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The Development of Methods for the Description of Adsorption Isotherms within the Framework of the Fundamental Postulates of Langmuir's Theory

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The review deals with the problem of the form of isotherms for adsorption on homogeneous and inhomogeneous surfaces with and without dissociation when the adsorbate molecule occupies a single elementary site on the surface or several such sites, for polymolecular adsorption, and for adsorption in the micropores.
The bibliography includes 74 references.

CONTENTS

I. Introduction of fundamental postulates 421
II. Adsorption isotherms on a homogeneous surface in the absence of interaction between the adsorbed molecules 422
III. Adsorption isotherms on inhomogeneous surfaces in the absence of interaction between the adsorbed molecules 425
IV. Adsorption isotherms on a homogeneous surface with interaction between the adsorbed species 427
V. Polymolecular adsorption isotherms on a homogeneous surface 429
VI. Polymolecular adsorption isotherms on inhomogeneous surfaces 431
VII. Isotherm for adsorption in micropores 432
VIII. Conclusion 432

I. INTRODUCTION OF FUNDAMENTAL POSTULATES

The equilibrium in adsorption can be characterised by specifying the adsorption isotherm:

$$v = f(p), \tag{1}$$

where v is the amount of adsorbed gas (or vapour) and p the equilibrium pressure, and the form of the function

$$Q = f_1(v), \tag{2}$$

where Q is the differential heat of adsorption.

Depending on the characteristics of the surface, the nature of the adsorbent, temperature, and pressure, the functions expressed by Eqns. (1) and (2) may be varied.

In the present review, adsorption is considered mainly within the framework of the adsorption theory the foundations of which were laid by Langmuir. However, initially we shall consider briefly the pre-Langmuir concepts concerning the nature of the phenomena at the interface between the solid and the gas or vapour. The first theoretical ideas about the adsorption of gases and vapours were put forward by Arrhenius in 1911 [1] and were somewhat later treated mathematically by Eucken [2]. Arrhenius began with the van der Waals hypothesis that there is no sharp phase transition between the liquid and its vapour and that there is a transitional layer the properties of which vary continuously from those of the liquid to those of the vapour on moving away from the surface of the liquid. Since the adsorbability sequence for various gases and vapours agrees with the condensability sequence, Arrhenius assumed that the adsorption forces are of the same type as molecular forces and hence are functionally related to the force constant in the van der Waals equation.

Developing this view, Eucken believed the transitional layer to be a miniature atmosphere whose molecules are retained near the surface under the influence of a potential ϵ, which is a function of the distance between the adsorbed molecule and the surface [2]:

$$\varepsilon = c/f(r), \tag{3}$$

where c is a constant which depends on the nature of the adsorbent and the adsorbate. In contrast to Eucken, Bakker [3] assumed that the molecules in the transitional layer attract one another with a force that decreases exponentially with increase of the distance between them.

Polanyi went further than other investigators in his development of Arrhenius's ideas, his first studies on this problem having been published in 1916. [4] He believed that the force field near the adsorbent should have the same properties as the gravitational field, i.e. it cannot be shielded, does not influence the interaction of the adsorbed molecules, and is independent of temperature, but, in contrast to the gravitational field, is specific. The degree of adsorption was calculated from the distribution of the potential, i.e. it was necessary to know the form of the relation $\epsilon = f(\varphi)$, which defines the volume of the space over the adsorbent surface in which the potential is greater then ϵ. In Polanyi's theory, this relation defines an infinite family of isotherms and permits the calculation of the degree of adsorption at any specified temperature. The nature of the $f(\varphi)$ curve, expressing the distribution of the potential, was determined from a single adsorption isotherm recorded below the critical temperature of the adsorbate. The required distribution was obtained as a result of the simultaneous solution of the equations

$$\varepsilon = RT \ln(p_0/p) \tag{4}$$

and

$$\varphi = v/d, \tag{5}$$

where p_0 is the vapour pressure at a temperature T and d the density of the adsorbed substance in the liquid state at the temperature T. Polanyi assumed that the forces of cohesion between the molecules are due to the fact that the latter are polarised in a specific manner.

Later London showed [5] that, when two particles are sufficiently close to one another, their electrons move in such a way that the states in which the electrons of both species are displaced in the same direction relative to

their nuclei are statistically preferable. This phenomenon is a result of the interaction of the instantaneous dipole moments, and is responsible for the presence of the cohesion forces.

The postulates constituting the basis of Polanyi's theory have been frequently criticised (see, for example, McBain[6]), and, although numerous experimental data are consistent with this theory, towards the beginning of the 1930's it was already widely believed that not only the adsorption of gases but also the adsorption of vapours (in the initial stage) must be described in terms of Langmuir's ideas and not those of Polanyi (see, for example, Dubinin[7]). On this basis of the physical concepts of Polanyi's theory, Zhukhovitskii[8] formulated in 1938 a theory of adsorption from real solutions and compared its conclusions with experimental data. Quantitative tests showed that the formulae of the potential theory conflict with experiment; for example, in order to explain the position of the adsorption maximum as a function of the concentration of carbon tetrachloride in benzene, it was necessary to assume an average adsorption potential of 85 000 cal, which is quite unrealistic for van der Waals forces. The predictions of the theory were not fulfilled even qualitatively. Thus the component for which the theory predicted negative adsorption underwent position adsorption from solutions which were dilute with respect to it. Zhukhovitskii's results[8] throw doubt on the physical picture of adsorption constituting the basis of Polanyi's theory.

The foundations of the modern adsorption theory were laid in 1916 by Langmuir[9], who assumed that, on each unit area of the crystal surface, there should be a definite number of sites capable of adsorbing gaseous molecules. More molecules can be adsorbed only as a result of the formation of additional molecular layers. The forces acting between two layers of adsorbed gas molecules must be much smaller than those acting between the surface layer of the crystal and the first layer of adsorbed molecules. The rate of evaporation from the second layer is usually much higher than from the first layer, so that the number of molecules in the second layer must be negligibly small. When a gas molecule collides with a section of the surface already coated by a layer of adsorbed molecules, it usually re-evaporates so rapidly that the phenomenon is indistinguishable from reflection. According to Langmuir, in the adsorption of vapours at pressures approaching the saturation vapour pressure there should be a tendency for the thickness of the adsorbed films to become greater than one monolayer.

Langmuir began with the postulate that the forces acting between the atoms of the crystal and those of the adsorbed substance are of the same type as the forces acting between the adjacent atoms of the crystal; the manifestation of these forces is a result of the chemical unsaturation of the surface atoms in the crystal. (A similar idea had been expressed somewhat earlier by Haber[10].) The residence time of the adsorbed molecules on the surface depends on the strength of the surface forces.

Langmuir considered quantitatively the following six cases of adsorption.

(1) The surface consists of elementary areas of the same kind (henceforth we shall refer to such a surface as homogeneous) and the gas is adsorbed in the form of molecules each of which occupies a single elementary site.

(2) The surface consists of more than one kind of elementary site and adsorption takes place as in case 1.

(3) Adsorption on an amorphous surface (henceforth such surfaces will be referred to as inhomogeneous).

(4) Adsorption on a homogeneous surface, but on each elementary site more than one adsorbed molecule may be retained.

(5) Adsorption with dissociation on a homogeneous surface.

(6) Deformation of adsorbed films on a homogeneous surface having a thickness greater than the value corresponding to one molecule.

The process leading to the formation of adsorbed films with a thickness greater than the value corresponding to one molecule is referred to as polymolecular adsorption, in contrast to monomolecular adsorption (cases 1–5), in which the thickness of the adsorbed layer does not exceed the value corresponding to one molecule.

The Langmuir isotherms are considered below and the progress in adsorption theory for the cases enumerated above is analysed. To facilitate the exposition, the different cases of adsorption have been grouped in a manner different from that used in Langmuir's study[11].

II. ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE IN THE ABSENCE OF INTERACTION BETWEEN THE ADSORBED MOLECULES

1. Each Adsorbate Molecule Occupies One Elementary Site on the Adsorbent Surface

In 1916[9] and then in 1918[11] Langmuir published a kinetic derivation of the equation of the isotherm for this simplest case. Suppose that θ_0 is the fraction of the free adsorbent surface, i.e. the ratio L/N, where N is a number of adsorbed molecules per cm^2 of the surface under the conditions of maximum adsorption (i.e. in this case the number of elementary sites per cm^2) and L the number of adsorbed molecules per cm^2 of the surface, θ_1 the fraction of the occupied surface ($\theta_1 = 1 - \theta_0$), and Z_0 the number of collisions of the adsorbate molecules with 1 cm^2 of the adsorbent surface per second, and, according to the kinetic theory of gases, we have

$$Z_0 = \frac{N_0 p}{\sqrt{2\pi MRT}} \tag{6}$$

(N_0 is the Avogadro number and M the molecule weight of the gas); if the pressure is expressed in mmHg, then

$$Z_0 = 3.52 \times 10^{22}\, p/\sqrt{MT}. \tag{7}$$

Suppose that α is the probability of adhesion, i.e. the ratio of the number of molecules adsorbing to the number of molecules colliding with the surface per unit time (on a completely free surface) and β is the rate of desorption of the adsorbed molecules from the fully coated surface.

We then have at equilibrium

$$(1 - \theta_1)\alpha Z_0 = \beta\theta_1, \tag{8}$$

whence

$$\theta_1 = \alpha Z_0/(\beta + \alpha Z_0). \tag{9}$$

If $\alpha/\beta = \sigma_1$, the Eqn. (9) transforms into

$$\theta_1 = \sigma_1 Z_0/(1 + \sigma_1 Z_0). \tag{10}$$

This is the required adsorption isotherm. Introducing the notation $ap = \sigma_1 Z_0$, where a is a constant, we have

$$\theta_1 = ap/(1 + ap). \tag{11}$$

Eqn.(11) can be formulated in the form of the equation of a rectangular hyperbola:

$$\theta_1 = a\left(\frac{1}{p} + a\right)^{-1}. \quad (12)$$

For this reason, Eqn.(11) is sometimes referred to as the hyperbolic adsorption isotherm. For values of p so small that $ap \ll 1$, we have

$$\theta_1 = ap, \quad (13)$$

i.e. Henry's equation holds. If p is so large that $ap \gg 1$, then

$$\theta_1 \to 1. \quad (14)$$

Under these conditions, Eqn.(11) can be written in the form

$$ap(1 - \theta_1) = 1, \quad (15)$$

i.e.

$$1 - \theta_1 = \theta_0 = 1/ap. \quad (16)$$

Thus, when the degree of surface coverage tends to unity, the fraction of the free surface is inversely proportional to the pressure.

The problem of whether or not experimental data are described by isotherm (11) is usually elucidated with the aid of one of the following methods.

One can use the equation

$$\frac{p}{\theta_1} = \frac{1}{a} + p, \quad (17)$$

obtained by rearranging Eqn.(11). Eqn.(17) describes a linear plot of p/θ_1 against p and makes it possible to determine a from experimental data.

The second method involves the use of the equation of a linear plot of p/v against p:

$$\frac{p}{v} = \frac{p_{1/2}}{v_\infty} + \frac{p}{v_\infty} \quad (18)$$

where v_∞ is the maximum degree of adsorption corresponding to the formation of a monolayer and $p_{1/2}$ the pressure at which $v = \frac{1}{2}v_\infty$. Eqn.(18) can be obtained from the expression

$$v = v_\infty p/(p_{1/2} + p), \quad (19)$$

which in its turn can be obtained from Eqn.(11) if account is taken of the fact that $\theta_1 = v/v_\infty$ and $1/a = p_{1/2}$ [the latter is a consequence of Eqn.(11)]. This method makes it possible to determine $p_{1/2}$ and hence also a and v_∞, provided that Eqn.(18) holds.

The following procedure is sometimes used to compare experimental data with isotherm (11).[12] After some rearrangement, logarithms are taken in Eqn.(8), which yields

$$\ln(\theta_1/p) = \ln a + \ln(1 - \theta_1). \quad (20)$$

For not unduly high values of θ, we have

$$\ln(1 - \theta_1) \simeq -\theta_1, \quad (21)$$

since the series expansion

$$\ln(1 - \theta_1) = -\left[\theta_1 + \frac{1}{2}\theta_1^2 + \frac{1}{3}\theta_1^3 + \ldots\right] \quad (22)$$

is valid. For this reason Eqn.(20) can be replaced approximately by the equation

$$\ln(\theta_1/p) = \ln a - \theta_1, \quad (23)$$

which describes a linear plot of $\ln(\theta_1/p)$ against θ_1. If isotherm (11) describes the experimental data, the slope of the straight line should be -1; the value of a can then be determined from the intercept on the ordinate axis.

Temkin[13] obtained Eqn.(11) by a statistical method. He used for this purpose the partition function for the adsorbed layer (Z_a):

$$Z_a = (f_a)^N \cdot \frac{L!}{N!(L-N)!}, \quad (24)$$

where f_a is the partition function of the molecule adsorbed in a specific manner, N the number of molecules in the adsorbed layer, L the number of surface sites, and $(f_a)^N$ the partition function of the adsorbed layer in which the molecules can be accommodated in only one way. Substitution of Z_a in the expression for the Helmholtz free energy and differentiation with respect to L yield the equation of the chemical potential of the adsorbed state. After setting the chemical potential of the adsorbed state equal to the chemical potential of the gas, i.e. assuming equilibrium, Temkin obtained Eqn.(11). This shows that Eqn.(11) is valid for the given case of adsorption regardless of the mechanism by which adsorption equilibrium is attained. Temkin established a relation between the constant a in Eqn.(11) and the heat of adsorption†. We shall restrict the treatment by quoting only the approximate equation, analogous to the approximate Nernst formula[16] for interphase equilibria, since the exact equation contains the heat capacity of the adsorbed layer, which is as yet unknown for the vast majority of adsorbent–adsorbate systems. The approximate equation is

$$\lg\frac{1}{a} = -\frac{Q}{4.57T} + 1.75\lg T + i', \quad (25)$$

where i' is the so called conventional chemical constant, which can be assumed to be approximately equal to 3 for molecules and 1.5 for atoms, and Q is the heat of adsorption.

2. The Adsorption Isotherm for Polyatomic Molecules Dissociating on the Surface into Mobile Atoms (Mobile Films)

Suppose that the adsorption of each atom requires a single elementary site. The necessary condition for the adsorption of a diatomic molecule colliding with the surface is then the presence of two adjacent free elementary sites. The probability that any of the elementary sites on the surface is free equals $1 - \theta_1$. When the adsorbed atoms can migrate on the surface (mobile films), the probability that any two adjacent sites on the surface are free is equal to the product of the probabilities that each is free, i.e. equals $(1 - \theta_1)^2$. The necessary condition for the desorption of diatomic molecules from the surface is the presence of adsorbed atoms on two adjacent elementary sites on the surface. The probability of such an event is θ_1^2. Then the condition for the equality of the rates of adsorption and desorption at equilibrium is

$$\alpha(1 - \theta_1)^2 Z_0 = \beta\theta_1^2. \quad (26)$$

† In non-Soviet literature, priority in the statistical derivation of isotherm (11) is frequently given to Fowler (see, for example, Trapnell[14]), who published his study two years later than Temkin[13].

This equation was obtained by Langmuir [11]. After substitutions, we obtain

$$ap(1-\theta_1)^2=\theta_1^2. \tag{27}$$

The positive solution of Eqn.(27) is

$$\theta_1=\sqrt{ap}/(1+\sqrt{ap}). \tag{28}$$

For low coverage, when $\theta_1 \ll 1$, Eqn.(28) becomes

$$\theta_1=\sqrt{ap}, \tag{29}$$

i.e. the degree of adsorption is proportional to the square root of the pressure. For an almost completely covered surface, where $(1-\theta_1) \ll 1$, we have

$$(1-\theta_1)=\sqrt{1/ap}. \tag{30}$$

If the molecule dissociates on the surface into three species, each of which occupies a single elementary site, then, when $\theta_1 \ll 1$, we have

$$\theta_1=\sqrt[3]{ap}, \tag{31}$$

and, when $(1-\theta_1) \ll 1$, we have

$$(1-\theta_1)=\sqrt[3]{1/ap}. \tag{32}$$

In order to test whether or not the experimental data are described by Eqn.(28), it is convenient to put the latter in the form

$$\frac{\sqrt{p}}{v}=\frac{1}{\sqrt{a}\cdot v_\infty}+\frac{\sqrt{p}}{v_\infty}. \tag{33}$$

Eqn.(33) describes a linear plot of $\sqrt{p}/v$ against $\sqrt{p}$, its slope yielding the volume of the monolayer v_∞ and the intercept on the ordinate axis yielding the value of a.

A second method for comparing the experimental data with Eqn.(28), which is applicable at pressures such that $\sqrt{ap} \ll 1$, is as follows. One can use the equation

$$\ln(\theta_1/\sqrt{p})=\ln\sqrt{a}-\sqrt{a}\sqrt{p}, \tag{34}$$

which is obtained by rearranging Eqn.(28) and taking logarithms, provided that one subsequently replaces $\ln(1+\sqrt{ap})$ by the first term of the series expansion

$$\ln(1+\sqrt{ap})=\sqrt{ap}-\frac{1}{2}ap+\frac{1}{3}ap\sqrt{ap}-\frac{1}{4}a^2p^2+\ldots \tag{35}$$

Eqn.(34) describes the straight line

$$\ln(\theta_1/\sqrt{p})-\sqrt{p}.$$

Temkin [13] derived Eqn.(28) by a thermodynamic method and showed that, in order to describe the relation between the coefficient a and the heat of adsorption, one can employ the approximate Eqn.(25).

3. The Adsorption Isotherm of a Gas Each Molecule of which Occupies More than one Elementary Site on the Surface (Mobile Films)

If the molecules are adsorbed without dissociation, then the activation energy for their migration on the surface must be lower than the activation energy for desorption, since migration does not require the complete dissociation of the bonds between the adsorbed molecules and the adsorbent. Therefore, when the gas adsorbed without dissociation is desorbed at an appreciable rate at any temperature, the adsorbed film cannot be stationary.

The exact adsorption isotherm for this case is unknown in a general form, although various workers undertook the solution of this problem, which is frequently encountered in practice. An approximate solution in the most general form has been given by Ostrovskii and Temkin [17,18]. The calculation is performed by a kinetic method, i.e. by equating the expressions for the rates of adsorption and desorption. The resulting equation is solved for p (or θ_1). The equation for the rate of adsorption will be formulated as follows:

$$r_+=\alpha p\, f(\theta_1), \tag{36}$$

where $f(\theta_1)$ is a function of the degree of surface coverage, which has to be determined. We shall consider, as an example, the adsorption of molecules (for example those of benzene) such that each requires seven elementary sites ($n=7$) distributed on the surface as shown in the Figure; each adsorbent atom has six nearest neighbours; $z=18$ is the number of surface sites which can be occupied on rotation of the adsorbed molecule about the fixed site which it occupies (0), which is not included in the number z; such a surface corresponds to the (111) face of a cubic crystal. We shall consider on the adsorbent surface a group of atoms (each of which is the centre of an elementary site), consisting of the central atom 0 and its 18 neighbours 1, 2, 3, ..., 18 (see Figure). If the central atom is occupied, the implication is that one of the septets of atoms 0, 6, 7, 8, 9, 2, 1 or 0, 1, 9, 10, 11, 3, 2 or 0, 2, 11, 12, 13, 4, 3, etc. is occupied, while the other sites can be occupied or free. If the central atom is free, then any of the atoms 1–18 can be either occupied or free. One must take into account the fact that the adsorption of each molecule reduces the probability of adsorption on the neighbouring sites; for example, the centre of the molecule adsorbed next to that shown in the Figure can no longer be located at points, 5, 4, 3, etc.

$f(\theta_1)$ was calculated in terms of Bethe's approximation [19]. It was assumed that the probability of any given distribution can be formulated thus:

$$g\xi_0^{An_0+Bn_1}\xi_{S1}^{n_0}\xi_{S2}^{n_1}, \tag{37}$$

where ξ_1 is the probability that the central atom is occupied, ξ_2 the probability that any one of the 18 atoms closest to the central atom is occupied, $n_0=0$ if the central atom is free, $n_0=1$ if the central atom is occupied, n_1 is the number of occupied atoms nearest to the central atom (with the exception of those contained in the same septet as the central atom if the latter is occupied), ξ is introduced to take into account the fact that ξ_1 and ξ_2 are not independent, A and B are constants, and g is the statistical weight of the given distribution.

The relative probability of any given distribution is

$$g\varepsilon_1^{n_0}\varepsilon_2^{n_1}, \tag{38}$$

where

$$\varepsilon_1=\xi^{A}\xi_{S1} \text{ and } \varepsilon_2=\xi^{B}\xi_{S2}. \tag{39}$$

The values of g corresponding to various combinations of n_0 and n_1 were calculated [17]. Next the average number of species at the sites closest to the central site were determined for cases where the central atom is occupied and free and $\epsilon_2=f(\theta_1)$ was calculated. The probability expressed in terms of ϵ_2, that there are on the surface seven free sites distributed in such a way that the given molecule can be adsorbed on them, was determined. Having expressed ϵ_2 in terms of θ_1, the required equation of the rate of adsorption was obtained. For the adsorption of a molecule resembling that of benzene on the (111) face of a cubic crystal, one obtains

$$r_+=\alpha'\,\alpha_0'\,p(1-\theta_1)^7\left(\frac{3}{3-\theta_1}\right)^6. \tag{40}$$

Apart from Eqn.(40), Ostrovskii and Temkin [17] also derived the corresponding equations for the adsorption of a molecule on four sites, as shown in Figs.*b* ($n = 4$, $z = 8$) and *c* ($n = 4$, $z = 6$). Generalisation by induction of the three equations obtained leads to the expression

$$r_+ = \alpha'(n, z)\, \alpha_0' p (1-\theta_1)^n \left[\frac{z}{z-(n-1)\theta_1}\right]^{n-1}. \quad (41)$$

For $n = 2$ [when $n = 2$, $\alpha'(n,z) = 1$ and $\alpha = \alpha b$], Eqn.(41) yields

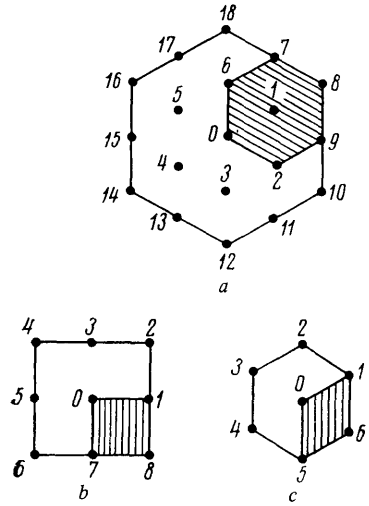
$$r_+ = \alpha_0' p (1-\theta_1)^2 \frac{z}{z-\theta_1}, \quad (42)$$

which agrees with the equation obtained earlier by Roberts and Miller using the same approximation [20]. Ostrovskii and Temkin [17] quote numerical values of $\alpha'(n,z)$ for certain typical combinations of n and z. In the case under consideration, the equation for the rate of desorption (r_-) is

$$r_- = \beta\theta_1. \quad (43)$$

Eqns.(41) and (43) lead to an adsorption isotherm of the following type [18,21]:

$$p = \frac{1}{a} \cdot \frac{\theta_1}{(1-\theta_1)^n} \cdot \left[1 - \frac{1}{z}(n-1)\theta_1\right]^{n-1}. \quad (44)$$



A model of adsorption on the (111) face of a face-centred cubic crystal (*a* and *c*) and on the (100) face of a cubic crystal (*b*).

When $n = 1$, Eqn.(44) leads to Eqn.(11). When $n = 2$ and $z = 2$, i.e. for the adsorption of a molecule on two sites in the case of a linear arrangement of sites, Eqn.(44) yields

$$p = \frac{1}{a} \frac{\theta_1}{(1-\theta_1)^2} \cdot \frac{2-\theta_1}{2}. \quad (45)$$

As a result of an exact solution by the thermodynamic method, Temkin [22] obtained the adsorption isotherm for molecules resembling carbon monoxide on two centres for a linear arrangement of sites:

$$p = \frac{1}{a} \frac{\theta_1 (2-\theta_1)}{2(1-\theta_1)^2}. \quad (46)$$

In comparing isotherms (46) and (45), one must bear in mind that, for molecules such as carbon monoxide, the factor 2 appears in the partition function owing to the asymmetry of the molecule. In the adsorption of symmetrical molecules, for which Eqn.(44) was derived, this factor should not appear. This implies that isotherms (45) and (46) agree numerically. Thus Bethe's approximation leads to the exact result for the one dimensional case.

If $1/a$ is defined as the proportionality coefficient between p and θ_1 in the range where $\theta_1 \ll 1$, isotherm (44) predicts a more rapid increase of p with θ_1 then isotherm (11). For example, in the case considered above with $n = 7$, $z = 18$, and $\theta_1 = 0.5$, we obtain, according to Eqn.(11), $p = 1/a$ and, according to Eqn.(43), $p = 10.7/a$. In order to show whether or not the experimental data for the relation between p and θ_1 are described by Eqn.(44), one determines $1/a$, as described above, from data obtained in the region where $\theta_1 \ll 1$. Theoretical $\theta_1 - p$ curves calculated by Eqn.(44) are then plotted for the postulated value of n and for values of z corresponding to the presence of four or six nearest neighbours at each surface adsorbent atom (the most frequently encountered cases for crystalline materials). The points corresponding to the experimental results are then drawn on the same plot and their positions are compared with the positions of the theoretical curves.

III. ADSORPTION ISOTHERMS ON INHOMOGENEOUS SURFACES IN THE ABSENCE OF INTERACTION BETWEEN THE ADSORBED MOLECULES

The problem of the form of adsorption isotherms on inhomogeneous surfaces was formulated for the first time by Langmuir [11], who called such surfaces "amorphous", assuming that, as a rule, on the surfaces of [crystalline] solids there are elementary sites of only one or a few different types, while on amorphous materials such as glass all the areas can have different adsorption capacities. In such cases the surface may be regarded as divided into infinitesimally small regions $d\rho$, each of which is characterised by a specific value of a. If the law governing the distribution of sites with respect to adsorption capacity is known, i.e. if the form of the function $a(\rho)$ is known, the overall adsorption can be obtained by integration with respect to all the values of ρ:

$$\frac{L}{N} = \int_0^1 \frac{pa(\rho)\, d\rho}{1 + pa(\rho)}. \quad (47)$$

Later Taylor [23,24] developed the idea that the surface of crystalline materials must be inhomogeneous with respect to catalytic activity and adsorption capacity. According to Taylor, the atoms located on the surface of the crystal faces are the most "saturated" (the saturation of valence forces is considered); the atoms located on the crystal edges are less saturated and those at the crystal vertices are saturated to a still smaller extent. If this is the case, there may be differences also between the atoms located on different crystal faces, near lattice defects, etc. As

a result, the activation energy for adsorption and the rates of adsorption and desorption will differ at different surface sites.

1. The Adsorption Isotherm on a Surface Characterised by a Linear Distribution of Elementary Sites with Respect to Adsorption Capacity

The adsorption isotherm for this case was obtained by Temkin[25]. Following Temkin, we shall assume that the different areas on the surface are characterised by different adsorption capacities, i.e. different values of a in Eqn.(11). The interaction forces between the adsorbed species will be neglected, so that the relative distribution of the adsorbed molecules may be disregarded. We shall imagine that all the elementary areas on the surface are numbered in order of decreasing values of a (1, 2, 3, ..., N, ..., L). We shall denote by s the fraction of the surface traversed on moving along it from area to area in the direction of increasing ordinal number of the latter, i.e. the relative number of the site (N/L). According to the earlier hypothesis concerning the multiplicity of the values of a, the latter is a monotonic function of s. At the same time, in order to examine the dependence of a on s, Temkin considered the variation of the heat of adsorption (per molecule) ϵ with s on the basis that a and ϵ are linked by the equation

$$a = \frac{F_a}{F_g kT} \cdot e^{\varepsilon/kT}, \tag{48}$$

where F_a and F_g are the partition functions of the adsorbate molecule in the adsorbed and gaseous states. Suppose that the relation between ϵ and s is given by the equation

$$\varepsilon = \varepsilon^0 - cs, \tag{49}$$

where c is a constant and $\epsilon^0 = \epsilon$ when $s = 0$. According to Eqn.(48),

$$a = a_0 e^{-f_1 s}, \tag{50}$$

where $a_0 = a$ for $s = 0$ and

$$f_1 = c/kT. \tag{51}$$

Following Temkin, we shall refer to surfaces for which Eqn.(49) is satisfied as linearly inhomogeneous surfaces.

For adsorption without dissociation, we have

$$\theta_1 = \int_0^1 \frac{ap\,ds}{1+ap}. \tag{52}$$

After substituting Eqn.(50) in (52), we obtain

$$\theta_1 = \int_0^1 \frac{a_0 e^{-f_1 s} p\,ds}{1 + a_0 e^{-f_1 s} p}, \tag{53}$$

and after integration we have

$$\theta_1 = \frac{1}{f_1} \ln \frac{1+a_0 p}{1+a_1 p}, \tag{54}$$

where $a_1 = a_0 e^{-f_1}$, i.e. $a_1 = a$ when $s = 1$, so that

$$f_1 = \ln (a_0/a_1). \tag{55}$$

If the surface is strongly inhomogeneous, i.e. if $a_0 \gg a_1$, it is possible to distinguish a range of pressures in which the following inequalities hold:

$$\begin{aligned} a_0 p &\gg 1, \\ a_1 p &\ll 1, \end{aligned} \tag{56}$$

i.e. the most strongly adsorbing areas are almost all occupied, while the least strongly adsorbing areas are almost all free. Temkin refers to this region as the region of moderate surface coverages. If inequality (56) holds, then we have the approximate relation

$$\theta_1 = \frac{1}{f_1} \ln a_0 p. \tag{57}$$

In the literature, Eqn.(57) is usually referred to as the Temkin isotherm. An isotherm of this type was put forward for the first time by Frumkin and Shlygin[26] as an empirical formula for the description of the behaviour of the platinum electrode in acid solutions in the region of the so called hydrogen arrest.

At low surface coverages, where $a_0 p \ll 1$, the Temkin isotherm transforms into the equation

$$\theta_1 = (a_0 - a_1)\, p/f_1, \tag{58}$$

if following the series expansion

$$\ln(1+x) = x - x^2/2 - x^3/3 - \ldots \tag{59}$$

only the first term is retained. Eqn.(58) is analogous to Henry's law. If $a_0 \gg a_1$, then

$$\theta_1 = a_0 p/f_1. \tag{60}$$

This equation leads to an interesting conclusion. The heat of adsorption calculated from the proportionality coefficient between the adsorption and pressure in the Henry region on a uniformly inhomogeneous surface should differ by only RT from the heat of adsorption on the most active sites (since f_1 is inversely proportional to T). This conclusion may be of interest, particularly for gas chromatography, where the method for the determination of the heats of adsorption from Henry's constant is widely used.

For the adsorption of diatomic molecules with dissociation into atoms on a uniformly inhomogeneous surface, the isotherm is

$$\theta_1 = \frac{1}{f_1} \ln \left(\frac{1 + \sqrt{a_0 p}}{1 + \sqrt{a_1 p}} \right)^2, \tag{61}$$

which gives rise at moderate coverages to the following approximate equation equivalent to Eqn.(57):

$$\theta_1 = \frac{1}{f_1} \ln a_0 p, \tag{62}$$

At low coverages, Eqn.(61) leads to the expression

$$\theta_1 = \frac{2}{f_1} \sqrt{a_0 p} \tag{63}$$

[cf. Eqn.(29) for a homogeneous surface]. In order to test whether or not the experimental data at moderate coverages are described by Eqn.(57) or (62), it is sufficient to demonstrate the linearity of the plot of θ_1 against $\ln p$. The slope of the resulting straight line is equal to the ratio kT/c and a_0 can be determined from the intercept on the ordinate axis.

2. The Adsorption Isotherm on a Surface Characterised by Exponential Inhomogeneity

Exponentially inhomogeneous surfaces are those with an exponential distribution of the elementary areas with respect to adsorption capacity. We shall define the distribution function in the form

$$dL = CL\, e^{-\frac{\varepsilon - \varepsilon_1}{k\theta}} d\varepsilon, \tag{64}$$

where ϵ_1 is the minimum heat of adsorption on the least strongly adsorbing sites, Θ a constant having the dimensions of temperature, and the constant C can be found from the normalisation condition

$$\int \mathrm{d}L = L, \tag{65}$$

which yields

$$C = \gamma/kT, \tag{66}$$

where

$$\gamma = T/\Theta. \tag{67}$$

The equation of the adsorption isotherm will be formulated as follows:

$$\frac{L}{N} = \int_{\varepsilon_1}^{\varepsilon_0} C\mathrm{e}^{-\frac{\varepsilon-\varepsilon_1}{k\Theta}} \frac{a_1 p \exp[(\varepsilon-\varepsilon_1)/kT]}{1+pa_1\exp[(\varepsilon-\varepsilon_1)/kT]}\,\mathrm{d}\varepsilon. \tag{68}$$

The problem of the form of the isotherm for the case under consideration was examined for the first time by Zel'dovich[27], who showed that, in the range of moderate coverages [which corresponds to the integration of Eqn.(68) in the range from $\epsilon_0 = \infty$ to $\epsilon_1 = 0$], an isotherm of the following form is obtained:

$$\theta_1 = \frac{\pi\gamma a_1^{\gamma}}{\sin\pi\gamma}\cdot p^{\gamma}. \tag{69}$$

Temkin and Levich[28], who, unlike Zel'dovich, carried out the integration with respect to surface coverages and not energies, later obtained the same equation for the region of moderate coverages. The constant γ is proportional to T and $0 < \gamma < 1$. When it is assumed that $\Theta = \infty$ (i.e. $\gamma = 0$) in Eqn.(64), then at moderate coverages, i.e. with $(1/a_0) \ll p \ll (1/a_1)$, Eqn.(69) leads approximately to the logarithmic Temkin isotherm [Eqn.(62)]. If $\gamma = 1$, then the following equation holds approximately at moderate coverages[28]:

$$\theta_1 = a_1 p \ln(1/a_1 p). \tag{70}$$

A general solution of Eqn.(68), from which it is possible to obtain Eqn.(69) as a special case, was published recently[29].

An equation of type (69) is usually referred to as the Freundlich isotherm. Freundlich[30] was the first to use the expression

$$v = cp^{1/n} \tag{71}$$

for the description of numerous data on adsorption equilibria over a wide range of pressures and temperatures. If the Freundlich isotherm is valid, then at moderate surface coverages the plot of θ_1 against $\lg p$ is a straight line whose slope is equal to γ.

Apart from the derivation of the equation for monomolecular adsorption on the basis of a specified law governing the distribution of sites with respect to adsorption capacity, Temkin and Levich[28] solved in a general form the converse problem of the determination of the type of distribution of sites with respect to their adsorption capacity when the form of the adsorption isotherm is known. The solution was applied to the logarithmic isotherm, the Freundlich isotherm, and certain other isotherms. In particular, it was shown by this method that the Schmidt–Il'in isotherm[31,32] cannot be obtained for any distribution of sites on an inhomogeneous surface with respect to adsorption capacity. In other words, this isotherm cannot be represented as the limiting sum of isotherms (11).

IV. ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE WITH INTERACTION BETWEEN THE ADSORBED SPECIES

The decrease of the heat of adsorption with increasing surface coverage of the adsorbent can be caused either by the inhomogeneity of the surface or by the operation of repulsion forces between the adsorbed species. Repulsion forces consist of the repulsion forces between the filled electron shells of the adsorbed species, which diminish rapidly with distance, and the forces which decrease comparatively slowly with distance. The latter can be of different types. The possibility of effects associated with the mutual influence of the adsorbed species was pointed out for the first time by Langmuir[33]. Somewhat later the results of measurements of the heats of adsorption of hydrogen on tungsten were explained[34] with the aid of the hypothesis of repulsion forces.

Langmuir[33] assumed that the interaction forces between the adsorbed molecules in a two-dimensional monolayer film are the same type as the forces responsible for the deviation of the equation of state for real gases from the equation for an ideal gas. In the derivation of the equation of state for the adsorbed layer, the virial equation for a two-dimensional gas is used:

$$FS_0 = RT - \frac{1}{2}\Sigma rf, \tag{72}$$

where F is the two dimensional pressure, S_0 the surface area containing 1 gram-atom of the adsorbate, and f the interaction force, which is a function of the distance r; the summation is carried out with respect to all the pairs of adsorbed atoms on the surface. Langmuir obtained the equation of the adsorption isotherm in the form

$$\theta_1 = \frac{ap\,\mathrm{e}^{m/T}}{A_{1.5}T^{3/2}}, \tag{73}$$

where $A_{1.5} = 7.98 \times 10^6$ atm $\mathrm{K}^{-3/2}$ is a constant and m is a constant related to the heat of adsorption Q by the equation $Q = n(m + lT)$, where n and l are constants and $m = f(\theta_1)$. Later the problem of the role of the interaction of the adsorbed species due to the operation of dipolar forces was examined by Temkin[25], who obtained an equation for the isotherm representing in an explicit form the relation between the pressure and the degree of coverage. Like Langmuir, Temkin began with the virial theorem for a two-dimensional gas, but, unlike Langmuir, restricted the treatment to surface coverages for which it is possible to neglect the cases of the simultaneous interaction of three and more gas molecules. The interaction law was used in the following form:

$$\varepsilon(r) = \mu^2/r^3, \tag{74}$$

where μ is the dipole moment of the adsorbed molecule. Temkin derived the equation of the adsorption isotherm from the equation of state for the adsorbed layer with the aid of the Gibbs equation:

$$L = \frac{1}{kT}\frac{\partial F}{\partial \ln p}. \tag{75}$$

This leads to the Williams isotherm, proposed[35] as the empirical formula

$$\ln(p/L) = BL + C\ , \tag{76}$$

where B and C are constants. If the interaction forces are fairly large, then, as shown by Temkin[25], Eqn.(76) differs little from that of the logarithmic isotherm for not

unduly low values of L (in the region of moderate coverages). Under these conditions, Eqn. (76) is close to

$$\theta_1 = \frac{1}{A} \ln a_0 p. \tag{77}$$

The constant a_0 has the same significance as a_0 in the logarithmic isotherm [Eqn. (57)]. We have $A = BN$, where

$$B = 2\pi \int_0^\infty (1 - e^{-\varepsilon(r)/kT}) r\, dr.$$

Thus the physical significance of the constant A differs from that of the constant f_1 in Eqn. (57) and is characterised by a different temperature dependence.

The authors [25,33] assume that the interaction is determined by forces of the same type as that in molecules of real gases. The physical picture underlying these equations can explain only a decrease of the heat of adsorption per mole of gas of the order of RT. In practice an appreciably greater reduction of the heat of adsorption is frequently observed as the surface becomes saturated.

Kobozev and Gol'dfel'd [36] examined the interactions associated with the effect involving the fixation of the adsorbed atoms on the surface. They assumed that, in the adsorption at any centre, there is a change in the adsorption potential not only of the given centre, in consequence of the saturation of the adsorption forces, but also a decrease of the adsorption potential extending over a number of neighbouring adsorption centres (since the atoms of the solid are close-packed). On moving away from the occupied centre, the attenuation of the adsorption potential decreases in accordance with a law of the type

$$\varphi_r = \varphi_0 - \varphi_0 \cdot f(r) = \varphi_0 [1 - f(r)], \tag{78}$$

where φ_r is the potential of the adsorption centre at a distance r from the occupied centre with $[\partial f(r)/\partial r] < 0$. A characteristic feature of this approach is the assumption that the repulsion of the molecules in the adsorbed layer is due to the polarisation of the adsorbent itself and not to the interaction of the adsorbent molecules. According to the authors, interactions of this type can extend over extremely long distances, are intense, and should occur for both polarised and electrically symmetrical adsorbed species. The adsorption isotherm is derived using the equation of state of a two-dimensional gas in the form

$$\left(F - \frac{\Delta}{A_2^2}\right)(A_2 - A_1) = RT, \tag{79}$$

where A_2 is the area of the entire surface, A_1 twice the area of the adsorbed molecules themselves, and $\Delta = f_1[\varphi_0, f(r)]$. The equation of the adsorption isotherm is

$$p/\theta_1 = p + C \cdot \exp[\varphi_0 (1 - \psi(\theta))/RT] \ddagger, \tag{80}$$

where $\varphi_0[1 - \psi(\theta)]$ is the adsorption energy and C a constant.

A graphical method for the calculation of the values of $C \exp\{\varphi_0[1 - \psi(\theta)]/RT\}$ from the experimental $p/\theta - p$ adsorption isotherms has been described [36]. It makes it possible to compare the theory with experimental results.

Vol'kenshtein [37] examined the problem of the form of the adsorption isotherm for different laws governing the interaction between the adsorbed species. He assumed that the interaction is independent of the relative orientation of the molecules and that the interaction forces are not capable of being saturated. The equations for the rates of adsorption (r_+) and desorption (r_-) are

$$r_+ = Z_0 \alpha (1 - \theta_1) \cdot \exp[-E(\theta_1)/RT], \tag{81}$$

$$r_- = \beta \theta_1 \exp[-(\Delta Q(\theta_1) + E(\theta_1))/RT], \tag{82}$$

where E is the activation energy for adsorption.

Under conditions of equilibrium, Eqns. (81) and (82) lead to the expression

$$\Delta Q(\theta_1) + RT \ln[(1 - \theta_1)/\theta_1] = RT \ln(1/\sigma_1 p). \tag{83}$$

Assuming that the adsorbed atoms on the surface are located at the sites of a square lattice, Vol'kenshtein found that

$$\theta_1 = (r_0/r)^2 \tag{84}$$

(r_0 is the minimum possible distance between two adsorbed molecules and r the shortest distance between two adsorbed molecules). Assuming that

$$\Delta Q(\theta_1) = -\Delta\Phi(r)|_{r = r_0/\sqrt{\theta_1}}, \tag{85}$$

he obtained the equation

$$RT \ln[(1 - \theta_1)/\theta_1] - \Delta\Phi(r_0/\sqrt{\theta_1}) = RT \ln(1/p\sigma_1). \tag{86}$$

The solution of this equation for θ_1 with the specified $\Delta\Phi(r)$ interaction law yields the equation of the adsorption isotherm. In the region of very low and very high coverages, it is possible to neglect the second term in Eqn. (86). One then obtains the Langmuir isotherm [Eqn. (11)]. In the region of moderate coverages, the form of the adsorption isotherm depends on the interaction law. However, Vol'kenshtein does not consider the problem of the convergence of the sums expressing the interaction energy between the adsorbed molecules and their neighbours on the surface, which throws doubt on the validity of his conclusions§.

There has been a fairly large number of studies whose authors describe the repulsion of molecules from one another by statistical procedures such as the Bethe–Peierls [38,39] and Bragg–Williams [40] methods and the method of correlation functions [41]. In terms of the Bragg–Williams approximation, when the interaction between the molecules is taken into account by introducing an average molecular field, the adsorption isotherm is [40]

$$\theta/(1 - \theta) = ap \cdot \exp(z_1 J \theta_1/kT), \tag{87}$$

where z_1 is the number of adsorption centres on the surface closest to the given centre and J is the overlap integral (a constant).

Fedyanin [41] took into account the correlation between the adsorbed molecules, which was neglected in the Bragg–Williams approximation, and obtained the adsorption isotherm

$$\theta/(1 - \theta) = ap/[1 + ap\varphi(1/kT, z_1, J)], \tag{88}$$

where

$$\varphi(1/kT, z_1, J) = -z_1[1 - \exp(J/kT)/1 + ap \exp(J/kT)]. \tag{89}$$

A novel idea concerning the nature of the long-range forces, leading to the repulsion of the adsorbed species, has been put forward by Breger and Zhukhovitskii [42]. Treating the electrons of the adsorbent as a Sommerfeld electron gas, they postulated that the electrons are

‡ In the formulation of Eqn. (80) for the isotherm, there is a misprint in the paper of Kobozev and Gol'dfel'd [36] [Eqn. (10a)].

§ Pointed out by M. I. Temkin.

combined with the adsorbed species and are not involved in the motion of the remaining electrons forming the electron gas of the adsorbent. Thus adsorption results in the formation of nodes, the number of which increases as adsorption proceeds. The presence of the nodes increases the overall energy of the adsorbent electrons, which is manifested as the repulsion between the adsorbed species. The authors showed that such repulsion is inversely proportional to the distance and that, even with $r = 20$ Å, the repulsion energy is still 0.08 eV.

The electronic nature of the long-range forces in adsorption was assumed also in other investigations. Boudart [43] explained the decrease of the heat of adsorption with surface coverage on metals by the increase in the potential energy of the electrons due to the appearance of an additional potential jump in adsorption. He regarded the surface layer as a planar condenser with the charge uniformly distributed over the plates. Since for a given capacitance the energy of the condenser is proportional to the square of the charge, Boudart obtained a linear relation between the heat of adsorption and surface coverages. However, the "smearing" of the charge over the surface has been inadequately justified in physical terms.

In contrast to Boudart, Temkin [44] explained the decrease of the heat of adsorption with coverage by an increase of the kinetic energy of the electrons. He treated the layer of adsorbed atoms on the metal surface as a surface alloy, assuming that the electrons of the adsorbate atoms on the surface are combined with the free electrons of the surface metal atoms, forming a two-dimensional electron gas. The charge density at the surface increases, since the excess positive charge of the adsorbed atoms must be compensated. In the adsorption of an atom, there is a gain of some energy, part of which is evolved in the form of heat of adsorption and another part is used in increasing the kinetic energy of the electron gas. The treatment in such terms was carried out within the framework of the simplest Sommerfeld model on the assumption of a non-interacting electron gas. In contrast to the adsorption models postulating interaction between the chemisorbed species, which decreases with distance in accordance with some law, in the electron gas model the energy of the adsorbed layer depends only on the total number of adsorbed species but not on their relative positions. If the effective charge of the adsorbed species η is independent of θ_1, the adsorption energy is

$$\varepsilon = \varepsilon^0 - \eta^2 \frac{h^2 N}{4\pi m^*} \theta_1, \qquad (90)$$

where ϵ^0 is the value of ϵ corresponding to $\theta_1 = 0$, η is expressed in units of the elementary electric charge, h is the Planck constant, and m^* is the effective mass of the electron. The equation of the isotherm corresponding to Eqn.(90) is [45,46]

$$\ln ap = \frac{\eta^2 h^2 N}{4\pi m^* kT} \theta_1 + \ln \frac{\theta_1}{1-\theta_1}. \qquad (91)$$

If the treatment is restricted to the first term of the expansion in Taylor's series of the second term on the right-hand side of Eqn.(91),

$$\ln \frac{\theta_1}{1-\theta_1} = 4\left(\theta_1 - \frac{1}{2}\right) + \frac{16}{3}\left(\theta_1 - \frac{1}{2}\right)^3 + \ldots + \frac{4^n}{2n-1}\left(\theta_1 - \frac{1}{2}\right)^{2n-1} + \ldots\text{¶}, \qquad (92)$$

then Eqn.(91) is converted into Eqn.(57), with

$$f_1 = \eta^2 \frac{h^2 N}{4\pi m^* kT} \text{ and } a_0 = a e^2. \qquad (93)$$

Fedyanin [47] estimated the contribution of the interaction of electrons to the overall kinetic energy of the electron gas. The theory of the mutual influence of adsorbed species was also investigated by Osherov [48], who considered the delocalisation of the wave functions of the electrons in the adsorbent crystal during adsorption.

V. POLYMOLECULAR ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE

If the pressure of the adsorbate vapour is close to the vapour pressure at the experimental temperature, the average thickness of the layer adsorbed on the surface of the adsorbent may exceed that of one molecule. As stated above, the adsorption isotherm for this case was obtained for the first time by Langmuir [11]. We shall now reproduce briefly Langmuir's derivation. Suppose that θ_0 is the fraction of the free surface and θ_{01}, θ_{02}, ... θ_{0n}, etc. are the fractions of the surface occupied by 1, 2, ..., n layers of adsorbed molecules. Then

$$\theta_0 + \theta_{01} + \theta_{02} + \ldots + \theta_{0n} = 1. \qquad (94)$$

The average degree of surface coverage by adsorbed molecules is

$$v/v_m = \theta_{01} + 2\theta_{02} + 3\theta_{03} + \ldots + n\theta_{0n}, \qquad (95)$$

where v_m is the degree of adsorption corresponding to the coverage of each site on the surface by one molecule. The rate of desorption of molecules from the nth layer is

$$\underleftarrow{r_n} = \beta_n' \theta_{0n}, \qquad (96)$$

where β_n' is the rate of desorption of molecules from the nth layer when $\theta_{0n} = 1$. The rate of adsorption in the nth layer is

$$\underrightarrow{r_n} = \alpha_n' p \theta_{(n-1)}, \qquad (97)$$

where α_n' is the rate of adsorption of molecules in the nth layer at the given pressure for $\theta_{n-1} = 1$. Having formulated the equilibrium conditions for each layer and using Eqns.(94) and (95), Langmuir obtained

$$\frac{v}{v_m} = \frac{a_1 p + 2a_1 a_2 p^2 + 3a_1 a_2 a_3 p^3 + \ldots}{1 + a_1 p + a_1 a_2 p^2 + a_1 a_2 a_3 p^3 + \ldots}, \qquad (98)$$

where $a_n = \alpha_n'/\beta_n'$. After dividing the numerator and denominator on the right-hand side of Eqn.(98) by the numerator, we obtain

$$\frac{v}{v_m} = \frac{a_1 p}{1 + Ap + Bp^2 + Cp^3 + \ldots}, \qquad (99)$$

where

$$\begin{aligned} A &= a_1 - 2a_2, \\ B &= a_2(4a_2 - 3a_3 - a_1), \\ C &= 2a_2(6a_2 a_3 - 2a_3 a_4 + a_1 a_2 - a_1 a_3 - 4a_2^2). \end{aligned} \qquad (100)$$

Eqn.(99) represents the adsorption isotherm for the case under consideration formulated in a general form. As a special case, Langmuir analysed the situation where $a_1 \neq a_2$, but $a_2 = a_3 = a_4 = \ldots, a_n$. This corresponds to approximately identical adsorption capacities in all the layers except the first. After appropriate rearrangements, Eqn.(99) is converted into

$$\frac{v}{v_m} = \frac{a_1 p}{(1 - a_2 p)(1 - a_2 p + a_1 p)}. \qquad (101)$$

¶ In Temkin's paper [46], there is a misprint in the formulation of the general term of the expansion.

Later Brunauer, Emmett, and Teller[49] assumed that the adsorption in all the layers other than the first takes place with a heat change equal to the heat of condensation E_Z. We then have in Eqn.(101)

$$a_1 = a_1^0 \exp(E_1/RT) \tag{102}$$

and

$$a_2 = a_2^0 \exp(E_L/RT). \tag{103}$$

After the notation

$$c = \frac{a_1^0}{a_2^0} \exp[(E_1 - E_L)/RT] \tag{104}$$

and

$$u = pa_2 \tag{105}$$

has been introduced, Eqn.(101) is converted into

$$v/v_m = cu/[(1-u)(1-u+cu)]. \tag{106}$$

It is seen from Eqn.(106) that $v \to \infty$ when $u \to 1$. Therefore and also on the grounds that $v/v_m \to \infty$ when $u \to 1$, Brunauer, Emmett, and Teller assumed that

$$u = p/p_0, \tag{107}$$

where p_0 is the vapour pressure over the liquid adsorbate.

It follows from Eqns.(103), (105), and (107) that

$$p_0 = 1/a_2^0 \exp(E_L/RT). \tag{108}$$

After substituting Eqns.(107) and (108) and algebraic rearrangements the following equation is obtained for the isotherm:

$$\frac{p}{v(p_0-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p_0}, \tag{109}$$

which is the equation of a linear plot of $p/v(p_0-p)$ against p/p_0. This equation is usually called the BET equation. It makes it possible to calculate the values of v_m and c when experimental data are available for the relation between v and p. If it is assumed that the area occupied by the adsorbed molecule of the given gas is constant and independent of the nature of the surface, then it is possible to determine the surface areas of adsorbents with the aid of Eqn.(109). This possibility is widely used in practice. The physical picture of adsorption constituting the basis of the derivation of the BET equation has been frequently discussed in the literature. It follows from Eqn.(104) that the coefficient c may be determined from the heat of adsorption in the first layer, provided that the ratio a_1^0/a_2^0 is known. In their publication[49], Brunauer et al. assumed that $a_1^0/a_2^0 = 1$. Then

$$c = \exp[(E_1 - E_L)/RT]. \tag{110}$$

However it has been shown, for example by Harkins and Boyd[50] and Beebe et al.[51], that c can be calculated from heats of wetting $E_1 - E_L$ or from calorimetric measurements of E_1, which are much higher than the values obtained from the BET isotherm when it is assumed that c is defined by Eqn.(110).

This may be due to three causes[52]. Firstly, a_1^0/a_2^0 may differ from unity. Secondly, the heat of adsorption in the second and succeeding layers may differ from the heat of condensation of the adsorbate, approaching it only gradually with increase of the number of adsorbed layers. Thirdly, in view of the inhomogeneity of the adsorbent surface, the BET equation is valid only in the region $\theta \gtrsim 0.5$, where the surface inhomogeneity does not have an appreciable effect. For this reason, the values of E_1 are calculated from the BET isotherm using data obtained for $\theta > 0.5$. As a result, one may expect that average values of E_1 will be obtained only for those molecules of the first layer which are adsorbed at sites with lower adsorption energies and not for the entire first layer. On the other hand, in the determination of the heats of wetting one obtains data averaged over the entire adsorbent surface. Statistical calculations have shown[53-55] that there are in fact no adequate grounds for believing that $a_1^0/a_2^0 = 1$ in the general case.

The second of these possible causes of disagreement between the values of c obtained in calculations from adsorption isotherms and from measurements of $E_1 - E_L$ was examined in detail by Clampitt and German[56]. These investigators based their treatment on the finding that, with increase in the thickness of the adsorbed film starting from two monolayers, the heat of adsorption of molecules from the gas phase to the film varies smoothly up to the heat of condensation. Using a method analogous to that described by Brunauer et al.[49], they derived an equation for polymolecular adsorption formally agreeing with the BET equation. The difference between these equations is that Clampitt and German[56] obtained

$$c = (a_1^0/a_2^0) \exp[(E_1 - 2E_L + E_S)/RT], \tag{111}$$

where

$$E_S = E_L - 1.35[RT + \gamma_0 (M/d)^{2/3}] \tag{112}$$

(γ_0 is the surface tension of the film and d the adsorbate density in the liquid state). In the next paragraph we shall return to the third cause of the disagreement between the values of c.

The problem of the validity of Eqn.(107), which is one of the principal components of the BET theory, has been frequently discussed in the literature. It has been stated (for example in Refs. 57-59), that there is no sufficient evidence for adopting this equation. It is more correct to assume that

$$u = p/g, \tag{113}$$

where $g \neq p_0$. The use of Eqn.(107) may be justified only because it can be derived from the simple equation of the BET isotherm, which can be readily used to determine the specific surfaces of solids.

When adsorption does not take place on a smooth surface but within the adsorbent pores whose diameter cannot be regarded as very large compared with the dimensions of the molecules, then there is a possibility of adsorbing a finite number of layers of adsorbate molecules on such a surface. An equation has been obtained for the polymolecular adsorption isotherm in pores bounded by two parallel planes[49], which, in contrast to the simple BET equation [Eqn.(109)], contains three parameters:

$$\frac{v}{v_m} = \frac{cu}{1-u} \cdot \frac{1-(n+1)u^n + nu^{n+1}}{1+(c-1)u - cu^{n+1}}, \tag{114}$$

where n is the number of adsorbed layers. When $n = 1$, this equation is converted into the equation of the Langmuir isotherm [Eqn.(11)] and, for $n \to \infty$, it is converted into the BET equation [Eqn.(109)].

The case where adsorption saturation is reached at pressures lower than p_0 has been investigated[60]. The authors suggested that this effect is associated with capillary condensation. By taking into account capillary condensation, equations were obtained for adsorption isotherms in which there is a fourth parameter, whose value depends on the heat of condensation of the adsorbent

vapour, in addition to the parameters in Eqn.(114). These equations are extremely complex and have hardly any practical value.

VI. POLYMOLECULAR ADSORPTION ISOTHERMS ON INHOMOGENEOUS SURFACES

This equation of the BET isotherm [Eqn.(109)] can be used only in the range $0.05 < p/p_0 < 0.3$. One of the main causes of the failure of the BET isotherm for $p/p_0 < 0.05$ is surface inhomogeneity and, under the conditions where $p/p_0 > 0.3$, the interaction between the adsorbed molecules becomes significant. None of these effects can be taken into account by the BET theory. We shall consider the problem of the form of polymolecular adsorption isotherms on inhomogeneous surfaces. The first attempts to describe polymolecular adsorption processes on such surfaces were made by McMillan [61] and Walker and Zettlemoyer [62]. In these studies the surface was treated as a mixture of a finite number of adsorption centres with different adsorption energies. Then

$$v = \frac{u}{1-u}\left[\frac{v_{mA}c_A}{1+(c_A-1)u} + \frac{v_{mB}c_B}{1+(c_B-1)u} + \ldots + \frac{v_{mi}c_i}{1+(c_i-1)u}\right], \quad (115)$$

where c_A, c_B, ..., c_i and v_{mA}, v_{mB}, ..., v_{mi} are constants analogous to the constants c and v_m in Eqn.(109), which, however, refer to adsorption centres of types A, B, ..., i respectively. Eqn.(115) can be used to describe adsorption on an adsorbent consisting of a mechanical mixture of substances, each of which has a homogeneous surface.

The case where i is very large is more general. In order to obtained the adsorption isotherms on such a surface, simple summation must be replaced by integration. The integration requires that one specifies the law governing the distribution of sites on the surface with respect to heats of adsorption or standard Gibbs free energies of adsorption $\Delta G^0_{a_1}$. It is known from monomolecular adsorption data that the distribution of surface sites with respect to adsorption capacity can be usually described with the aid of a linear or exponential distribution law. The problem has been examined of finding the form of the polymolecular isotherms for any distribution of surface sites with respect to standard Gibbs free energies, when the monomolecular adsorption isotherm for the corresponding site distribution law is known [63].

The equation of the polymolecular adsorption isotherm can be put in the form

$$v = \frac{v_m c p}{(p_0 - p)[1 + (c-1)p/p_0]}, \quad (116)$$

and comparison of Eqns.(102), (103), (104), and (108) shows that

$$c = a_1 p_0. \quad (117)$$

Having substituted Eqn.(117) in (116), we obtain

$$v(1-u) = v_m \frac{a_1 p/(1-u)}{1 + [a_1 p/(1-u)]}. \quad (118)$$

Comparison of Eqn.(118) with the equation of the Langmuir isotherm for monomolecular adsorption

$$v = v_m \frac{a_1 p}{1 + a_1 p} \quad (119)$$

shows that the equation of the monomolecular adsorption isotherm can be converted into the equation of the polymolecular adsorption isotherm by replacing

$$\left.\begin{array}{l} v \text{ by } v(1-u) \\ p \text{ by } p/(1-u) \end{array}\right\} \quad (120)$$

and

The reverse conversion can be achieved by assuming that $p_0 = \infty$ in the equation of the polymolecular adsorption isotherm. If the surface is uniformly inhomogeneous, the monomolecular adsorption isotherm is described by an equation of type (62). Having replaced θ_1 by v/v_m and having substituted the variables in Eqn.(62) in accordance with Eqn.(110), we obtain the polymolecular adsorption isotherm on a uniformly inhomogeneous surface:

$$v = \frac{v_m}{f_1(1-u)} \ln \frac{1 + a_0 p/(1-u)}{1 + a_1 p/(1-u)}. \quad (121)$$

For a strongly inhomogeneous surface, where $a_0 \gg a_1$, in the region of moderate coverages Eqn.(121) becomes

$$v = \frac{v_m}{f_1(1-u)} \ln \frac{a_0 p}{(1-u)}. \quad (122)$$

In the case of an exponentially inhomogeneous surface, the adsorption isotherm has the following form in the region of moderate monolayer coverages under the conditions of polymolecular adsorption:

$$v = c \frac{p^\gamma}{(1-u)^{(1+\gamma)}}, \quad (123)$$

where

$$c = \frac{\gamma \pi v_m a_1^\gamma}{\sin \pi\gamma}. \quad (124)$$

Eqn.(123) can be obtained from the equation of the Freundlich isotherm, which describes monomolecular adsorption on an exponentially inhomogeneous surface at moderate coverages when the variables are substituted in accordance with formula (120).

In polymolecular adsorption, transition to the region of high surface coverages occurs already when $p/p_0 \simeq 0.05$. For this reason, in the case of polymolecular adsorption it is of interest to consider the adsorption not only in the region of moderate coverages but also in the region of high coverages. The equation of the adsorption isotherm for moderate and high surface coverages has therefore been obtained [64] by integrating the degrees of adsorption at sites with different adsorption capacities up to a minimal heat of adsorption in the first layer. When adsorption in layers above the first was considered [64], the same assumptions were made as in the derivation of the BET isotherm. The equation of the isotherm is

$$\frac{v}{v_m} = \frac{\pi\gamma \exp[E_L\gamma(h-1)/RT]}{\sin\pi\gamma} \cdot \frac{u^\gamma}{(1-u)^{(\gamma+1)}} - \frac{\gamma u \cdot \exp[E_L\gamma(h-1)/RT]}{(1-\gamma)(1-u)^2} \times \times\left[1 - \frac{1-\gamma}{2-\gamma}\cdot\frac{u}{(1-u)} + \frac{1-\gamma}{3-\gamma}\left(\frac{u}{1-u}\right)^2 - \frac{1-\gamma}{4-\gamma}\left(\frac{u}{1-u}\right)^3 + \ldots\right], \quad (125)$$

where h is the ratio of the minimum heat of adsorption in the first layer to the heat of condensation E_L. For fairly small values of u, Eqn.(125) is converted into

$$\frac{v}{v_m} = \frac{\pi\gamma \exp[E_L\gamma(h-1)/RT]}{\sin\pi\gamma} \cdot \frac{u^\gamma}{(1-u)^{(1+\gamma)}}. \quad (126)$$

By taking logarithms in Eqn.(126), it is possible to obtain an expression which permits the determination of γ and h from a plot of $\lg[v(1-u)]$ against $\lg[u/(1-u)]$ using adsorption measurements in the region of fairly small

values of u. The observed values of γ and h can then be used to describe the adsorption at high surface coverages using for this purpose Eqn.(125).[65] This makes it possible to determine whether or not the theory described above describes the experimental results.

By substituting Eqn.(107) in Eqn.(125) and assuming that $p_0 = \infty$, it is possible to obtain the equation of the monomolecular adsorption isotherm for moderate and high coverages corresponding to an exponential distribution of surface sites with respect to adsorption capacity.

VII. ISOTHERM FOR ADSORPTION IN MICROPORES

Adsorption by microporous adsorbents (i.e. adsorbents containing pores whose radius exceeds only slightly the size of the adsorbate molecules) at temperatures so low that dispersion forces are of decisive importance in the adsorption interaction constitute a special case. Langmuir did not consider it. We shall examine it in order to illustrate the view frequently encountered in the literature that the physical picture of polymolecular adsorption is not always adequate for the description of the adsorption of vapours when the amount adsorbed is greater than the volume of the adsorbate monolayer on the adsorbent surface. The theory of adsorption in micropores has been developed mainly by Dubinin and his coworkers[66,67]. It is assumed that micropores are filled at once and not layer by layer. The theory of the bulk saturation of micropores uses the temperature invariance of the characteristic adsorption equation noted by Polanyi. The characteristic adsorption equation is

$$\theta_1 = \exp[-(A'/E)^2]. \qquad (127)$$

It is usually called the Dubinin–Radushkevich equation. Here θ_1 is the degree of bulk saturation of the adsorption space, E the characteristic adsorption energy (a parameter of the distribution function), and A' the differential molar work of adsorption, which is defined in the theory of bulk saturation of micropores as the decrease in the Gibbs free energy:

$$A' = RT\ln(p_0/p) \quad , \qquad (128)$$

where p is the vapour pressure of the given substance in the standard state at a temperature T. The equation of the adsorption isotherm for the case under consideration can be formulated as follows[67]:

$$\theta_1 = \exp[-(A'/\beta E_0)^2], \qquad (129)$$

where $\beta = E/E_0$ (E_0 is the characteristic adsorption energy for a standard vapour, benzene being usually employed as the standard. For adsorption in very small pores, where the adsorption interactions are strongest, the more general equation

$$\theta_1 = \exp[-(A'/E)^n], \qquad (130)$$

where n is an integer, has been suggested[68] for the distribution function of θ_1 with respect to A'. Eqn.(127) can be regarded as a special case of Eqn.(130).

The theory of the bulk saturation of micropores is widely used to describe adsorption on activated charcoals, zeolites, microporous silica gels, etc.

VIII. CONCLUSION

The foundation of the modern theory of adsorption were laid by Langmuir in 1916–1918. The Soviet scientists Frumkin, Dubinin, Roginskii, Zel'dovich, Temkin, and others have contributed much to the development of the theory. The Langmuir, Freundlich, and Temkin isotherms are most widely used in studies on adsorption and the kinetics of heterogeneous catalytic processes and electrode processes (see for example, Refs.14 and 69–71). The Dubinin–Radushkevich isotherm together with the Brunauer–Emmett–Teller isotherm, which is generally employed to determine the specific surfaces of solids, are extensively applied in the description of physical adsorption.

The above discussion permits the conclusion that the formal description of adsorption isotherms within the framework of Langmuir's fundamental postulates can now be regarded as largely completed. In certain cases the solutions may be refined. However, with present experimental techniques and the accuracy currently achieved in the results, refinements in the solutions cannot be of any practical value.

Apparently the most serious of the currently unsolved problems in the field under consideration is that of the quantitative elucidation of the physical causes of the inhomogeneity of catalysts and adsorbents. In this sense calorimetric studies and also studies of isotope exchange on catalyst surfaces are most promising. Methods for the investigation of surface inhomogeneity with the aid of measurements of the rates of isotope exchange have been developed and have been used successfully by Boreskov and the catalytic school of which he is the Head (see, for example, Refs. 72–74).

The problem of which physical (or physicochemical) parameters determine the nature of the distribution of surface sites with respect to adsorption capacity and of the quantitative expression of the relation between these parameters and the adsorption capacity is of special interest (in particular, it is not clear why experimental data frequently yield an exponent in the equation of the Freundlich isotherm close to 0.5). In other words, although adsorption isotherms can in fact successfully describe experimental data, the hypotheses concerning the distribution of surface sites with respect to adsorption capacity used in their derivation have no adequate physical justification at the present time.

In the adsorption of vapours on porous bodies, the observed surface inhomogeneity may be due to the presence of narrow pores. The heats of adsorption of vapours do not differ very greatly from the heats of their condensation, exceeding the latter usually by a factor of only 2–3 even in the region of low surface coverages. Thus the adsorption of vapours can be as a rule explained by the action of van der Waals forces. Since such forces are additive, the heats of adsorption of vapours in pores whose size is comparable to the size of the adsorbate molecules should be greater than on a smooth surface. In this case the distribution of surface sites with respect to heats of adsorption can be related functionally to the distribution of adsorbate pores with respect to radii. In the chemisorption of permanent gases, for example in the adsorption of oxygen or hydrogen at the usual temperatures of catalytic experiments, the heat of adsorption frequently exceeds the heat of condensation even by an order of magnitude. In such cases the decrease of the heats of adsorption with surface coverage can amount to tens of kcal $mole^{-1}$. This effect cannot be accounted for by the operation of van der

Waals forces. One of the possible causes may be the presence of impurities. However, the adsorption can be frequently described by the Freundlich isotherm, but it is not clear why the presence of impurities should lead so often to an exponential distribution of sites with respect to adsorption capacity.

We shall consider briefly the possibility of reaching conclusions concerning the nature of surface site distribution with respect to adsorption capacity or about the adsorption mechanism (for example, how many elementary areas on the surface are required for the adsorption of each molecule) solely on the basis of the form of the adsorption isotherm. In practice, adsorption isotherms are as a rule investigated over a fairly narrow pressure range (electrochemical studies in which the change of potential may correspond to a pressure change by a factor of 10^5 constitute an exception). In this case the possibility of describing the results with the aid of, for example, a power or logarithmic isotherm does not by itself demonstrate the validity of the corresponding distribution of surface sites with respect to adsorption capacity. In order to deduce the nature of the inhomogeneity, it is necessary to consider the isotherms together with the results obtained by other methods, for example the calorimetric method, the method of surface isotope exchange, the ESR method, studies of the kinetics of adsorption and desorption, etc.

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