A. V. KISELEV

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. KISELEV

ADSORPTION OF VAPORS WITH THE FORMATION ON THE SURFACE OF COMPLEXES FROM ADSORBATE MOLECULES

(Presented by Academician M. M. Dubinin on 27 VI 1957)

Along with polymolecular adsorption of vapors, well described by the BET equation at large adsorption energies, when interactions between adsorbate molecules may be neglected (^{1,2}), cases are very common in which the interaction of adsorbed molecules plays a major role, leading to the formation of complexes on the surface; in the case of water, the molecules in these complexes are bound by hydrogen bonds ($^{3-5}$). In this connection it is of interest to consider vapor adsorption with allowance for the distribution of complexes of adsorbate molecules both perpendicular to the surface and along it.

The distribution of complexes along the surface after localization of molecules on primary active centers was considered in works ($^{4-9}$). However, in cases such as the adsorption of water vapor on graphitized carbon blacks, such centers are absent. Therefore we shall consider here the case of vapor adsorption on a homogeneous surface that bears no centers specific to the given adsorbate. At the same time, as in the BET picture, we shall consider the general case of van der Waals interactions in the surface layer.

Let us apply the method of quasi-chemical equilibria, which we used in the thermodynamic derivation of the BET equation (^{1}). Consider the chain of quasi-chemical reactions:

1. **Primary reaction of formation of unit complexes:**

vapor molecule + free surface ⇄ unit complex

Equilibrium constant (^{1})

$$K_1 = \theta_1 / p\theta_0 \quad \text{or} \quad K_1' = \theta_1 / h\theta_0, \tag{1}$$

where θ_1 is the fraction of the surface occupied by a unit complex; θ_0 is the fraction of free surface; p is the vapor pressure, and $h = p/p_s$ is the relative vapor pressure; $K_1' = K_1 p_s$.

2. **Formation of multiple complexes along the surface:**

unit complex + unit complex ⇄ double horizontal complex,

unit complex + double horizontal complex ⇄ triple horizontal complex, etc.*

The constants of these equilibria are

$$K_2 = \theta_2/\theta_1\theta_1; \quad K_3 = \theta_3/\theta_1\theta_2, \dots, \tag{2}$$

* We neglect the possibility of formation of multiple complexes from multiple complexes.

where $\theta_2, \theta_3, \dots$ are the fractions of the adsorbent surface occupied by double, triple, etc., horizontal complexes. These constants, strictly speaking, are not identical, since the energy and entropy of adsorption depend on coordination. Taking this dependence into account, however, introduces a new constant[6]. Therefore, by analogy with the assumption in the BET equation for vertical complexes[10], let us assume that

$$K_2 \approx K_3 \approx \dots = K_n. \tag{3}$$

If adsorption remains monomolecular, i.e., no vertical complexes are formed, then the total degree of filling of the monolayer, according to (1) and (2) under condition (3), is

$$\theta' = \frac{a}{a_m} = \theta_1 + \theta_2 + \theta_3 + \dots =$$

$$= \theta_1[1 + K_n\theta_1 + (K_n\theta_1)^2 + \dots] = \frac{\theta_1}{1 - K_n\theta_1} \tag{4}$$

(expressing the corresponding sum of terms of the geometric progression through $1/(1-K_n\theta_1))^*$. Introducing θ_1 from (1) and substituting $\theta_0 = 1-\theta'$, we obtain

$$\theta' = \frac{K_1' h(1-\theta')}{1 - K_n K_1' h(1-\theta')} \tag{5}$$

or

$$\alpha = \frac{\alpha_m K_1' h(1-\alpha/\alpha_m)}{1 - K_n K_1' h(1-\alpha/\alpha_m)}. \tag{6}$$

The obtained equation of the adsorption isotherm is solved with respect to h:

$$h = \frac{\theta'}{K_1'(1-\theta')(1+K_n\theta')}. \tag{7}$$

In linear form it has the form

$$\theta'/h(1-\theta') = K_1' + K_n K_1' \theta'. \tag{8}$$

Equations (5), (6), (7) contain three constants: α_m, K_1', and K_n; therefore, in the general case, to determine K_1' and K_n, α_m must be found independently.

In the absence of association, i.e., at $K_n \approx 0$, this equation becomes the Langmuir equation $\alpha = \alpha_m K_1' h/(1 + K_1' h)$. For strongly adsorbing substances ($K_1' \gg 1$), large θ' values are reached even at small h; therefore the product $h(1-\theta')$ is small for all θ', and the equation practically becomes the Langmuir equation, i.e., it describes a convex isotherm even for $K_n > 0$.

As K_1' decreases, isotherm (5) is expressed by an S-shaped curve—it is initially concave, then passes through an inflection point and approaches a limiting value. At small K_1', in this case the formation of vertical complexes can no longer be neglected.

3. Formation of vertical complexes. Let us assume approximately that the appearance of vertical complexes does not change the horizontal interactions in the first layer**, so that adsorption in the first

* α is the adsorption value; α_m is the adsorption value in a dense monolayer.

** In what follows it is necessary to take into account this influence, as well as the horizontal interactions in each layer, which sometimes lead to wave-like adsorption isotherms.

in the layer is expressed by equations (5), (6). Above horizontal complexes of different multiplicity, vertical complexes are built up.

a) The formation of double vertical complexes occurs on that part θ' which does not carry multiple vertical complexes. We shall denote this top free part θ' by θ_0'. Then, according to (1), for the quasichemical reaction:

$$\text{vapor molecules} + \text{complexes of the first layer open at the top} \rightleftarrows \text{double vertical complexes}$$

$$K'' = \theta''/h\theta_0', \tag{9}$$

where θ'' is the fraction of the surface corresponding to all double vertical complexes.

b) Formation of triple, quadruple, etc. vertical complexes:

$$\text{vapor molecules} + \text{double vertical complexes} \rightleftarrows$$

$$\rightleftarrows \text{ triple vertical complexes, etc.}$$

The constants of these equilibria are

$$K''' = \theta'''/h\theta''; \qquad K'''' = \theta''''/h\theta'''; \ldots \tag{10}$$

We assume*, as in the derivation of the BET equation, that

$$K'' \simeq K''' \simeq \ldots \simeq K_l. \tag{11}$$

The total adsorption is equal to the sum of the adsorption quantities in vertical complexes of each kind (10), i.e.

$$\alpha = \alpha_m(\theta'_0 + 2\theta'' + 3\theta''' + \ldots) =$$

$$= \alpha_m\theta'_0[1 + 2K_{lh} + 3(K_{lh})^2 + \ldots]. \tag{12}$$

Further, by the definition of θ'_0 and from (9), (10), and (11):

$$\theta' = \theta'_0 + \theta'' + \theta''' + \ldots =$$

$$= \theta'_0\{1 + K_{lh}[1 + K_{lh} + (K_{lh})^2 + \ldots]\} = \frac{\theta'_0}{1 - K_{lh}}. \tag{13}$$

The sum in square brackets in (12) is the derivative of the sum in square brackets in (13) (10); therefore the total degree of filling, taking (13) into account, is

$$\theta = \frac{\alpha}{\alpha_m} = \frac{\theta'_0}{(1 - K_{lh})^2} = \frac{\theta'}{1 - K_{lh}} = \frac{\theta'}{1 - h} \tag{14}$$

($K_l = 1$, because at $h = 1$, $\alpha = \infty$). Thus, $\theta' = \theta(1-h)$, where θ' represents the adsorption in the first layer (5), (6). Therefore the equation of polymolecular adsorption, taking into account the formation of horizontal complexes, takes the form

$$\theta(1 - h) = \frac{K'_1 h[1 - \theta(1 - h)]}{1 - K_n K'_1 h[1 - \theta(1 - h)]}, \tag{15}$$

or, in linear form:

$$\frac{\theta(1-h)}{h[1-\theta(1-h)]} = K_1' + K_n K_1' \theta(1-h). \tag{16}$$

---

* Approximately, since the contribution of the adsorbent field to the adsorption energy decreases with distance from the surface, i.e., as the vertical complex increases. This makes the derivation inaccurate at large h, as in the case of the BET equation (1).

This equation describes polymolecular adsorption isotherms both with a convex and with a concave initial part (with one and with two inflection points). For $K_n \approx 0$ it passes into an equation with a convex initial part

$$\theta = \frac{K_1' h}{(1-h)(1+K_1' h)}; \qquad \frac{h}{a(1-h)} = \frac{1}{a_m K_1'} + \frac{1}{a_m} h. \tag{17}$$

This equation coincides with the BET equation if $K_1' \gg 1$, i.e., for strongly adsorbed substances. For weakly adsorbed substances (small K_1', large K_n), at large h, θ remains still small; therefore (17) passes into

$$\theta(1-h) \approx \frac{K_1' h}{1 - K_n K_1' h}, \qquad \frac{h}{a(1-h)} \approx \frac{1}{a_m K_1'} - \frac{K_n}{a_m} h, \tag{18}$$

i.e., it becomes linear in the coordinates of the BET equation, but with a negative slope.

The description given above of vapor adsorption with the formation of both vertical and horizontal complexes is approximate, since it contains assumptions (3) and (11). In reality, the energy and entropy of adsorption depend on the coordination of molecules in the complexes. This also applies to the completion of adsorption in each layer, which may be associated with an increased energy.

Of great interest are cases in which an isotherm, concave at the beginning, passes through two inflection points, for example in the adsorption of methanol and methylamine vapors on graphitized carbon black ([3,11,12]). These cases are well described by equation (15). In work ([13]), isotherms of this type were described by methods of statistical thermodynamics on the basis of the concept of a localized layer with an appropriate choice of constants. Isotherms of monomolecular adsorption with allowance for adsorbate–adsorbate interaction can be described on the basis of a two-dimensional analogue of the van der Waals equation ([14])*. A comparison of various equations of isotherms of mono- and polymolecular adsorption with experiment will be made in the following communication.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
26 VI 1957

CITED LITERATURE

1. N. N. Avgul, G. I. Berezin et al., ZhFKh, **30**, 2106 (1956).
2. N. N. Avgul, G. I. Berezin et al., Izv. AN SSSR, OKhN, **1957**, 1021.
3. A. V. Kiselev, N. N. Kovaleva, ZhFKh, **30**, 2775 (1956).
4. N. N. Avgul, O. M. Dzhigit, A. V. Kiselev, DAN, **86**, 95 (1952).
5. N. N. Avgul, O. M. Dzhigit et al., DAN, **92**, 105 (1952); **101**, 285 (1955).
6. O. Theimer, Trans. Farad. Soc., **48**, 326 (1952).
7. M. M. Dubinin, V. V. Serpinskii, DAN, **99**, 1033 (1954).
8. M. M. Dubinin, E. D. Zaverina, V. V. Serpinskii, J. Chem. Soc., **1955**, 1760.
9. L. N. Kurbatov, *Collection: Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 223.
10. S. Brunauer, *Adsorption of Gases and Vapors*, IL, 1948.
11. R. A. Beebe, R. M. Dell, J. Phys. Chem., **59**, 754 (1955).
12. C. Pierce, R. N. Smith, J. Phys. Chem., **54**, 356 (1950).
13. R. M. Barrer, W. I. Stuart, J. Chem. Soc., **1956**, 3307.
14. J. H. de Boer, *The Dynamical Character of Adsorption*, Oxford, 1953.

* To the adsorption-isotherm equation (5) there corresponds the equation of state

$$\pi\omega = kT(1 + B_1/\omega + B_2/\omega^2 + ...), \qquad (19)$$

where π is the two-dimensional pressure, ω is the area in the monolayer per adsorbate molecule, and B_1, B_2 are coefficients.

Equation (5) is also obtained upon introducing activity coefficients into (1), if it is assumed that their dependence on θ' is expressed by a linear function in the exponent and this function is expanded in a series, retaining only the linear term.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.