplified below with the respective cases of the molecular and atomic adsorption.

(1) Molecular adsorption

We have

$$\mu^{H_2} = \mu_G \,, \tag{5}$$

where μ^{H_2} denotes particularly the chemical potential μ of the adsorbate in this case, hence from (2), (3) and (5)

$$\theta = \left\{1 + \mathfrak{a}^{H_2} \exp\left(\frac{E^{H_2}}{RT}\right) \Big/ P\right\}^{-1}, \tag{6.θ}$$

where

$$\mathfrak{a}^{H_2} = \exp(-\mu_1/RT) \tag{6. a}$$

and E^{H_2} denotes E in this case. Eq. (1) is now

$$v_1 P^c = \int_{-\infty}^{+\infty} \frac{F(E^{H_2})\,dE^{H_2}}{1 + \mathfrak{a}^{H_2} \exp(E^{H_2}/RT)/P} \,, \tag{7}$$

hence we have according to the theory of LAPLACE or STIELTJES transform[17][18]

$$F(E^{H_2}) = \frac{v_1 (\mathfrak{a}^{H_2})^c}{RT} \frac{\sin \pi c}{\pi} \exp\left(\frac{cE^{H_2}}{RT}\right). \tag{8}$$

(2) Atomic adsorption

Particular value μ^H of μ in this case is given as

$$\mu^H = \mu_G/2 \,, \tag{9}$$

so that we have by (2) and (3)

$$\theta = \left\{1 + \mathfrak{a}^H \exp(E^H/RT)/P^{1/2}\right\}^{-1}, \tag{10.θ}$$

where

$$\mathfrak{a}^H = \exp(-\mu_1/2RT) \tag{10. a}$$

and E^H denotes E in this case. Eq. (1) is now written according to (4) and (10. θ) as

$$v_1 P^c = \int_{-\infty}^{+\infty} \frac{F(E^H)dE^H}{1 + a^H \exp(E^H/RT)/P^{1/2}}, \tag{11}$$

from which we have similarly*)

$$F(E^H) = \frac{v_1 (a^H)^{2c}}{RT} \frac{\sin 2\pi c}{\pi} \exp\left(\frac{2cE^H}{RT}\right) \tag{12}$$

This procedure is associated, as it is, with a physical difficulty, as remarked by SIPS[17], that the total number of sites $\int_{-\infty}^{+\infty} F(E)dE$ is infinite in either case of molecular or atomic adsorption. SIPS[17] proposed, in order to get around the difficulty, an alternative expression of the average covered fraction $\bar{\theta}$, *i.e.*

$$\bar{\theta} = \frac{v_1 P^c}{1 + v_1 P^c},$$

which leads, instead, to a finite total number of sites. However, the latter isotherm reproduces the observed result (4) only when $v_1 P^c$ and in consequence $\bar{\theta}$ are negligible as compared with unity according to the above equation. The $\bar{\theta}$ is not at all small, however, but even near unity[12)13)] over the range, where the FREUNDLICH's law strictly holds. Another alternative of SIPS[19] could neither be accepted on the same ground.

This difficulty associated with (8) or (12) arises from the implicit assumption that the FREUNDLICH's law (4) holds over the whole range of P, which is however by no means substantiated. We know only that it holds good over a limited range of P. We should rather investigate the range of (8) or (12), which is solidly founded upon that of observation, leaving the value of $F(E^{H_2})$ or $F(E^H)$ outside the range unknown but just subject to the condition of the finite total number of adsorption sites than to turn away from the the definite experimental fact of (4).

KEII[8] has applied the SOMMERFELD's method of evaluating μ, hence the

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*) Let

$$e^{-E^H/RT} = x, \quad a^H/P^{1/2} = y.$$

Eq. (11) is now written as

$$v_1 (a^H)^{2c}/RTy^{2c} = \int_0^{\infty} \frac{\varphi(x)dx}{x+y},$$

where

$$\varphi(x) = F(-RT \ln x).$$

The $\varphi(x)$ is given according to the STIELTJES transform[17] as

$$\varphi(x) = \frac{v_1 (a^H)^{2c}}{RT} \frac{x^{-2c} e^{2\pi i c} - x^{-2c} e^{-2\pi i c}}{2\pi i} = \frac{v_1 (a^H)^{2c}}{RT} x^{-2c} \frac{\sin 2\pi c}{\pi},$$

which leads to (12) on substitution back of x.

mean energy and the specific heat of FERMI gas from known $F(E)$ inversely to the present problem of finding the latter from known μ. The SOMMERFELD's method leads, in terms of the present notation, to the equation*)

$$v=\int_{-\infty}^{\mu}F(E)dE+2\sum_{m=1}^{\infty}\frac{(\pi RT)^{2m}}{(2m)!}(2^{2m-1}-1)B_m\left\{\frac{d^{2m-1}F(E)}{dE^{2m-1}}\right\}_{E=\mu}, \qquad (13)$$

where B_m is the BERNOULLI's number, *i.e.* 1/6, 1/30, 1/42, $\cdots$ for $m=1,2,3,\cdots$ respectively. KEII[8] has shown on the basis of (13) that the ROGINSKY's approximation[6] for evaluating $F(E)$ from v corresponds to the first term of (13) only being retained and he[8] advanced further with the approximation reserving the first two terms to work out $F(E)$ and the heat of adsorption.

It is now shown in Appendix retaining the whole terms of the infinite series of (13), that

$$F(E^{H_2})_{E^{H_2}=\mu^{H_2}}=\frac{v_1(a^{H_2})^c}{RT}\frac{\sin\pi c}{\pi}\exp\left(\frac{c\mu^{H_2}}{RT}\right), \qquad (14.\text{a})$$

or

$$F(E^{H})_{E^{H}=\mu^{H}}=\frac{v_1(a^{H})^{2c}}{RT}\frac{\sin 2\pi c}{\pi}\exp\left(\frac{2c\mu^{H}}{RT}\right), \qquad (14.\text{b})$$

respectively for the case of the molecular or the atomic adsorption. Eq. (14.a) or (14.b) reproduces (8) or (12) respectively deduced according to the theory of LAPLACE or STIELTJES transform[17][18][19], under the assumption that (4) holds over the whole range of P, but gives the particular values of $F(E^{H_2})$ or $F(E^{H})$ as based on observations, since according to (3), (4), (5) and (6.a), or (3), (4), (9) and (10.a)

$$v=v_1(a^{H_2})^c\exp(c\mu^{H_2}/RT), \text{ or } v=v_1(a^{H})^{2c}\exp(2c\mu^{H}/RT), \qquad (15)$$

hence by (14)

$$F(E^{H_2})_{E^{H_2}=\mu^{H_2}}=\frac{v}{RT}\frac{\sin\pi c}{\pi} \qquad (16.\text{a})$$

or

$$F(E^{H})_{E^{H}=\mu^{H}}=\frac{v}{RT}\frac{\sin 2\pi c}{\pi}. \qquad (16.\text{b})$$

Eq. (16) gives the value of $F(E^{H_2})$ or $F(E^{H})$ determined by *observed* v and c as a function of E^{H_2} or E^{H} respectively, which equals μ^{H_2} or μ^{H} defined by *observed* P. $F(E^{H_2})$ or $F(E^{H})$ is thus determined over the range relevant, according to (16), to the observed range of v. We have no reason to extrapolate $F(E)$ beyond the range to be confronted with the difficulty of the infinite total

*) *Cf.* ref. (21).

number of sites.

The distribution function $F_0(E_0)$ is derived in subsequent sections from $F(E)$ thus obtained, hence the heterogeneous model is put to test in later sections by comparing $F_0(E_0)$ thus determined at different temperatures first assuming the atomic adsorption and then later the molecular adsorption.

§ 2. Ground state energy E_0^{H} of adsorbed hydrogen atom

Consider a macroscopic system at constant temperature and constant total volume, consisting of a definite amounts respectively of hydrogen and adsorbent, which are in equilibrium of atomic adsorption. The ratio of the probability θ of a certain definite site of being occupied to that $1-\theta$ of the same site of being unoccupied is given statistical-mechanically by the ratio of the partition functions of the whole macroscopic system at the respective states as formulated below[4)15)]. Let the above macroscopic system be at a particular state of the definite site being unoccupied. Draw out one of constituent hydrogen atoms from the macroscopic system keeping the definite site unoccupied and then put the hydrogen atom just drawn out to the definite unoccupied site as an adsorbed atom. Let $1/p^{\mathrm{H}}$ be the factor of increase of the partition function of the macroscopic system caused by the withdrawal first and q^{H} that caused by putting the atom to the definite unoccupied site next. It follows that[4)15)]

$$\frac{\theta}{1-\theta} = \frac{q^{\mathrm{H}}}{p^{\mathrm{H}}} . \tag{17}$$

The p^{H} is identified with the Boltzmann factor of the chemical potential μ^{H}, *i. e.*

$$p^{\mathrm{H}} = \exp(-\mu^{\mathrm{H}}/RT) , \tag{18}$$

inasmuch as the partition function behaves as the BOLTZMANN factor of the free energy, the effect on μ^{H} or p^{H} of the microscopic constraint of the definite site being kept unoccupied being ignored. The probability θ is of course identical with the covered fraction of a group of sites of the same θ.

It follows from (2), (17) and (18) that

$$q^{\mathrm{H}} = \exp(-E^{\mathrm{H}}/RT) , \tag{19}$$

identifying E or μ in (2) with E^{H} or μ^{H} for this case, hence that E^{H} is the free energy increase according to the definition of q^{H} as mentioned in the foregoing section.

The function q^{H} is developed in terms of the ground state energy E_0^{H} of adsorbed hydrogen atom and its vibrational frequencies, ν_j, $j=1,2,3$, as[4)]

$$q^{\mathrm{H}} = q_0^{\mathrm{H}} \exp(-E_0^{\mathrm{H}}/RT) , \tag{20. a}$$

where

$$q_0^{\mathrm{H}} = \prod_{j=1}^{3} \left\{1-\exp(-h\nu_j/kT)\right\}^{-1}. \tag{20. b}$$

It follows from (19), (20. a) and (20. b) that

$$E^{\mathrm{H}} = E_0^{\mathrm{H}} - RT\ln q_0^{\mathrm{H}}. \tag{20. c}$$

The function q^{H} as given by (20. a) is derived as follows[4] under the assumption that the coordinates of heavy particles composing the adsorbent are separable from those of the adsorbed hydrogen atom and that the latter vibrates harmonically around its equilibrium position.

The partition function of the macroscopic system with the hydrogen atom adsorbed on the site is now Qq^{H}, according to the former assumption, where q^{H} is the partition function of the adsorbed hydrogen atom alone moving in the mean potential field provided by the adsorbent, which is expressed according to the latter assumption as (20. a) and Q is the partition function of the rest of the macroscopic system, *i. e.* that which results from the original one by extracting a hydrogen atom from it with the definite site unoccupied; the appropriate factor of increase of the partition function is hence

$$Qq^{\mathrm{H}}/Q = q^{\mathrm{H}}.$$

§ 3. $F_0(E_0)$

The function $F_0(E_0)$ is now given explicitly by substituting $\mu^{\mathrm{H}} = E^{\mathrm{H}}$ from (20. c) into (14. b) and referring to (10. a), as

$$\begin{aligned}\log F_0(E_0^{\mathrm{H}}) &= \log F(E^{\mathrm{H}}) \\ &= \log\frac{v_1\sin 2\pi c}{\pi RT} - \frac{c\mu_1}{2.30RT} - 2c\log q_0^{\mathrm{H}} + \frac{2cE_0^{\mathrm{H}}}{2.30RT}.\end{aligned} \tag{21. a}$$

The μ_1 is expressed as

$$\mu_1 = -2.30ART - \frac{7}{2}RT\ln T, \tag{21. b}$$

where*)

$$A = \log\frac{(2\pi mk)^{3/2}4\pi^2 Ik^2}{1.360\times 980.5\times h^5} = -0.49176. \tag{21. c}$$

We have from (21. a) and (21. b)

*) The A was calculated on the base of the data,

$m = 2.0152/6.0254\times 10^{23}$ gm,

$k = 1.3803\times 10^{-16}$ erg deg^{-1},

$h = 6.6238\times 10^{-27}$ erg sec

and $I = 0.46637\times 10^{-40}$ gm cm^2.

$$\log F_0(E_0^{\mathrm{H}}) = \log F(E^{\mathrm{H}})$$
$$= \log \frac{v_1 \sin 2\pi c}{\pi RT} + cA + \frac{7c}{2} RT \log T - 2c \log q_0^{\mathrm{H}} + \frac{2cE_0^{\mathrm{H}}}{2.30\, RT}. \tag{22}$$

Eq. (21. b) is derived as follows. The chemical potential μ_G of gaseous hydrogen is given with sufficient accuracy as

$$\mu_G = -RT \ln \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 IkT}{h^2 N^{\mathrm{H}_2}}$$

taking the ground state of hydrogen molecule at rest as the standard state of energy, where m or I is the mass or the moment of inertia of hydrogen molecule, N^{H_2} its concentration in gas and k or h the BOLTZMANN or PLANCK constant. The concentration N^{H_2} is given in terms of P in mmHg as

$$N^{\mathrm{H}_2} = 1.360 \times 980.5\ P\ \mathrm{mmHg}/kT,$$

where 1.360 is the pressure of 1 mmHg in gm cm^{-2} and 980.5 cm sec^{-2} the acceleration of gravity. We have from the above two equations with reference to (21. c)

$$\mu_G = -2.30\, ART - \frac{7}{2} RT \ln T + RT \ln P, \tag{23}$$

hence (21. b) according to (3).

Eq. (22) gives thc distribution function as a linear function $\log F_0(E_0^{\mathrm{H}})$ of E_0^{H}; the upper and the lower extremities of observed v specify, in accordance with (16. b), a segment of the linear function as based upon the observation.

§ 4. Distribution function

The segment of the distribution function $F_0(E_0^{\mathrm{H}})$ appropriate to the observation is now quantitatively determined according to (22) by evaluating q_0^{H} involved. Eq. (20. b) shows that q_0^{H} approaches unity as all the values of ν_j/T tend to infinity. It may be adequate to assume with the heterogeneous model that the set of ν_j's depends on E_0^{H} similarly as the vibrational frequency of diatomic molecule increases with increase of the dissociation energy. Nevertheless, we may work out $F_0(E_0)$ for a set of constant ν_j-values to examine the heterogeneous model by comparison of $F_0(E_0)$ thus derived from observations at different temperatures because of the following reason. If any set of constant ν_j's be relevant to a certain value of E_0^{H}, which is covered commonly by the ranges of distribution functions based upon observations at different temperatures, the latters should intersect each other at the value of E_0^{H}, insofar as the heterogeneous model is valid. The intersection is thus the necessary condition for the assigned set to be appropriate to such a common value of E_0^{H}.

It may be noted that, for infinite ν_j's, E_0^{H} equals E^{H} according to (20), hence $F_0(E_0^{\mathrm{H}})$ is congruent with $F(E)$, since then q_0^{H} is unity or $RT \ln q_0^{\mathrm{H}}$ vanishes by

(20.b).

Table 1 shows the values of v_1 and c, and the upper extremity v_u and the lower one v_l respectively of observed v. These values are given in absolute amounts of adsorption on a definite catalyst or in percent of full coverage respectively in the case of nickel or tungsten, relative change of v being here only of significance.

TABLE 1. Observed values of v_1, v_u, v_l and c for H_2 adsorbed on Ni and W

t°C	Ni				W			
	v cc NTP			c	v % of saturation			c
	v_1	v_u	v_l		v_1	v_u	v_l	
0	2.513	2.97	2.04	0.0435	33.3	37.1	20.4	0.0524
100	1.841	2.51	1.12	0.0795	27.7	32.4	14.7	0.0690
200	1.170	2.12	0.50	0.1515	20.6	26.5	4.5	0.1104
300	0.617	1.72	0.29	0.251	14.0	20.0	3.3	0.158

The distribution function $F_0(E_0^{\mathrm{H}})$ is calculated from these data at different temperatures according to (22) as shown in Figs. 1, 2, 3 and 4.

The upper and the lower ends of the segment of $F_0(E_0^{\mathrm{H}})=F(E)$ based on observation are respectively fixed to v_u and v_l by (16.b) irrespective of ν_j's. Hence the segment shifts between the two horizontal lines with constant slope against E_0^{H} monotonously rightwards along with decrease of ν_j's, or with increase of q_0^{H} according to (20.b) and (22).

The leftmost segment "300°C; $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3\to\infty$" and the segment "0°C; $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3\to\infty$" at the middle in Fig. 1 show the distribution functions $F_0(E_0^{\mathrm{H}})$ of nickel computed respectively at 300°C and 0°C by (22) for infinite ν_j's. The segments give identically those of $F(E)$ as mentioned above. Since the segments at 300°C and 0°C lie wide apart from each other without intersection, the infinite ν_j's assigned must be irrelevant to any value of $F_0(E_0)$ commonly covered both by the segments.

Fig. 1 shows the segments for the set of wave numbers[4], $\tilde{\nu}_1=1900\ \mathrm{cm}^{-1}$, $\tilde{\nu}_2=417\ \mathrm{cm}^{-1}$ and $\tilde{\nu}_3=479\ \mathrm{cm}^{-1}$. The appropriate segments at 300°C and 0°C are still far from intersecting each other, yet the segment at 300°C shifts rightwards much more than that at 0°C does. It is analytically shown by (20.b) and (22), that any segment shifts rightwards monotonously with decrease of ν_j's, but the more, the higher the temperature, to which the segment is appropriate. They may hence be brought to intersect each other by decreasing ν_j's further.

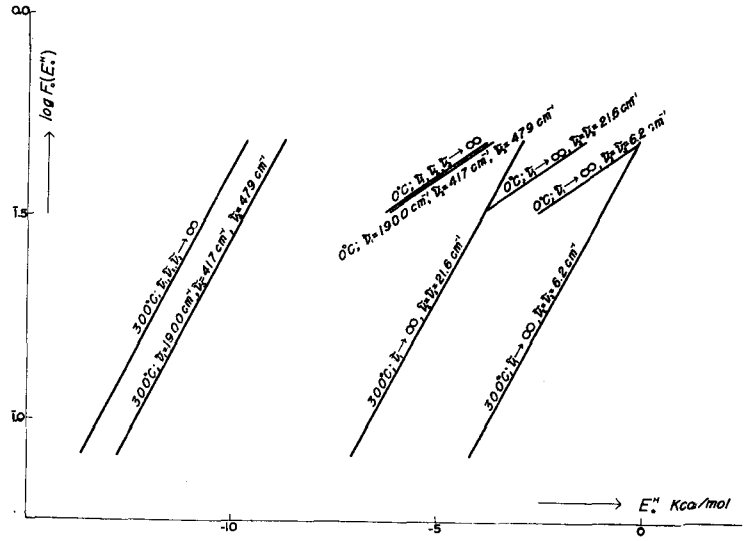

Fig. 1. Distribution functions. Atomic adsorption of H_2 on Ni. 0° and 300°C.

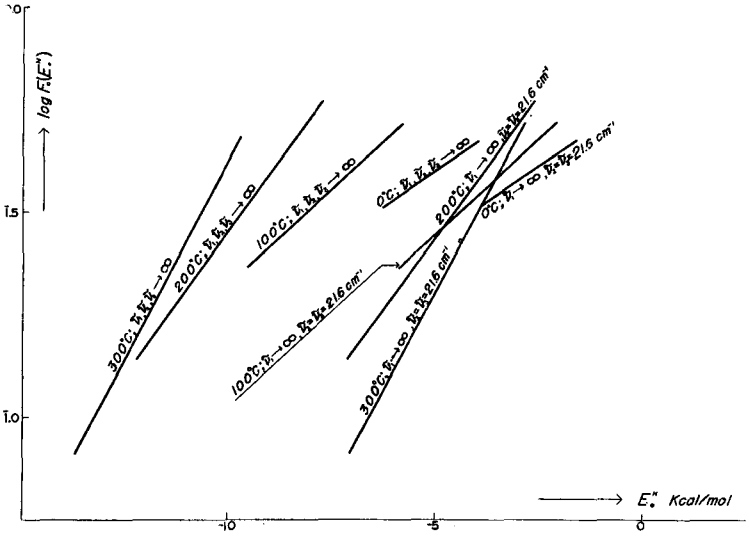

Fig. 2. Distribution functions. Atomic adsorption of H_2 on Ni. 0°, 100°, 200° and 300°C.

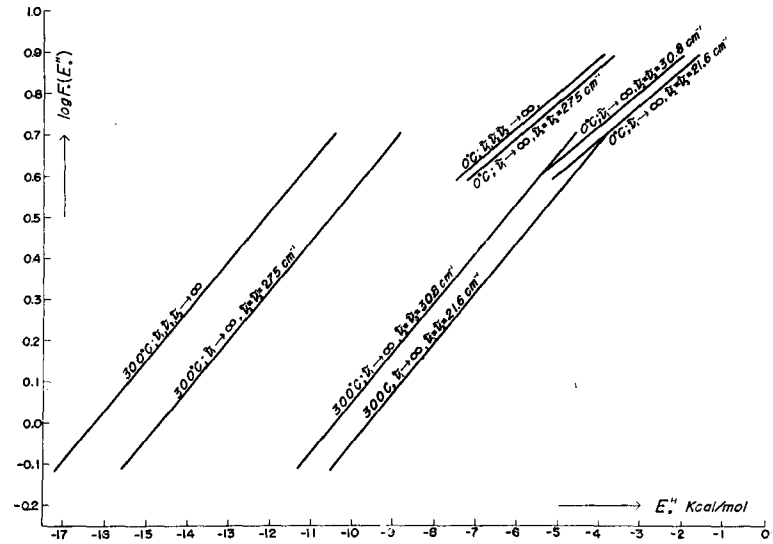

Fig. 3. Distribution functions. Atomic adsorption of H_2 on W. 0° and 300°C.

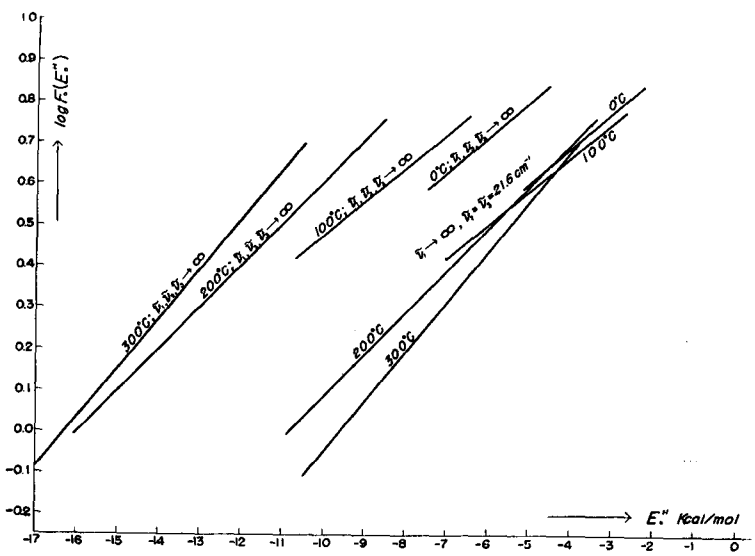

Fig. 4. Distribution functions. Atomic adsorption of H_2 on W. 0°, 100°, 200° and 300°C.

The ν_j's are now varied according to the following considerations. One of the three normal vibrations must be that of valence bond, while the other two those of deformation or lateral vibrations, so that the wave number $\tilde{\nu}_1$ of the first one must be large compared with those $\tilde{\nu}_2$ and $\tilde{\nu}_3$ of the other two, which are expected nearly equal to each other as in the above example*), whether based on the homogeneous or the heterogeneous model. The factor $\{1-\exp(-h\nu_1/kT)\}^{-1}$ of the stiff vibration of $\tilde{\nu}_1=1900\ \mathrm{cm}^{-1}$ amounts to 1.00004 at 0°C and to 1.0085 at 300°C, so that it contributes to the term $-2c\log q_0^{\mathrm{H}}$ practically as good as that of $\nu_1\to\infty$.

On the ground of the above consideration, we assume ν_1 infinite and that $\nu_2=\nu_3$, to evaluate the latter for the intersection of segments. We then have from (20.b)

$$\log q_0^{\mathrm{H}} = -2\log\left\{1-\exp(-h\nu/kT)\right\}, \tag{24}$$

where

$$\nu = \nu_2 = \nu_3 .$$

The value of $\tilde{\nu}$ is determined as below respectively at the point, where the segment at 300°C just overtakes that at 0°C at its left end or just passes over the latter at its right end as seen on the right part of Fig. 1, respectively as

$$\tilde{\nu} = 21.6\ \mathrm{cm}^{-1} \tag{25.l}$$

or

$$\tilde{\nu} = 6.2\ \mathrm{cm}^{-1} . \tag{25.u}$$

The $\tilde{\nu}$-value for the intersection of the segments lies between the two values of (25) as deduced from (22) and (24).

The result of (25) is obtained as follows. The lowest value $\{\log F_0(E_0^{\mathrm{H}})\}_l$ of $\log F_0(E_0^{\mathrm{H}})$ at the left end of the segment is determined at $\bar{1}.509$ for 0°C by (16.b) from the appropriate values of v_l and c for nickel in Table 1, hence we have from (21.c), (22) and (24)

$$\bar{1}.509 = \bar{1}.949+0.174\log\left\{1-\exp(-h\nu/kT_0)\right\}+0.0679\,E_0^{\mathrm{H}},$$

where T_0 is the absolute temperature of 0°C. We have, on the other hand, from the condition of the segment at 300°C to pass through the same point according to (22), that

$$\bar{1}.509 = 1.536+1.004\log\left\{1-\exp(-h\nu/kT_{300})\right\}+0.1916\,E_0^{\mathrm{H}},$$

*) The wave number $1900\ \mathrm{cm}^{-1}$ is that of the valence bond vibration, whereas $417\ \mathrm{cm}^{-1}$ and $479\ \mathrm{cm}^{-1}$ are those of the lateral vibrations, which were worked out by taking account of the repulsive interactions between the adsorbed hydrogen atom and metal atoms other than that to which the hydrogen atom was bonded[4]. The small difference of the latter two wave numbers was due to the anisotropic pattern of the (110)-lattice plane of f.c.c. Ni crystal.

where T_{300} is the absolute temperature of 300°C. Solving the above two equations simultaneously for $\tilde{\nu}$, we have the result of (25.*l*). That of (25.*u*) is similarly obtained.

Fig. 2 shows the segments of nickel at 0°, 100°, 200° and 300°C respectively for $\tilde{\nu}_1 \to \infty$ and $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$, keeping $\tilde{\nu}_1$ constantly to infinity.

Fig. 3 shows $\log F_0(E_0^{\mathrm{II}})$ of tungsten at 300° and 0°C computed by (22) for different sets of ν_j's from data given in Table 1. As in the case of nickel, $\tilde{\nu}$ is varied, to which $\tilde{\nu}_2$ and $\tilde{\nu}_3$ are equated, while $\tilde{\nu}_1$ kept constantly to infinity. The segments at 300° and 0°C lie widely apart from each other for $\tilde{\nu}\to\infty$ and $\tilde{\nu}=275\,\mathrm{cm}^{-1}$, while the former segment shifts rightwards with decrease of $\tilde{\nu}$ more than that at 0°C does just as in the case of nickel. The former overtakes the latter, along with decrease of $\tilde{\nu}$, just touching its left end at $\tilde{\nu}=30.8\,\mathrm{cm}^{-1}$ and severs it rightwards at $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$. The $\tilde{\nu}$-value of the intersection should lie between these limits.

Fig. 4 shows the segments of $\log F_0(E_0^{\mathrm{II}})$ of tungsten at 0°, 100°, 200° and 300°C both for $\tilde{\nu}\to\infty$ and for $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$. Those for $\tilde{\nu}\to\infty$ lie wide apart from each other, whereas those for $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$ group close together intersecting each other similarly as in the case of nickel.

It is concluded both for nickel and tungsten that the wave number of the lateral vibration of adsorbed hydrogen atoms must be as low as that of microwave or far infrared, should the heterogeneous model be valid. The "microwave" frequencies are now examined in the next section.

§ 5. Frequency of lateral vibration

We first investigate whether the "microwave" frequency of lateral vibrations were consistent with the premise of the localized adsorption. The normalized eigenfunction ϕ_0 of the ground state of the two-dimentional lateral vibration is

$$\phi_0 = \sqrt{\alpha/\pi}\exp(-\alpha r^2/2)\,, \qquad (26.\phi)$$

where

$$\alpha = 4\pi^2 m\nu/h\,, \qquad (26.\alpha)$$

r is the distance of the adsorbed hydrogen atom from the fixed bond axis and m its mass. We have from the above eigenfunction the probability that the adsorbed hydrogen atom is localized above the metal atom to which it is bonded or $r \leqq \mathrm{R}$ on the plane of the motion as

$$\omega = \int_0^{\mathrm{R}}\int_0^{2\pi}\phi_0^2 r\,dr\,d\theta = 1-\exp(-\alpha \mathrm{R}^2)\,, \qquad (27)$$

where R is the radius of the metal atom. The ω is calculated by (26.α) and (27) for $\tilde{\nu}$-values dealt with in the foregoing section as shown in Table 2.

The wave number $\tilde{\nu}=448\,\mathrm{cm}^{-1}$ is the average of those[4] $\tilde{\nu}_2=417\,\mathrm{cm}^{-1}$ and $\tilde{\nu}_3=479\,\mathrm{cm}^{-1}$ on nickel mentioned in the preceding section.

TABLE 2. The probability ω of localization

Adsorbent	Ni			W		
$R\times10^8$ cm	1.245			1.370		
$\tilde{\nu}=\tilde{\nu}_2=\tilde{\nu}_3\,\mathrm{cm}^{-1}$	448	21.6	6.2	275	30.8	21.6
$\omega=1-\exp(-\alpha R^2)$	$1-10^{-9}$	0.63	0.25	$1-2\times10^{-7}$	0.82	0.70

As shown in the Table, adsorbed hydrogen atom could hardly be termed localized for the "microwave" frequencies, whereas it is practically perfectly for $448\,\mathrm{cm}^{-1}$ of nickel and for $275\,\mathrm{cm}^{-1}$ of tungsten. The locarization is still worse at the excited states as deduced from the appropriate eigenfunction $\psi_{m,n}(x,y)=\psi_0 H_m(\sqrt{\alpha}x)H_n(\sqrt{\alpha}y)/(2^{m+n}m!n!)^{1/2}$ of the rectangular coordinates x and y, where $H_m(\sqrt{\alpha}x)$ or $H_n(\sqrt{\alpha}y)$ is the HERMITE polynomial of m-th or n-th degree corresponding respectively to m-th excited vibrational state in x-direction or n-th one in y-direction. The factor $H_m(\sqrt{\alpha}x)H_n(\sqrt{\alpha}y)/(2^{n+n}m!n!)^{1/2}$ thus modulates the eigenfunction ψ_0 of the ground state to give those of the excited states, weighting the probability $|\psi_{m,n}|^2$ at larger value of x and y, hence reducing the probability of localization still worse.

The "microwave" frequencies are further disproved as follows on the ground of an experimental result of GOMER[20]. He has found by means of field emission microscope that the activation energy for jump of an adsorbed hydrogen atom from a metal atom to another varied from 16 to 6 kcal with increase of adsorbed amount. It follows that

$$\frac{f}{2}R^2-Z_e+Z^*-\Delta V^*\geqq 6\ \mathrm{kcal\ mol}^{-1},$$

admitting that the parabolic potential $fR^2/2$ of adsorbed hydorgen atom is reduced by the quantum mechanical resonance energy ΔV^* around the activated state of the jump at $r=R$, where f is the force constant and Z_e or Z^* the zero point energy at the equilibrium position or at the activated state. It may safely be assumed that Z_e is greater than Z^*, the latter being usually even neglected. It follows then that

$$\frac{f}{2}R^2>6\ \mathrm{kcal\ mol}^{-1},$$

or $f>12/R^2\ \mathrm{kcal\ mol^{-1}cm^{-2}}$, hence we have

$$\tilde{\nu} = \frac{1}{2\pi}\sqrt{\frac{f}{m}}\Big/3\cdot 10^{10} > \frac{10^{-10}}{6\pi}\sqrt{\frac{6\times 4.187\times 10^{10}}{1/2\times(1.37\times 10^{-8})^2\times 1.008}} = 275\ \mathrm{cm}^{-1}, \tag{28}$$

for $R = 1.37\times 10^{-8}$ cm of tungsten. The above unequality limits the frequencies to those which conform with the condition of localization*) on the one hand and excludes the "microwave" frequencies on the other hand. The heterogeneous model is thus disproved in the case of atomic adsorption.

§ 6. Molecular adsorption

The E^{H_2} is expressed similarly as in the case of (20. c) for atomic adsorption, as

$$E^{H_2} = E_0^{H_2} - RT\ln q_0^{H_2}, \tag{29. E}$$

where

$$q_0^{H_2} = \prod_{j=1}^{6}\left\{1-\exp(-h\nu_j/kT)\right\}^{-1} \tag{29. q}$$

for six degrees of freedom of adsorbed molecule. We have on substitution of $\mu^{H_2} = E^{H_2}$ from (29. E) into (14. a), referring to (6. a)

$$\log F_0(E_0^{H_2}) = \log F(E^{H_2}) = \log\frac{v_1\sin\pi c}{\pi RT} - \frac{c\mu_1}{2.30RT} - c\log q_0^{H_2} + \frac{cE_0^{H_2}}{2.30RT}. \tag{30}$$

Let us first assume that

$$2\log q_0^{H} = \log q_0^{H_2}, \tag{31}$$

which is the case, if each frequency of the normal vibration of an adsorbed atom just doubles for an adsorbed molecule. We see from (21. a), (30) and (31), that $\log F_0(E_0^{H_2})$ is less than $\log F_0(E_0^{H})$ for $E_0^{H} = E_0^{H_2}/2$ by $\log(\sin 2\pi c/\sin\pi c)$ or that the segment of $\log F_0(E_0^{H_2})$ plotted against $E^{H_2}/2$ is obtained by lowering that of $\log F_0(E_0^{H})$ against E_0^{H} vertically by the same amount. Figs. 5 and 6 show $F_0(E_0^{H_2})$ thus derived respectively from those of Fig. 2 and Fig. 4 on the base of the c-values given in Table 1. Wave numbers $\tilde{\nu}_1$, $\tilde{\nu}_2$ and $\tilde{\nu}_3$ written in the figures are those of normal vibrations of adsorbed atom, which are assumed to be doubled for adsorbed molecule.

The general features of $F_0(E_0^{H_2})$ illustrated by Fig. 5 and 6 are similar to those of $F_0(E_0^{H})$ shown in Figs. 2 and 4 respectively, although the segment at

*) Eqs. (26. a), (27) and (28) limits ω to a value greater than that for $\tilde{\nu} = 275\ \mathrm{cm}^{-1}$ given in Table 2.

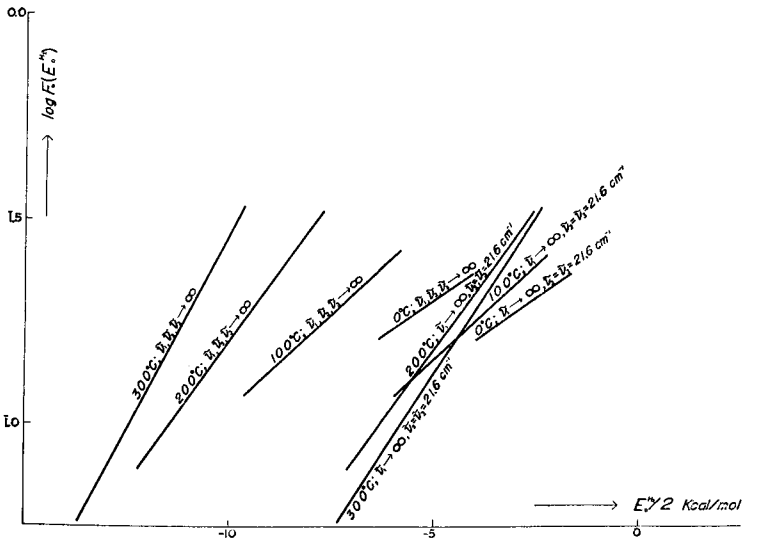

Fig. 5. Distribution functions. Molecular adsorption of H_2 on Ni. 0°, 100°, 200° and 300°C.

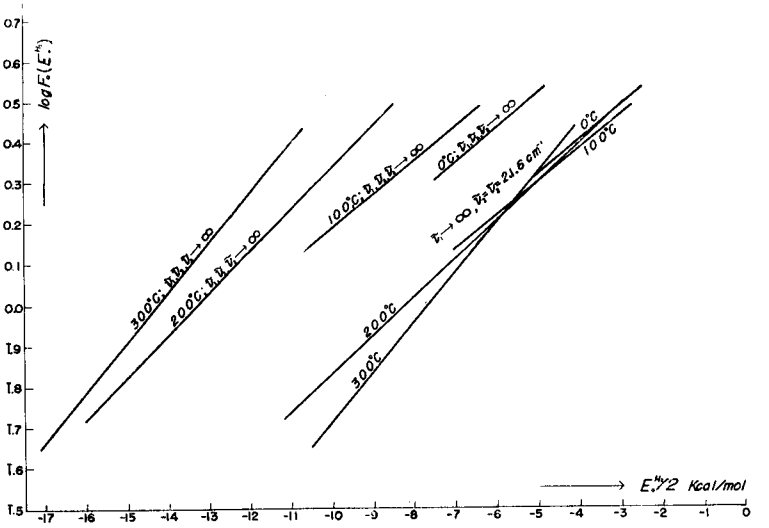

Fig. 6. Distribution functions. Molecular adsorption of H_2 on W. 0°, 100°, 200° and 300°C.

different temperatures deviate from each other somewhat worse than those of $F_0(E_0^H)$, for the depression $\log(\sin 2\pi c/\sin \pi c)$ increases with decrease of c, *i.e.* of temperature according to Table 1. It follows that $\tilde{\nu}$ must be further reduced in order that the segment at higher temperature catches that at lower temperature by the rightward shift associated with the decrease of $\tilde{\nu}$. In particular, the segment at 300°C of nickel does not yet catch that at 0°C for $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$ in this case as seen in Fig. 5, whereas it does just by the left end of the latter for the same value of $\tilde{\nu}$ in the case of atomic adsorption as seen in Fig. 2. We see besides in Fig. 4 that the segment of tungsten at 300°C just passes over, with decrease of $\tilde{\nu}$, that at 0°C rightwards for $\tilde{\nu}=21.6\,\mathrm{cm}^{-1}$ in the case of atomic adsorption, whereas the segment at 300°C just catches that at 0°C from left at the same $\tilde{\nu}$ in the case of molecular adsorption as seen in Fig. 6. The "microwave" frequencies must in consequence be still reduced, hence the difficulty associated is still worse.

We have based the above argument on the assumption that the normal frequencies of adsorbed hydrogen atom are just doubled in this case of molecular adsorption or that the two of the six normal vibrations of adsorbed molecule are so stiff that they contribute practically nothing to the term $RT\ln q_0^{H_2}$ of (29.E), whereas other four of the same wave number are soft enough to vary $E_0^{H_2}$ considerably from E^{H_2}. It might be reasonable alternatively to assume in this case, that there exist three soft vibrations besides three stiff ones inclusive of the valence vibration of the two hydrogen atoms. If then, the frequency of the three soft vibrations must still be smaller than in the case of four soft ones at the intersection of segments at higher and lower temperatures as seen from (29.q) and (30). This conclusion conflicts with the premise of localized adsorption still worse than in the case of the four soft vibrations.

We might go too far in working out the frequencies of normal vibrations for a quantitative description of the situation without any reliable model existing; it would, however, be safely concluded that the alternative assumption of molecular adsorption brings no relief to the heterogeneous model so far disproved.

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Appendix

Derivation of (13) and (14)

Eq. (1) is written according to (2) as

$$v=\int_{-\infty}^{+\infty}\frac{F(E)}{1+\exp\left(\frac{E-\mu}{RT}\right)}dE$$

or by integration by parts as

$$v=\frac{\Phi(E)}{1+\exp\left(\frac{E-\mu}{RT}\right)}\Bigg|_{-\infty}^{\infty}+\frac{1}{RT}\int_{-\infty}^{+\infty}\Phi(E)\frac{\exp\left(\frac{E-\mu}{RT}\right)}{\left\{1+\exp\left(\frac{E-\mu}{RT}\right)\right\}^{2}}dE, \quad \text{(i. a)}$$

where

$$\Phi(E)=\int_{-\infty}^{E}F(E)dE. \quad \text{(i. b)}$$

We will assume that $F(E)$ is such a function as to make the first term of (i. a) vanish. Writting

$$x=\frac{E-\mu}{RT}, \quad \text{(ii)}$$

we have from (i. a)

$$v=\int_{-\infty}^{+\infty}\frac{\Phi(E)dx}{(1+e^{x})(1+e^{-x})}. \quad \text{(iii)}$$

Expanding $\Phi(E)$ around $E=\mu$, as

$$\Phi=\sum_{n=0}^{\infty}\frac{(E-\mu)^{n}}{n!}\left(\frac{d^{n}\Phi}{dE^{n}}\right)_{E=\mu},$$

we have from (iii) with reference to (ii)

$$v=\sum_{n=0}^{\infty}\frac{(RT)^{n}}{n!}\left(\frac{d^{n}\Phi}{dE^{n}}\right)_{E=\mu}\int_{-\infty}^{+\infty}\frac{x^{n}dx}{(1+e^{x})(1+e^{-x})}. \quad \text{(iv)}$$

The integral in the above equation is known as[21]

$$\left.\begin{aligned}&\int_{-\infty}^{+\infty}\frac{x^{n}dx}{(1+e^{x})(1+e^{-x})}=0, && n=2m+1,\\ &\text{and}\\ &\int_{-\infty}^{+\infty}\frac{x^{n}dx}{(1+e^{x})(1+e^{-x})}=2(n!)\beta(n), && n=2m,\end{aligned}\right\} \quad \text{(v)}$$

where

$$\beta(2m)=\sum_{j=1}^{\infty}\frac{(-1)^{j+1}}{j^{2m}}$$

and m is positive integer. The $\beta(2m)$ is expressed in terms of BERNOULLI's number B_m as

$$\beta(2m)=\frac{(2^{2m-1}-1)\pi^{2m}}{(2m)!}B_m\,. \tag{vi}$$

We have now from (iv), (v) and (vi)

$$v=\Phi_{E=\mu}+2\sum_{m=1}^{\infty}\frac{(\pi RT)^{2m}}{(2m)!}(2^{2m-1}-1)B_m\left(\frac{d^{2m}\Phi}{dE^{2m}}\right)_{E=\mu}.$$

Eq. (13) is obtained from the above equation with reference to (i. b).

Eq. (14) is now derived as follows. Differentiating (13) with respect to μ, we have

$$\frac{dv}{d\mu}=F(E)_{E=\mu}+2\sum_{m=1}^{\infty}\frac{(\pi RT)^{2m}}{(2m)!}(2^{2m-1}-1)B_m\left\{\frac{d^{2m}F(E)}{dE^{2m}}\right\}_{E=\mu} \tag{vii}$$

Let the particular solution of (vii) be

$$F(E)_{E=\mu}=\bar{k}\frac{dv}{d\mu}\,, \tag{viii}$$

where $\bar{k}$ is constant, hence

$$\left\{\frac{d^{2m}F(E)}{dE^{2m}}\right\}_{E=\mu}=\bar{k}\frac{d^{2m+1}v}{d\mu^{2m+1}}\,. \tag{ix}$$

The chemical potential μ is expressed for the case of molecular or atomic adsorption respectively as

$$\mu=\mu_G \quad \text{or} \quad 2\mu=\mu_G \tag{x. a), (x. b)}$$

in accordance with (5) or (9). We have from (3), (4) and (x. a) or (x. b)

$$\frac{dv}{d\mu}=\frac{cv}{RT} \quad \text{or} \quad \frac{dv}{d\mu}=\frac{2cv}{RT}\,, \tag{xi. a), (xi. b)}$$

hence

$$\frac{d^{2m+1}v}{d\mu^{2m+1}}=\left(\frac{c}{RT}\right)^{2m}\frac{dv}{d\mu} \quad \text{or} \quad \frac{d^{2m+1}v}{d\mu^{2m+1}}=\left(\frac{2c}{RT}\right)^{2m}\frac{dv}{d\mu}\,, \tag{xii. a), (xii. b)}$$

which gives on substitution into (ix)

$$\left\{\frac{d^{2m}F(E)}{dE^{2m}}\right\}_{E=\mu}=\bar{k}\left(\frac{c}{RT}\right)^{2m}\frac{dv}{d\mu} \tag{xiii. a)}$$

or

$$\left\{\frac{d^{2m}F(E)}{dE^{2m}}\right\}_{E=\mu} = \bar{k}\left(\frac{2c}{RT}\right)^{2m}\frac{dv}{d\mu} \qquad \text{(xiii. b)}$$

respectively. Substituting $F(E)_{E=\mu}$ from (viii) and $\{d^{2m}F(E)/dE^{2m}\}_{E=\mu}$ from (xiii. a) or (xiii. b) respectively into (vii), we have, for $dv/d\mu \neq 0$

$$\bar{k} = \left\{1+2\sum_{m=1}^{\infty}\frac{(\pi c)^{2m}}{(2m)!}(2^{2m-1}-1)\,B_m\right\}^{-1} \qquad \text{(xiv. a)}$$

or

$$\bar{k} = \left\{1+2\sum_{m=1}^{\infty}\frac{(2\pi c)^{2m}}{(2m)!}(2^{2m-1}-1)\,B_m\right\}^{-1} \qquad \text{(xiv. b)}$$

respectively in the case of molecular or atomic adsorption. The contents of the parentheses { } of (xiv.a) or (xiv.b) happen to be the expansion of $\frac{\pi c}{\sin \pi c}$ or $\frac{2\pi c}{\sin 2\pi c}$ respectively*), so that

$$\bar{k} = \frac{\sin \pi c}{\pi c} \quad \text{or} \quad \bar{k} = \frac{\sin 2\pi c}{2\pi c}\,. \qquad \text{(xv. a), (xv. b)}$$

Eq. (xv.a) or (xv.b) leads, according to (viii), (15) and (xi.a) or (xi.b), respectively to (14.a) or (14.b).

Solution (14.a) or (14.b) of (vii) must be unique in the respective case of (x.a) or (x.b), since it reproduces the unique solution (8) of (7) or (12) of (11) obtained according to the theory of STIELTJES transform. We see on the other hand from (14) that the first term of (i.a) actually vanishes as assumed, inasmuch as $0<2c<1$ as seen in Table 1.

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