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THEORY OF MULTILAYER ADSORPTION—METHOD OF SURFACE AREA DETERMINATION

By

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Summary

Multilayer adsorption on solid adsorbents was statistical mechanically formulated taking into account of lateral attractions between adsorbate molecules in extension of the similar treatment of condensed state of adsorbate in the foregoing paper.¹⁾ The theory was first developed with regard to an immobile adsorption on localized adsorption sites and subsequently generalized to a mobile adsorption on a flat, homogeneous surface.

Followings were concluded for a layer of adsorbate assumed to be formed either directly on the surface of solid adsorbent or otherwise exclusively above a completed layer. In case where the Boltzmann factor, ξ , of attractive potential between any pair of adsorbate molecules in contact with each other lies below 2.48, the layer of adsorbate is a homogeneous two-dimensional phase, whose covered fraction increases monotonously with increase of the concentration of adsorbate molecules in gas phase in equilibrium with the two-dimensional phase. Even in case where $\xi \geq 2.48$, there appears a single two-dimensional phase, as molecules in gas phase is rare enough. The covered fraction of the single two-dimensional phase increases with increase of concentration of the molecules in gas phase until it attains a certain definite value $\theta_{n,I}$, when a denser two-dimensional phase of covered fraction, $\theta_{n,II}$, begins to coexist with the former. The covered fractions both of the two-dimensional phases remain respectively constant, so far as they coexist; the total amount of adsorption increases with increase of the area covered by the denser two-dimensional phase at the cost of that covered by the sparser one, while the equilibrium concentration of molecules in gas phase keeps sharply constant throughout the coexistence of the two-dimensional phases. The adsorbed amount is thus so far increased that the whole surface of adsorbent is covered by the denser two-dimensional phase alone. The adsorbed amount increases further with increase of the covered fraction of the single, two-dimensional phase beyond $\theta_{n,II}$ along with increase of the equilibrium concentration of molecules in gas phase.

The $\theta_{n,I}$ and $\theta_{n,II}$ are respectively unique, universal functions of ξ and tend respectively to zero and unity with increase of ξ , although the equilibrium concentration of molecules in gas phase depends, in general, on the potential of adsorbed molecule and temperature.

On the basis of the above development a method is advanced for area measurement of flat, homogeneous surfaces of solid adsorbents.

1. Introduction

Equilibrium of molecules in gas phase and its liquid condensation has been statistical mechanically investigated in the foregoing paper¹⁾ preparatory to the present work on the theory of multilayer adsorption; the process of condensation has been treated as a piling up of layers of molecules adsorbed on the surface of its own bulk liquid allowing for lateral attractions, *i. e.* those between neighbouring adsorbed molecules in the same layer. It has thus been concluded that the "adsorbate" forms two coexistent two-dimensional phases on the surface of "adsorbent" under a certain condition.

On the basis of the above conclusion followings have been shown in the present work on the adsorption by an adsorbent of primary sense, *i. e.* a solid phase of substance different from the adsorbate. There exists a single two-dimensional phase on the surface of adsorbent, insofar as the concentration of molecules in gas phase is sparse enough. There arises two different cases as the concentration of molecules in gas phase is increased according as the Boltzmann factor, ξ , of attractive potential of a pair of molecules, with their spherical models in contact with each other, lies below 2.48 or not. In the former case the covered fraction of a single two-dimensional phase existing increases monotonously with increase of the concentration of molecules in gas phase. In the latter case the covered fraction, θ_n , of a single two-dimensional phase increases as far as $\theta_{n,I}$, when there appears the second two-dimensional phase of a higher covered fraction, $\theta_{n,II}$. The equilibrium between molecules in gas phase and both the two-dimensional phases is characterized by a sharply defined concentration of the former and such covered fractions of the latter; the total amount of adsorbate varies with the relative expanses of the two-dimensional phases. The equilibria in these cases are statistical mechanically investigated, on which basis an experimental method of surface area determination of solid adsorbents is advanced assuming a simple pattern of potential of adsorbed molecule, *e. g.* that postulated in the BET method.

We have called in the foregoing paper¹⁾ the bulk liquid of adsorbate metaphorically an adsorbent, whereas in the present paper the term adsorbent is reserved with its primary sense unless otherwise stated, *i. e.* with a solid adsorbent of substance different from the adsorbate. The adsorbate is taken to be one of pure rare gases. Bulk liquid condensation of the adsorbate molecules is called simply a liquid and adsorbate molecule a molecule and every treatment is referred to a constant temperature. Equations, Tables, Figures and Sections in the foregoing paper are denoted with F attached to their notations as Eq. (1.a.F), Table 1.F, Fig. 1.F and 3.3.F in distinction

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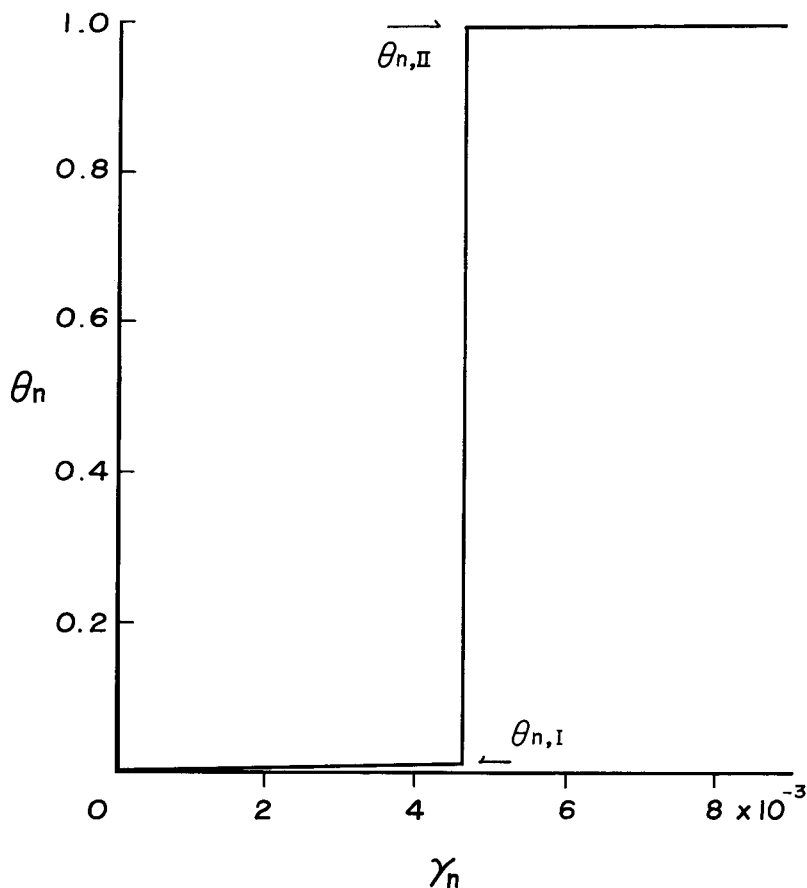


Fig. 1. Universal function $\theta_n = \theta_n(i_n)$ for $\xi = 6$.

from those in the present paper.

2. Model of adsorption

Theory of adsorption is developed first with the model specified below, which is subsequently generalized in 6.

a) The potential of interaction among molecules is attractive, additive and significant only for those pairs with their spherical models in contact with each other.

b) Sites of adsorption are physically identical and arrayed in a (111)-lattice, whose nearest neighbours are apart from each other by the diameter of the spherical model of molecules.

c) The q_0 defined in 3.1.1.F is valid and has the same magnitude for the same adsorbate molecule, as regards the adsorption site specified in b).

d) The first layer, when completed, provides sites of adsorption of second layer as b), 2.F and so on. The formation of a layer requires the completion of the layer underlying it.

3. Statistical mechanical functions

We have introduced in the foregoing paper¹⁾ a function, γ_0 , in the statistical mechanical treatment of the condensation of adsorbate molecules as consecutive formation of adsorption layers one upon another. A function, γ_n , now defined as below with reference to the n -th layer of adsorbate including γ_0 as its special case on the surface of its own liquid.

3.1. γ_1 .

Let \mathfrak{A} be the assembly in equilibrium consisting of the adsorbent, molecules adsorbed on it and molecules in gas phase. The γ_1 is defined as the factor of multiplication of the partition function of \mathfrak{A} due to transfer of a molecule from gas phase to a definite, preliminarily evacuated adsorption site on the adsorbent apart from interaction with other molecules; γ_1 is expressed according to c), 2., similarly to Eq. (1.b.F), as

$$\gamma_1 = q_0 \zeta_1 / p_G, \quad (1. a)$$

where ζ_1 is the Boltzmann factor of the potential, $\Delta\epsilon_1 + \epsilon_0$, of adsorbed molecule on the site apart from interactions with other molecules, *i. e.*

$$\zeta_1 = \exp \left\{ -(\Delta\epsilon_1 + \epsilon_0) / kT \right\}; \quad (1. b)$$

$\Delta\epsilon_1$ is the excess, due to the adsorbent, of the potential over ϵ_0 defined in 2.F. The q_0/p_G in Eq. (1.a) is expressed according to Eqs. (12.F) and (20.F) as

$$q_0/p_G = v_L N. \quad (2)$$

3.2. γ_n .

The $\gamma_{n(>1)}$ is introduced similarly to γ_1 , as

$$\gamma_{n(>1)} = q_0 \zeta_{n(>1)} / p_G, \quad \zeta_{n(>1)} = \exp \left\{ -(\Delta\epsilon_{n(>1)} + \epsilon_0) / kT \right\}, \quad (3. a), (3. b)$$

where $\Delta\epsilon_{n(>1)}$ is the potential of a molecule of $n(>1)$ -th layer due to the adsorbent, hence $\Delta\epsilon_{n(>1)} + \epsilon_0$ its total potential apart from the lateral interactions.

Eqs. (1.b.F) and (2.b.F) are transcribed, on the other hand, as

$$\gamma_0 = q_0 \zeta_0 / p_G, \quad \zeta_0 = \exp(-\epsilon_0 / kT). \quad (4. a), (4. b)$$

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Both $\Delta\varepsilon_1 + \varepsilon_0$ and $\Delta\varepsilon_{n(>1)} + \varepsilon_0$ are the total potential of an adsorbed molecule due to the underlying substance in the respective case, while $\Delta\varepsilon_n$ is the excess over ε_0 of the potential due to the adsorbent, which alone underlies the first layer; with this definition of $\Delta\varepsilon_1$ and the convention, $\Delta\varepsilon_0 = 0$, Eqs. (1), (3) and (4), inclusive of Eqs. (1.b.F) and (2.b.F), are formally incorporated in the form

$$\gamma_n = q_0 \zeta_n / p_G, \quad \zeta_n = \exp \left\{ -(\Delta\varepsilon_n + \varepsilon_0) / kT \right\}, \quad n = 0, 1, 2, \dots \quad (5. a), (5. b)$$

4. Isotherm of individual layer

Investigations are now made on the basis of the model specified in 2. into the adsorption isotherm of individual layer, *i. e.* the covered fraction of n -th layer, θ_n , as a function of γ_n .

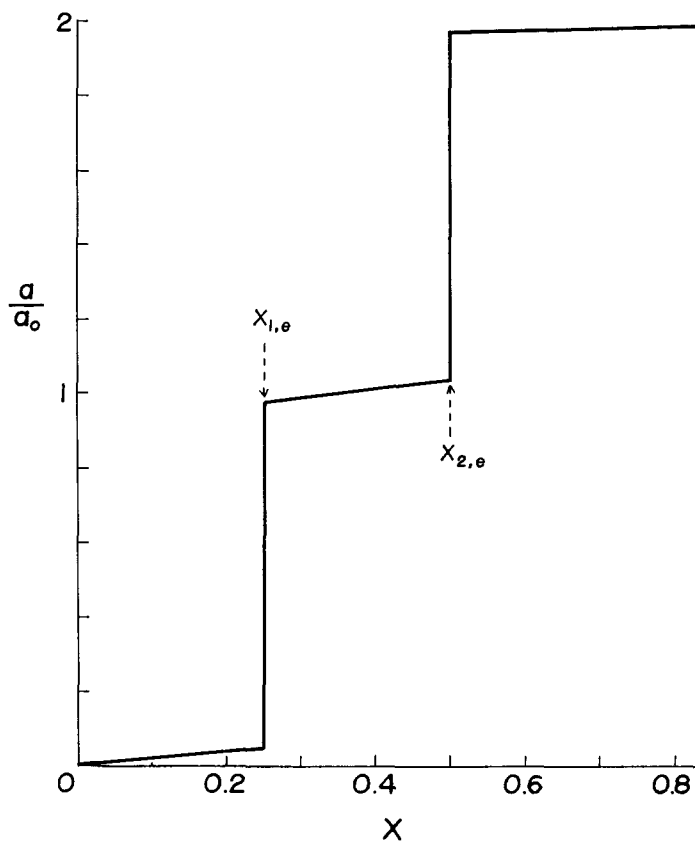


Fig. 2. Overall amount of adsorption *vs.* x , where $\Delta\varepsilon_1 < \Delta\varepsilon_2 < 0$, $\Delta\varepsilon_{n(>2)} = 0$, and $\xi = 4$.

4.1. Universal function, $\theta_n = \theta_n(\gamma_n)$.

Reasoning similarly to 3.F on the base of the model specified in 2., we arrive at a set of simultaneous equations for θ_n , γ_n and ξ , which is derived from the set of Eqs. (1.a.F), (3.F), (4.F) and (6.F) just by replacing θ_0 and γ_0 there by θ_n and γ_n respectively. It follows that the solution, $\theta_n = \theta_n(\gamma_n)$, is derived from $\theta_0 = \theta_0(\gamma_0)$ shown in Fig. 2.F just by replacing θ_0 and γ_0 with θ_n and γ_n respectively, hence that inferences from $\theta_0 = \theta_0(\gamma_0)$ applies universally to $\theta_n = \theta_n(\gamma_n)$.

It has been shown in 3.2.F with isotherms for $\xi \geq 2.48$ that there existed two coexistent two-dimensional phases at a certain value, $\gamma_{0,e}$, of γ_0 , hence the similar coexistence at a value, $\gamma_{n,e}$, of γ_n , which is identical function of ξ with $\gamma_{0,e}$ and covered fractions, $\theta_{n,I}$ and $\theta_{n,II}$, of the sparser and denser coexistent two-dimensional phases, which are identical functions of ξ with $\theta_{0,I}$ and $\theta_{0,II}$ respectively.

Fig. 1 is the transfer of the curve for $\xi = 6$ in Fig. 2.F tracing particularly the horizontal part shown there by a broken line, with θ_n and γ_n respectively substituted formally for θ_0 and γ_0 . The θ_n in Fig. 1 thus rises slowly with increase of γ_n up to $\gamma_{n,e}$, where θ_n increases vertically from $\theta_{n,I}$ to $\theta_{n,II}$, tending slowly to unity beyond $\theta_{n,II}$ with increase of γ_n .

Previous conclusions on θ_0 , γ_0 , $\theta_{0,I}$ and $\theta_{0,II}$ are thus transcribed in general terms as follows.

- a) Function, $\theta_n(\gamma_n)$, tends to be accurate as θ_n approaches unity.*)
- b) The $\theta_{n,I}$ and $\theta_{n,II}$ tend to zero and unity respectively with increase of ξ .**)

4.2. $\theta_n = \theta_n(x)$.

Universal function $\theta_n = \theta_n(\gamma_n)$ is transformed into a function of

$$x = N/N_{0,e}, \quad (6. a)$$

which gives θ_n in terms of properties of the adsorbate and the layer in question, where $N_{0,e}$ is the concentration of saturated vapour over the liquid. We have from Eqs. (2) and (5.a)

$$\gamma_n = v_L \zeta_n N, \quad (6. b)$$

hence

$$\gamma_n/x = v_L \zeta_n N_{0,e}. \quad (6. c)$$

The right-hand side of Eq. (6.c) is the proportional constant of γ_n to x , which is calculable from the values of v_L , ξ given in Table 1.F and ζ_n derived from

*) Generalization of a conclusion in 4.1.F.

***) Generalization of a conclusion in 3.2.F.

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the given pattern of $\Delta\varepsilon_n$ by Eq. (5.b) with reference to Eq. (2.b.F). We have thus $\theta_n = \theta_n(x)$ from the universal function, $\theta_n = \theta_n(\gamma_n)$.

Let $\gamma_{n,e}$ and $N_{n,e}$ be the particular values of γ_n and N respectively under the coexistence of the two-dimensional phases of n-th layer; we have from Eq. (6.b)

$$\gamma_{n,e} = v_L \zeta_n N_{n,e}; \quad (7.a)$$

$N_{0,e}$ is the special case of $N_{n,e}$, where the adsorbent is liquid,¹⁾ while $\gamma_{n,e}$ is of a universal value among n according to 4.1.. Defining $x_{n,e}$ in accordance with Eq. (6.a) as

$$x_{n,e} = N_{n,e}/N_{0,e}, \quad (7.b)$$

we have, eliminating $N_{n,e}$ from Eqs. (7.a) and (7.b),

$$\gamma_{n,e} = v_L \zeta_n N_{0,e} x_{n,e}. \quad (7.c)$$

It follows from Eq. (7.c) with reference to Eq. (5.b) that

$$\gamma_{0,e} = v_L \exp\{-(\Delta\varepsilon_0 + \varepsilon_0)/kT\} \cdot N_{0,e} x_{0,e} = v_L \exp\{-(\Delta\varepsilon_n + \varepsilon_0)/kT\} \cdot N_{0,e} x_{n,e},$$

hence

$$x_{n,e} \exp(-\Delta\varepsilon_n/kT) = 1, \quad n=1, 2, \dots, \quad (8)$$

noting that $x_{0,e}=1$ by Eq. (7.b) and $\Delta\varepsilon_0=0$ by 3.2..

4.3. Completion of a layer.

Completion of n-th layer is defined in terms of θ_n as $\theta_n \geq \theta_{n,II}$. We see from Fig. 1 that the necessary condition of completion of a layer is that $\gamma_n > \gamma_{n,e}$ or by Eqs. (6.b) and (7.a), $N > N_{n,e}$, hence according to Eqs. (6.a) and (7.b)

$$x > x_{n,e}. \quad (9.a)$$

The similar condition has to be satisfied by all layers underlying the n-th one for it to exist according to d), 2., hence

$$x > x_{m,e}, \quad m=1, \dots, n \quad (9.b)$$

is the necessary and sufficient condition for the completion of n-th layer.

5. Overall amount of adsorption

Overall amount of adsorption is obtained by summing up isotherms of all layers inclusive of the uppermost one which may not be completed.

The completion of a layer is first investigated with different patterns of $\Delta\varepsilon_n$ in accordance with 4.3..

5.1. $\Delta\varepsilon_1 < 0$ and $\Delta\varepsilon_{n(>1)} = 0$.

We have from the superscribed premise according to Eq. (8)

$$x_{1,e} < 1, \quad x_{n(>1),e} = 1. \quad (10. a), (10. b)$$

For x lying between $x_{1,e}$ and unity the first layer is completed according to Ineqs. (9.a) and (10.a), but none of upper layers is. The isotherm of the first layer is derived from Fig. 1 with reference to Eq. (6.c), while that of the uncompleted second layer is given by Eq. (13.F), since the completed first layer provides sites of adsorption in accordance with **d**), **2.**

As x exceeds unity, the second layer is completed by Ineq. (9.b) and Eq. (10.b), but the branch of the isotherm which runs asymptotically to the horizontal, $\theta_n = 1$, in Fig. 1 does not appear, inasmuch as the upper layers pile up unlimitedly under the latter condition.

5.2. $\Delta\varepsilon_1 < 0$ and $\Delta\varepsilon_{n(>1)} < \Delta\varepsilon_1$.

It follows from the premise according to Eq. (8) that $x_{1,e} > 1$ and $x_{n(>1),e} < x_{1,e}$. The first layer is thus not formed, much less the upper layers by **d**), **2.** until x exceeds $x_{1,e}$. The gas phase is supersaturated for x lying between 1 and $x_{1,e}$. Bulk condensation occurs as soon as x exceeds $x_{1,e}$ as in the case of **5.1.**

5.3. $\Delta\varepsilon_k > \Delta\varepsilon_{n(<k)}$.

We have then by Eq. (8)

$$x_{k,e} > x_{n(<k),e}, \quad (11)$$

which states, according to **4.3.**, that all layers up to $k-1$ -th one are completed before x exceeds $x_{k,e}$. This is the case whether $\Delta\varepsilon_k$ is positive or negative; if positive, supersaturation occurs for x lying between unity and $x_{k,e}$ and, if $\Delta\varepsilon_{n(>k)} = 0$ in addition, a bulk condensation occurs as soon as x exceeds $x_{k,e}$ similarly to the case of **5.2.**

5.4. $\Delta\varepsilon_{k_{l+1}} > \Delta\varepsilon_{k_l} > \Delta\varepsilon_{m_l}$, $m_l = k_l + 1, \dots, k_{l+1} - 1$.

We have according to Eq. (8)

$$x_{k_{l+1},e} > x_{k_l,e} > x_{m_l,e}, \quad (12)$$

which states that from k_l -th to $k_{l+1}-1$ -th layers are completed as soon as x exceeds $x_{k_l,e}$.

5.5. $\Delta\varepsilon_{k_0} < \Delta\varepsilon_{k_1} < \dots < \Delta\varepsilon_{k_l} < \dots$, $k_0 < k_1 < \dots < k_l$.

Where $k_0 \equiv 1$ and there exists a set of $\Delta\varepsilon_{m_l}$ for every pair of ε_{k_l} and $\varepsilon_{k_{l+1}}$ in accordance with the premise of **5.4.**

It follows from the premise according to Eq. (8)

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$$x_{k_0,e} < x_{k_1,e} < \cdots < x_{k_l,e} < \cdots,$$

and that there exist, for every pair of $x_{k_l,e}$ and $x_{k_{l+1},e}$, $x_{m_l,e}$ -values which comply with Ineq. (12), hence according to 5.4. that from k_l -th to $k_{l+1}-1$ -th layers are completed as soon as x exceeds $x_{k_l,e}$; the adsorbed amount of thus increases stepwise with steady increase of x .

5.6. Overall amount of adsorption.

The overall amount of adsorption, $a(x)$, is the sum of $a_0\theta_n(x)$ over n , where a_0 is the amount of molecules in a closest packed monolayer. Fig. 2 exemplifies the construction of $a(x)$ in a simple case where $\Delta\varepsilon_1 < \Delta\varepsilon_2 < 0$ and $\Delta\varepsilon_{n(>2)} = 0$. The $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ in the latter inequality determine $x_{1,e}$ and $x_{2,e}$ respectively according to Eq. (8), which are marked on the abscissa in accordance with the premise.

6. Investigation of conclusions

Practically exact conclusions coherent to the model specified in 2. are obtained, as seen with reference to 4.2.F and 4.1., in case where separation of adsorbate takes place and $\theta_{n,I}$ and $\theta_{n,II}$ are respectively close to zero and unity.

We consider now an alternative case of mobile adsorption on a homogeneous, flat surface of adsorbent. The assembly to be dealt with consists of the adsorbent, molecules adsorbed on it and molecules of the same kind in gas phase in equilibrium with adsorbed one. The covered fraction, θ_1 , is defined in this case as the fraction of the number of molecules adsorbed over that of closest packed monolayer. The θ_1 is statistical mechanically formulated in terms of partition functions of the assembly similarly to 3.F with special reference to a portion, Σ , on the surface of adsorbent, which is a regular hexagon circumscribed about six orthographs of molecules contacting with another orthograph at the center.

Consider first that the Σ is fixed on the surface. The seven orthographs thus fixed play the part of fixed sites in the immobile adsorption. We thus have equations similar to Eqs. (1.a.F), (3.F), (4.F) and (6.F), which decide θ_1 as a function of γ_1 with parameter ξ ; γ_1 here is the factor of multiplication of partition function of the assembly due to transfer of a molecule from gas phase to right above a definite, clear orthograph apart from interactions with other adsorbate molecules.

The Σ is now shifted and turned on the surface to allow for the continuously variant positions of orthographs fixed to Σ in accordance with the premise of mobile adsorption. The appropriate partition function corresponding

to $\Omega \mathcal{A}_{\Sigma(0)}$ cancels by its manifold created by the shift and turn in final equations corresponding to Eqs. (4.F) and (6.F), which decide $\theta_1 = \theta_1(\gamma_1)$; no difference thus is eventually made by taking account of the manifold due to the mobile adsorption.

The above procedure admits, however, only the relative positions of sites of either single class mentioned in a), 4.1.F. The actual relative position may appreciably deviate from the latter qualitatively similarly to the case of immobile adsorption but tends to conform compulsorily with those admitted along with the increase of coverage as in the case of immobile adsorption referred to in 4.1.F and 4.2.F.

The above procedure implies another approximation similar to b), 4.1.F, but inaccuracies hence derived vanishes similarly as θ_1 approaches unity.

It is hence concluded that $\theta_1 = \theta_1(\gamma_1)$ thus derived is practically accurate even in the case of mobile adsorption, for sufficiently large ξ , where $\theta_{n,I}$ and $\theta_{n,II}$ are close enough to zero and unity respectively.

The alternative assumption of mobile adsorption in the first layer thus makes no difference either in the adsorption of the first layer or of upper layers for sufficiently large ξ .

7. Determination of surface area

A method of surface area determination of adsorbents is formulated on the basis of the foregoing development assuming that the surface is homogeneous and flat and the potential of molecules is that premised in 5.1. or in the BET method.

The covered fraction of a layer on completion approaches unity with increase of ξ according to b), 4.1. and 4.3.. The predominant terms in the coefficient of $\Omega \mathcal{A}_{\Sigma(0)}$ in Eqs. (1.a.F) and (3.F) are then those relevant to the highest occupation of Σ , *i. e.* $\gamma_0^6 \gamma^6 \xi^6$ in Eq. (1.a.F) and $\gamma_0^7 \gamma^6 \xi^{12}$ in Eq. (3.F). We hence have according to Eqs. (1.a.F), (3.F) and (4.F)

$$1 - \theta_0 = \theta_0 / \gamma_0 \xi^6$$

or by dint of the universality of function $\theta_n = \theta_n(\gamma_n)$ among n as shown in 4.1.

$$1 - \theta_1 = \theta_1 / \gamma_1 \xi^6$$

or substituting γ_1 from Eq. (6.c) into the above equation

$$\theta_1 = k_1 x / (k_1 x + 1), \quad (13. \theta)$$

where

$$k_1 = v_L \zeta_1 \xi^6 N_{0,e};$$

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ζ_1 is given by Eqs. (5.b) and (2.b.F) as $\zeta_1 = \xi^3 \exp(-\Delta\epsilon_1/kT)$, hence

$$k_1 = v_1 \xi^9 N_{0,e} \exp(-\Delta\epsilon_1/kT), \quad (13.k)$$

which is simplified according to Eq. (22.v_L.F) as

$$k_1 = \xi^3 \exp(-\Delta\epsilon_1/kT). \quad (13.k')$$

The $\theta_2 = N_A/N_L$ is given by Eq. (13.F) as $\theta_2 = 2q_0 \xi^3 N h^3 / (2\pi M k T)^{3/2}$ or substituting N from Eq. (6.a) and q_0 from Eq. (20.F)

$$\theta_2 = k_2 x, \quad (14.\theta)$$

where

$$k_2 = 2v_L N_{0,e} \xi^3, \quad (14.k)$$

or by Eq. (22.v_L.F)

$$k_2 = 2/\xi^3; \quad (14.k')$$

k_2 is numerically determined with special reference to krypton at 89.9°K, where $\xi = 6$,* as

$$k_2 = 9.26 \times 10^{-3}. \quad (15.a)$$

The k_1 is given, on the other hand, by Eq. (13.k') as

$$k_1 = 2.16 \times 10^2 \exp(-\Delta\epsilon_1/kT). \quad (15.b)$$

There occurs no adsorption in the third and upper layers on account of the uncompleted second layer according to **d**), **2.**, hence the overall amount, a , of adsorption is given as

$$a = a_0(\theta_1 + \theta_2),$$

where a_0 is the value of a for $\theta_1 + \theta_2 = 1$ or the amount of molecules in a closest packed monolayer, which indicates the surface area of adsorbent in question. Substitution of θ_1 and θ_2 from Eqs. (13. θ) and (14. θ) gives

$$a = a_0 \left(\frac{k_1 x}{k_1 x + 1} + k_2 x \right), \quad (16.a)$$

which holds for $x > x_{1,0}$ or $\theta_1 > \theta_{1,II}$ according to **d**), **2.**

The first term in the parentheses of Eq. (16.a) predominates over the second one, inasmuch as the ratio, $k_2(x+1/k_1)$, of the second to the first term is exceedingly smaller than unity throughout, as follows from Eqs. (15) and the premise, $\Delta\epsilon_1 < 0$. The same term or θ_1 by Eq. (13. θ) is now accurate

*) The ξ of krypton attains to 6.00 according to Eq. (2.b.F) and Table 1.F at the absolute temperature, $T = T_B \times \log 3.83 / \log 6.00 = 89.9^\circ\text{K}$.

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according to a), 4.1. when θ_1 approximates unity and is then accurately expanded into $1 - 1/k_1x$. Eq. (16.a) is thus written as

$$x(1 + k_2x) = 1/k_1 + ax/a_0, \quad (16. b)$$

i. e. as a linear relation between known quantities, $x(1 + k_2x)$ and ax , by which

TABLE 1. Suitable conditions of a_0 -determination

Adsorbate	Temperature °K	ξ	k_2	$\theta_{n,II}$	P mmHg*)
Ar	77.4 (Boiling pt. of N ₂)	4.48	2.22×10^{-3}	0.984	241
Ar	64.7	6.00	9.26×10^{-3}	0.994	33.3
Kr	89.9 (Boiling pt. of O ₂)	6.00	9.26×10^{-3}	0.994	36.9

*) Calculated vapour pressure of supercooled liquid at the specified temperature.

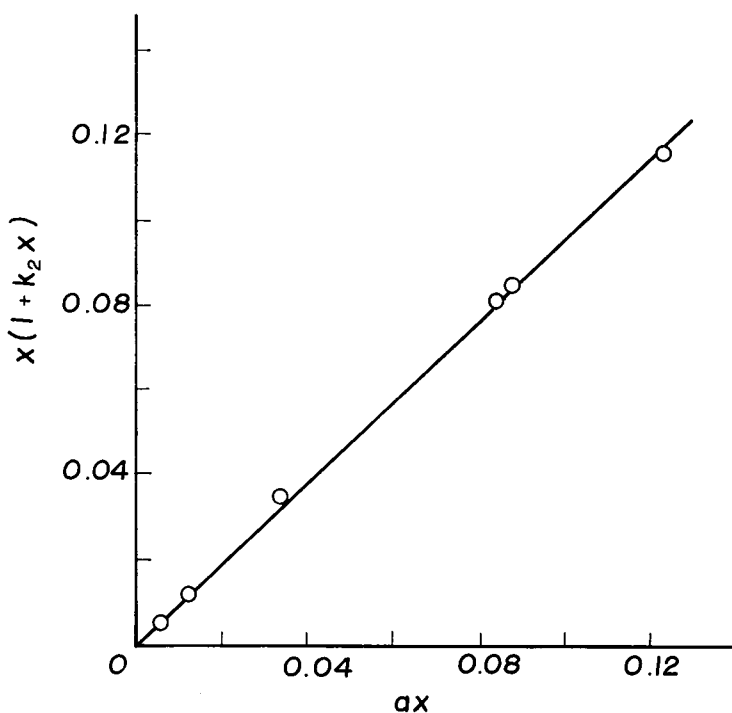


Fig. 3. Surface area determination by $x(1 + k_2x)$ vs. ax plots. $x = N/N_{0,e}$, where $N_{0,e}$ is the concentration of saturated vapour of supercooled liquid of krypton extrapolated from the boiling point at 77°K in terms of the heat of vaporization 2.158 kcal/mole. Fig. 3 shows the analysis of the adsorption isotherm, $a(x)$, derived from the observation of SINGLETON and HALSEY²⁾ on the adsorption of krypton on graphitized carbon black at 77°K.

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a_0 and k_1 are numerically determined by observation.

The lower bound to θ_1 on completion of the layer is $\theta_{1,II}$ according to 4.3. which increases with increase of ξ by b), 4.1.. Eq. (16.b) by which a_0 is determined is hence the more accurate, the greater ξ . The $\theta_{1,II}$ thus increases from 0.971 for $\xi=3.83$ of krypton at its boiling point to 0.994 for $\xi=6.00$ at 89.9°K, which temperature is approximately secured by liquid oxygen under one atmospheric pressure. This increase of ξ is, however, accompanied by the decrease of vapour pressure from ca. one atmosphere to 36.9 mmHg for supercooled liquid in terms of $\Delta H=2.158$ kcal/mole. A further depression of temperature to increase $\theta_{1,II}$ would make the $a(x)$ -measurement unhandy on account of decreased vapour pressure. Table 1 shows conditions of the $a(x)$ -measurement apparently suitable in this respect.

Fig. 3 exemplifies the surface area determination in accordance with Eq. (16.b). The data are taken from the adsorption isotherm of krypton on graphitized carbon black at 77°K by SINGLETON and HALSEY.²⁾ The a_0 is determined by the present method as shown in Fig. 3 to be 1.14 or 1.08 times as large as that obtained by the "point B" method or the "step height" method by the authors.²⁾ The x is determined in accordance with Eq. (6.a) assuming $N_{0,e}$ be the concentration of saturated vapour over supercooled liquid of krypton at the specified temperature. No difference is practically made, however, by an alternative assumption of $N_{0,e}$ to be that of saturated vapour over solid krypton along with the procedure of these authors.²⁾

References

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