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SIMULATION OF ADSORPTION AND ABSORPTION PROCESSES BASED ON PHENOMENOLOGICAL THERMODYNAMICS

A. V. Tvardovskii and V. Yu. Yakovlev UDC 541.183

Using the phenomenological-thermodynamics method, we have derived an equation which is one possible form of representation of interphase equilibrium. It has been shown that this equation yields, as particular cases, the well-known equations of Henry, Langmuir, Fowler–Guggenheim, Temkin, and Brunauer–Emmett–Teller. The equation proposed can provide a basis for simulating adsorption and absorption processes in highly diverse systems, including swelling ones.

Numerous equations of adsorption and absorption reflecting particular properties of systems have been derived at present by highly diverse methods. Moreover, the number of these equations is increasing constantly, and it is believed that this number can be completely unlimited, since the objects under consideration are so different and highly diverse in nature. The most useful are the investigations (for example, [1–8]), whose main objective is to systematize models and to describe equilibriums from a unified viewpoint.

In the enumerated works, equations are given that reflect, in different forms, the general condition of equilibrium of the phase. For example, in [9, 10] one more equation to analyze interphase equilibriums is presented. The application of the results of any of the mentioned works is determined by the complexity of the considered systems and the tests of the researchers themselves.

The derivation of an equation which is one form of representation of the general condition of interphase equilibrium, as applied to swelling systems, seems to be pressing. This is associated with the absence of reliable sorption equations for these systems and with the complexity of the latter. It should be noted here that the great interest in sorption on swelling sorbents is motivated by the increasing application of sorbents as a means for separation of gaseous mixtures and solutions, purification of waste water, degassing, distillation (desalination), environmental protection, etc. This problem is urgent in connection with the employment of facilities for individual and group protection from toxic agents. One should also include here the use of swelling sorbents in medicine, for example, to remove noxious substances from the blood (hemosorption), etc.

Let us consider a two-component (sorbent and retained gas) condensed phase which is in equilibrium with the gas; the sorbent is assumed to be nonvolatile. This condensed phase has energy E, entropy S, volume V, etc., and contains the number of moles n_{ant} and n_{ads}.

Such an approach is understood in the case where the sorbent with insignificant surface effects (compared to the volume effects) is considered. However, if the sorbent possesses noticeable surface effects, it is implied that in all the considered processes the change in the quantity n_{ant} by dn_{ant} is related to the addition of the pure sorbent with the same dispersion degree, specific surface, etc., as in the case of a pure component of the sorbent used to produce the initial specimen. Thus, in those cases where the expression "surface size" has a meaning, this size is in proportion to n_{ant} and is not an additional independent variable [11].

Using the conventional methods of the thermodynamics of solutions, we can, for example, write

$$dE = TdS - PdV + \mu_{\text{ads}}dn_{\text{ads}} + \mu_{\text{ant}}dn_{\text{ant}}\,, \quad d\mu_{\text{ads}} = -\bar{s}_{\text{ads}}dT + \bar{v}_{\text{ads}}dP + (\partial\mu_{\text{ads}}/\partial a)_{T,P}\,da\,,$$

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where $a = \dfrac{n_{\text{ads}}}{n_{\text{ant}}}$, $\bar{s}_{\text{ads}} = \left(\dfrac{\partial S}{\partial n_{\text{ads}}}\right)_{n_{\text{ant}}T,P}$, etc.

For the gas the following relation will hold:

$$d\mu_{\text{g}} = -\tilde{s}_{\text{g}}dT + \tilde{v}_{\text{g}}dp \;.$$

In the case of equilibrium between the gas and the condensed phase we have $d\mu_{\text{g}} = d\mu_{\text{ads}}$ and, consequently,

$$-\bar{s}_{\text{ads}}dT + \bar{v}_{\text{ads}}dP + \left(\frac{\partial \mu_{\text{ads}}}{\partial a}\right)_{T,P} da = -\tilde{s}_{\text{g}}dT + \tilde{v}_{\text{g}}dp \;.$$

Under ordinary experimental conditions, $P = p$; therefore, for the constant a we have

$$\left(\frac{\partial p}{\partial T}\right)_a = \frac{\tilde{s}_{\text{g}} - \bar{s}_{\text{ads}}}{\tilde{v}_{\text{g}} - \bar{v}_{\text{ads}}} \;.$$

Assuming that $\bar{v}_{\text{g}} >> \bar{v}_{\text{ads}}$, we write

$$\left(\frac{\partial p}{\partial T}\right)_a = \frac{\tilde{s}_{\text{g}} - \bar{s}_{\text{ads}}}{\tilde{v}_{\text{g}}} = \frac{q_{\text{st}}}{T\tilde{v}_{\text{g}}} \;. \tag{1}$$

Differentiation of the left-hand side of Eq. (1), under the assumption that the gaseous phase is ideal, gives

$$\left(\frac{\partial p}{\partial T}\right)_a = nk + kT\left(\frac{\partial n}{\partial T}\right)_a = nk + kT\frac{d_T n}{dT} \;. \tag{2}$$

In the last expression, $d_T n = \left(\dfrac{\partial n}{\partial T}\right)_a dT$ is the so-called partial differential of n with respect to T. Substituting Eq. (2) into Eq. (1) and rearranging it, we obtain

$$d \ln (n) = \frac{q_{\text{st}} - RT}{RT^2} dT \;.$$

Integration and rearrangement of the last expression is not a very complicated problem [12]. But the simplest derivation of the equation sought can be represented in the following manner.

As is known, $G = H - TS$. In equilibrium transition of one mole of the substance from the sorbed state to a gaseous state, we will have

$$\Delta\bar{g} = \Delta\bar{h} - T\Delta\bar{s} = 0 \quad \text{or} \quad \tilde{h}_{\text{g}} - \bar{h}_{\text{ads}} = T(\tilde{s}_{\text{g}} - \bar{s}_{\text{ads}}) \;.$$

The change in the entropy of the mole of the substance in its transition from one state to another is determined as follows [13]:

$$\Delta S = S(V, T) - S(V_0, T_0) = \int_{V_0,T_0}^{V_0,T} \frac{C_V dT}{T} + \int_{T,V_0}^{T,V} \left(\frac{\partial S}{\partial V}\right)_T dV \;.$$

It is obvious that at $T = \text{const}$ the change in the entropy depends only on the volumetric characteristics. To calculate the change in the molar entropy of an ideal gas at $T = \text{const}$ we use the formula [13]

$$\Delta S = R \ln \left(\frac{n_{\text{in}}}{n_{\text{fin}}} \right).$$

As applied to our situation, we can write

$$\Delta \bar{s} = - R \ln \left(\frac{n_{\text{g}}}{N_{\text{A}} / (V_{\text{ads}} - F_{\text{ads}})} \right). \tag{3}$$

Using formula (3) and the relation between the enthalpy and entropy changes of one mole of the substance in its equilibrium transition from the sorbed state to a gaseous state, we obtain

$$\frac{n_{\text{g}}}{N_{\text{A}} / (V_{\text{ads}} - F_{\text{ads}})} = \exp \left(- \frac{q_{\text{st}}}{RT} \right) \quad \text{or} \quad n_{\text{g}} = \frac{N_{\text{A}}}{V_{\text{ads}} - F_{\text{ads}}} \exp \left(- \frac{q_{\text{st}}}{RT} \right). \tag{4}$$

We multiply the left-hand side and the right-hand side of Eq. (4) by kT:

$$p = n_{\text{g}} kT = \frac{N_{\text{A}} kT}{V_{\text{ads}} - F_{\text{ads}}} \exp \left(- \frac{q_{\text{st}}}{RT} \right) \quad \text{or} \quad p = \frac{RT}{V_{\text{ads}} - F_{\text{ads}}} \exp \left(- \frac{q_{\text{st}}}{RT} \right). \tag{5}$$

If the gaseous phase is nonideal, then we have

$$p = z \frac{RT}{V_{\text{ads}} - F_{\text{ads}}} \exp \left(- \frac{q_{\text{st}}}{RT} \right). \tag{6}$$

We have presented the general thermodynamic approach to description of adsorption and absorption equilibriums. In Eqs. (5) and (6), the entropy and energy factors are the functions of a and of the temperature T. Using strictly definite models, i.e., assigning these functions, it is possible to obtain specific adsorption and absorption equations from expressions (5) and (6). We can demonstrate this with some examples.

The Henry Equation [14]. For this case of adsorption the assumptions $z = 1$ and $F_{\text{ads}} = 0$ will hold. Then Eq. (6) will be written as follows:

$$p = \frac{N_{\text{A}}}{V_{\text{ads}}} kT \exp \left(- \frac{q_{\text{st}}}{RT} \right). \tag{7}$$

in which $N_A / V_{\text{ads}} = n_{\text{ads}}$. In this case, the concentration n_{ads} can be expressed by the linear dependence

$$n_{\text{ads}} = \frac{a n_{\text{ads}}^{\text{s.layer}}}{a_{\text{s.layer}}}. \tag{8}$$

Taking into account the fact that in this simple adsorption model the lateral interactions of the adsorbed molecules are neglected and only the bonds between the adsorbate and the adsorbent occur ($q_{\text{st}} = \text{const}$ (the surface is homogeneous)), we obtain

$$p = Ka, \tag{9}$$

where

$$K = \frac{n_{\text{ads}}^{\text{s.layer}}}{a_{\text{s.layer}}} kT \exp \left(- \frac{q_{\text{st}}}{RT} \right) = \frac{RT}{\frac{V^{\text{s.layer}} \mu}{m}} \exp \left(- \frac{q_{\text{st}}}{RT} \right), \quad \frac{V^{\text{s.layer}}}{m} = s\tau.$$

Formula (9) has been obtained from Eq. (7) with account for Eq. (8).

The Langmuir Equation [15]. In this model, the following assumptions are used: $z = 1$ and the adsorbent surface is implied to be homogeneous as well. Compared to the Henry model, the size of the adsorbed molecules is here considered. Therefore, from Eq. (6) it follows that

$$p = \frac{RT}{CV_{\text{ads}}} \exp\left(-\frac{q_{\text{st}}}{RT}\right) = \frac{N_{\text{A}} kT}{CV_{\text{ads}}} \exp\left(-\frac{q_{\text{st}}}{RT}\right), \tag{10}$$

where $C = (V_{\text{ads}} - F_{\text{ads}})/V_{\text{ads}}$.

Since the lateral interactions of the molecules are neglected and it is assumed that $q_{\text{st}} = \text{const}$, from Eq. (10) with account for Eq. (8) we have

$$p = a \frac{n_{\text{ads}}^{\text{s.layerí}}}{a_{\text{s.layer}}} kT \frac{\exp\left(-\dfrac{q_{\text{st}}}{RT}\right)}{C} = \frac{Ka}{C} = \frac{Ka_{\text{s.layer}}\theta}{1-\theta} = \frac{K_{\text{adsorp}}\theta}{1-\theta}\ . \tag{11}$$

In Eq. (11), $K_{\text{adsorp}} = Ka_{\text{s.layer}} = \text{const}$, while $(1 - \theta)$ is nothing but C. Expression (11) is known as the Langmuir equation.

The Fowler–Guggenheim Equation [16]. The Langmuir model presupposes that adsorbed molecules interact with adsorption centers with a certain energy and at the same time do not interact with each other. The possibility for this lateral interaction is provided in the Fowler–Guggenheim model. The probability of molecular adsorption on this center is equal to θ (coverage). If each adsorption center has z' adjacent centers, then the probability of location of the adsorbed molecule on one adjacent center comprises $z'\theta$. Thus, the fraction of the adsorbed molecules interacting with each other is equal to $(z'\theta)/2$ (the factor 1/2 is introduced so as not to take account of each molecule twice). If the energy of the lateral interaction of two molecules is equal to w, then the mean energy of the adsorption increases additionally by $z'\omega\theta/2$, while the differential energy of adsorption increases by $z'\omega\theta$ [17]. Indeed, taking into account the relation between the mean and differential quantity $\partial(\tilde{u})/\partial N = \bar{u}$, we obtain

$$\frac{\partial\left[\left(\dfrac{z'\omega\theta}{2}\right)N\right]}{\partial N} = \frac{\partial\left[\left(\dfrac{z'\omega\dfrac{N}{N^*}}{2}\right)N\right]}{\partial N} = \frac{z'\omega\dfrac{N}{N^*}}{2} + \frac{z'\omega\dfrac{N}{N^*}}{2} = z'\omega\frac{N}{N^*} = z'\omega\theta\ .$$

Thus, if, under the same assumptions as in the case of the Langmuir model, we introduce the additional term $z'\omega\theta$, responsible for the lateral interaction of the molecules, into the heat q_{st} of Eq. (6), we obtain the Fowler–Guggenheim equation

$$p = \frac{K_{\text{adsorp}}\theta}{1-\theta} \exp\left(-\frac{z'\omega\theta}{RT}\right),$$

where ω is the energy of the lateral interaction of two molecules per mole.

The Temkin Equation [18]. This model refers to the case of monomolecular adsorption on the inhomogeneous surface of the adsorbent when q_{st} depends linearly on θ:

$$q_{\text{st}} = q_0\,(1 - \alpha\theta)\ .$$

By substituting the last expression into Eq. (7) and allowing that, as above, $z = 1$, we obtain the Temkin equation

$$p = \frac{K_{\text{adsorp}}\theta}{1-\theta} \exp\left(\frac{\alpha q_0 \theta}{RT}\right).$$

It should be noted that the models given by Henry, Langmuir, Fowler–Guggenheim, and Temkin can also be related to the sorption models. But in this case certain characteristics entering into the constants of the enumerated equations will have a somewhat different meaning associated with the special properties of absorption of the sorbate.

The Brunauer–Emmett–Teller Equation. As is known, this model refers to the case of polymolecular adsorption of a vapor on the homogeneous surface of the adsorbent. A distinguishing feature of vapor adsorption is the transition to volume condensation at a limiting pressure which is equal to the saturated vapor pressure of a liquid $p = p_S$. For the Brunauer–Emmett–Teller model it is assumed that under the indicated conditions the adsorption of the vapor of liquids, wetting a solid, becomes infinite. In derivation of the equation we neglected the lateral interactions of the adsorbed molecules but implied connections between the layers. Moreover, the assumption was made that in all the layers, except for the first one, the heat of adsorption was equal to the molar heat of condensation.

According to the Brunauer–Emmett–Teller model, the adsorption pattern for any value of the adsorption is a set of noninteracting complexes of the adsorbed molecules with different degrees of multiplicity.

If we consider the equilibrium of the complexes and the gaseous phase based on expression (6) and perform the corresponding summation, we can obtain a polymolecular-adsorption equation of the Brunauer–Emmett–Teller type with constants having a clear physical meaning.

Thus, using Eq. (6), first we consider the equilibrium of unit complexes with the gaseous phase. In so doing, the folowing equation is obtained:

$$p = \frac{n_1}{C_1} kT \exp\left(-\frac{q_{\mathrm{st},1}}{RT}\right). \tag{12}$$

The compressibility factor of the gaseous phase here and below is assumed to be equal to unity; $C_1 = (V_1 - F)/V_1 = 1 - \theta$. It is clear that V_1 is determined by the size of the adsorbent surface and by the diameter (or the linear dimension) of the adsorbed molecule. We should emphasize that the concentration n_1 allows only for those molecules which precisely refer to the unit complexes located in the volume V_1.

Now, taking into account the fact that the lateral interactions are absent, it is possible to assume that the adsorbent surface is uniformly covered with molecules. Therefore,

$$n_1(a) = \frac{a_1 n_{\mathrm{ads}}^{\mathrm{s.layer}}}{a_{\mathrm{s.layer}}}. \tag{13}$$

Expression (12) with account for Eq. (13) can be represented in the following manner:

$$p = a_1 \frac{n_{\mathrm{ads}}^{\mathrm{s.layer}}}{a_{\mathrm{s.layer}}} kT \frac{\exp\left(-\frac{q_{\mathrm{st},1}}{RT}\right)}{C_1} = \frac{K a_{\mathrm{s.layer}} \theta_1}{1 - \theta} = \frac{K_{\mathrm{adsorp}} \theta_1}{1 - \theta} = \frac{\theta_1}{K_1 (1 - \theta)}, \tag{14}$$

where $K = K_{\mathrm{adsorp}}/a_{\mathrm{s.layer}}$, and

$$\frac{1}{K_1} = K_{\mathrm{adsorp}} = K a_{\mathrm{s.layer}}. \tag{15}$$

In Eq. (14), the difference $(1 - \theta)$ can be replaced by the quantity θ_0 that characterizes the fraction of the free adsorbent surface. Thus, we have the Langmuir-type adsorption with allowance for the fact that on the adsorbent surface there are also complexes of another multiplicity.

Next, we also consider the Langmuir-type adsorption on the molecules interacting immediately with the surface. In this case $p = \theta_2/(K_2\theta_1)$, while the constant $1/K_2$ (with account taken of the model assumptions) is determined in the following manner:

$$\frac{1}{K_2} = n_{\mathrm{liq}} kT \exp\left(-\frac{q_{\mathrm{liq}}}{RT}\right). \tag{16}$$

In what follows, the adsorption on the molecules of the second, third, etc., layers is considered. In the general case we obtain

$$p = \frac{\theta_{i+1}}{K_{i+1}\theta_i} . \tag{17}$$

Taking into consideration the assumption of the Brunauer–Emmett–Teller model, we can write

$$K_2 \approx K_3 \approx ... \approx K_{\text{liq}} . \tag{18}$$

Next, from the general considerations it follows that with increase in the pressure, the smoothing will occur in the surface fractions covered with complexes of different types, i.e., for $p/p_s \to 1$, $\theta_{i+1}/\theta_i \to 1$. Therefore, Eq. (17) gives $p_s = 1/K_{\text{liq}}$.

Further derivation can be carried out according to a commonly accepted scheme. In this connection, the value of the adsorption is calculated as follows:

$$a = a_{\text{s.layer}} (\theta_1 + 2\theta_2 + 3\theta_3 + ...) = a_{\text{s.layer}} (\theta_1 + 2K_{\text{liq}}\, p\theta_1 + 3\, (K_{\text{liq}}\, p)^2\, \theta_1 + ...) =$$

$$= a_{\text{s.layer}} K_1 p\theta_0\, (1 + 2\, (p/p_s) + 3\, (p/p_s)^2 + ...) . \tag{19}$$

It is quite obvious that the series enclosed in the parentheses in Eq. (19) represents the derivative with respect to p/p_s of the following series: $\left(1 + \frac{p}{p_s} + \left(\frac{p}{p_s}\right)^2 + ...\right)$, which is a decreasing geometric progression whose sum is equal to $1 \Big/ \left(1 - \frac{p}{p_s}\right)$. Thus, taking the derivative, we obtain

$$a = \frac{a_{\text{s.layer}} K_1 p\theta_0}{\left(1 - \frac{p}{p_s}\right)^2} . \tag{20}$$

The fraction of the free adsorbent surface θ_0 can be found from the apparent formula

$$\theta_0 = 1 - (\theta_1 + \theta_2 + \theta_3 + ...) = 1 - K_1 p\theta_0 \left(1 + \frac{p}{p_s} + \left(\frac{p}{p_s}\right)^2 + \left(\frac{p}{p_s}\right)^3 + ...\right) = 1 - \frac{K_1 p\theta_0}{1 - \frac{p}{p_s}} . \tag{21}$$

In deriving Eq. (21), the decreasing geometric progression $\left(1 + \frac{p}{p_s} + \left(\frac{p}{p_s}\right)^2 + ...\right)$ was also replaced by its sum. From relation (21) it follows that

$$\theta_0 = \frac{1 - \frac{p}{p_s}}{1 + K_1 p - \frac{p}{p_s}} . \tag{22}$$

Substitution of Eq. (22) into Eq. (20) will yield

$$a = \frac{a_{\text{s.layer}} K_1 p}{\left(1 + K_1 p - \frac{p}{p_s}\right)\left(1 - \frac{p}{p_s}\right)} \tag{23}$$

or

$$\frac{a}{a_{\text{s.layer}}} = \frac{C\dfrac{p}{p_{\text{s}}}}{\left(1 - \dfrac{p}{p_{\text{s}}}\right)\left(1 + (C-1)\dfrac{p}{p_{\text{s}}}\right)}, \tag{24}$$

where $C = K_1/K_{\text{liq}}$. Taking into account Eqs. (14)–(16) and (18), we obtain

$$C = \frac{n_{\text{liq}}}{n_{\text{ads}}^{\text{s.layer}}} \exp\left(\frac{q_{\text{st,1}} - q_{\text{liq}}}{RT}\right). \tag{25}$$

As is known, expressions (23) and (24) correspond to the Brunauer–Emmett–Teller equation of polymolecular adsorption [19]. Unlike the classical variant, the pre-exponential factor or the entropy factor in Eq. (25) has a clear physical definition.

The Brunauer–Emmett–Teller Equation for a Finite Number of Layers f. Using this approach, it is possible to obtain the Brunauer–Emmett–Teller equation for a finite number of layers *f*. To do this, we must restrict ourselves in expressions (19) and (21) only to summation over *f* layers [20]:

$$a = \frac{a_{\text{s.layer}} K_1 p \left[1 - \left(\dfrac{p}{p_{\text{s}}}\right)^{f}\left(1 + f - f\dfrac{p}{p_{\text{s}}}\right)\right]}{\left(1 - \dfrac{p}{p_{\text{s}}}\right)\left(1 + K_1 p\left(1 - \left(\dfrac{p}{p_{\text{s}}}\right)^{f}\right) - \dfrac{p}{p_{\text{s}}}\right)}.$$

Thus, using the method of phenomenological thermodynamics and the concept of free volume, we have derived an equation which is one possible form of representation of interphase equilibrium. It has been shown that the well-known equations of Henry, Langmuir, Fowler–Guggenheim, Temkin, and Brunauer–Emmett–Teller with constants having a clear physical meaning follow from this equation as particular cases. The equation proposed can provide a basis for simulating adsorption and absorption processes in highly diverse systems, including swelling ones.

NOTATION

n_{ant} and n_{ads}, number of the sorbent (adsorbent) and sorbate (adsorbate) moles; T, temperature; P, hydrostatic pressure exerted by a hypothetical piston or, partly, by a hypothetical foreign inert gas; μ_{ads}, chemical potential of the sorbate; μ_{ant}, chemical potential of the sorbent; $\bar{s}_{\text{ads}}$, partial molar entropy of the sorbate; $\bar{v}_{\text{ads}}$, partial molar volume of the sorbate; a, sorption; μ_{g}, chemical potential of the gas; $\tilde{s}_{\text{g}}$, molar entropy of the gas; $\tilde{v}_{\text{g}}$, molar volume of the gas; p, gas pressure; n, concentration of molecules in the gaseous phase; k, Boltzmann constant; R, universal gas constant; G, Gibbs energy; H, enthalpy; $\tilde{h}_{\text{g}}$, molar enthalpy of the gaseous phase; $\bar{h}_{\text{ads}}$, partial molar enthalpy of the sorbed substance; C_V, molar heat capacity of the substance with $V = \text{const}$; V_0 and V, molar volumes of the substance in the initial and final state; T_0 and T, initial and final temperatures; n_{in} and n_{fin}, initial and final concentrations of molecules in the gas; n_{g}, concentration of molecules in the gaseous phase; N_A, Avogadro number; V_{ads}, molar volume of the sorbed substance changing uniformly to the gaseous phase; F_{ads}, inaccessible volume for motion of one mole of the sorbed substance; q_{st}, isosteric heat of sorption; z, compressibility factor of the gaseous phase; n_{ads}, running value of the concentration of the adsorbed molecules; $n_{\text{ads}}^{\text{s.layer}}$ and $a_{\text{s.layer}}$, limiting values of the concentration and adsorption in covering a single layer, respectively; $V^{\text{s.layer}}$, volume of a single layer; m, mass of the adsorbent; s, specific surface of the adsorbent; τ, height of a single layer; μ, molar mass of the adsorbate; K, Henry constant; θ, coverage of the adsorbent surface; z', number of adjacent adsorption centers for the adsorption center in the Fowler–Guggenheim model; $\tilde{u}$ and $\bar{u}$, mean and differential energies of adsorption, respectively; N, number of adsorbed molecules; N^*, number of adsorption centers; ω, energy of the lateral interaction of two molecules; q_0 and α, constant expressions for the heat in the Temkin model; p_{s}, saturated vapor pressure of the liquid; $q_{\text{st,1}}$, adsorption heat of the molecules of the first layer; n_1, concentration of the adsorbed molecules belonging to unit complexes; V_1, volume in which unit adsorption complexes (volume of a single layer) are located and F, volume inaccessible to these complexes; a_1, running value of the adsorption related to unit adsorption complexes; θ_0, fraction of the free adsorbent surface; θ_1, θ_2, ..., θ_i, and θ_{i+1}, fractions of the adsorbent surface covered with different types of complexes, respectively; n_{liq}, concentration of molecules in the liquid; q_{liq}, molar evaporation heat of the liquid; K_{adsorp}, constant in the models given by Langmuir, Fowler–Guggenheim, and Temkin; K_1, K_2, ..., K_i, K_{i+1}, and K_{liq}, constants in the Brunauer–Emmett–Teller model; p/p_s, relative vapor pressure of the adsorbed substance; f, maximum number of layers of the adsorbed substance in the Brunauer–Emmett–Teller model for a finite number of layers. Subscripts: ant, adsorbent; ads, adsorbate; g, gas; in, initial; fin, final; A, index at the Avogadro number; st, isosteric state of the system; s.layer, single layer; s, saturation; adsorp, adsorption; liq, liquid; 0, 1, 2, ..., i, and $i + 1$, indices characterizing differents states of the system.

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