

## **THE EQUIVALENCE OF QUASI-CHEMICAL AND STATISTICAL DESCRIPTION OF ADSORBATE MOLECULE ASSOCIATION IN A LOCALISED ADSORPTION MONOLAYER ON A HOMOGENEOUS SOLID SURFACE**

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### **ABSTRACT**

The analysis of Berezin and Kiselev's concept assuming linear association of molecules in a localised adsorption monolayer on the homogeneous surface of a solid adsorbent was carried out. An inconsistency due to the lack of consideration of equilibrium concentration of free adsorption sites in the formulation of the expression for the association constant has been pointed out. It was shown that the correct form of this function leads to the final adsorption equation being identical to the specific case of the Fowler-Guggenheim equation. The obtained result has been generalised to cases of branched adsorbate-adsorbate associations. A new adsorption equation limiting the association to at most the dimers has been introduced. Critical conditions for the two-dimensional condensation of the adsorption layer were determined. By applying the formalism of canonical ensemble, full equivalence of the phenomenological and statistical methods was demonstrated in the description of the intermolecular interactions in the localised adsorption monolayer.

**Keywords:** chemical equilibrium, adsorption, Berezin and Kiselev equation, adsorbate-adsorbate interactions.

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## INTRODUCTION

The development of effective methods of energy homogenisation of solid surfaces has made it possible to produce adsorbents with properties that satisfactorily imitate the model of an ideal homogeneous surface. At the same time, experimental studies using such adsorbents (e.g. graphitised carbon blacks, boron nitride, cationised zeolites, etc.) proved to be a source of qualitatively new data. Sigmoidal monolayer adsorption isotherms, with initial protuberance in the direction of the pressure axis, or increasing character of isosteric heat adsorption in area of low and average values of adsorbent surface filling, have proven the important role of adsorbate-adsorbate interactions in the process of adsorption equilibrium determination.

These results confirmed, on the one hand, the validity of the previous intuition of theoreticians, while on the other hand, they inspired further research on the possibility of including these interactions in the theoretical description of the phenomenon. Among numerous proposals for such a description, Berezin and Kiselev's concepts [1] play a pivotal role, in which adsorbate-adsorbate interactions in the localised adsorption monolayer are presented as the formation of linear associations parallel to the adsorbent surface [2]. The simplicity of the model and the ease of its application to describe experimental data resulted in a wide recognition of surface phenomena in the physicochemical environment.

In the opinion of the authors of the concept, shared by a significant portion of this academic environment, this solution was an alternative to the earlier, much less demonstrative, two-dimensional version of the Ising model [3], which in the form of the so-called quasi-chemical approximation was adapted by Fowler and Guggenheim [4]. The aim of this work is to provide a new insight into the relationship between the above-mentioned solutions. The analysis presented below utilises, first of all, the formalism of phenomenological thermodynamics, seeking, in the second stage, statistical justification of the obtained results. In a sense, the side-effect of this analysis is the authors' own proposal of a description of the dimerisation of adsorbed molecules.

### DETAILED ANALYSIS OF THE CONCEPT OF ADSORBATE-ADSORBATE ASSOCIATION ON A HOMOGENEOUS SOLID SURFACE

The concept of Berezin and Kiselev is an extension of the Langmuir model with an assumption concerning the association of pre-adsorbed molecules. The Langmuir part of the concept is limited to the description of the formation of so-called single adsorption complexes,  $A_1$ , as a result of the following "reaction" between the gas molecules of the adsorptive,  $M$  and the unoccupied binding locations of the adsorbent's surface,  $S$ :



The equilibrium of the above process is characterised by the isothermal constant  $K_1$  in the following form

$$K_1 = \frac{N_1}{p^{(B-N)}}, \quad (1)$$

where  $p$  is the pressure of the adsorbent,  $B$ ,  $N$  and  $N_1$  are the numbers of the binding sites, of all adsorbate molecules and individual adsorption complexes, respectively.

On the other hand, secondary interactions responsible for the formation of linear adsorbate-adsorbate associations are presented in the discussed concept in the form of recursion:

$$A_1 + A_{j-1} \rightleftharpoons A_j; j \geq 2 \quad (II)$$

The equilibrium constants,  $K_j$ , corresponding to the successive stages of scheme (II) are expressed by Berezin and Kiselev as follows:

$$K_j = \frac{N_j}{N_1 \cdot N_{j-1}} \quad (2)$$

where the lower index is, in each case, a multiplication of a given association.

Two more assumptions proved to be important for the completion of the model. The first one allows for the possibility of creating associations of any high factors ( $j \rightarrow \infty$ ), while the second one postulates the equality of individual  $K_j$  constants, i.e.:

$$K_2 = K_3 = \dots = K_j = K_{j+1} = \dots = K_n \quad (3)$$

The briefly presented theoretical construction leads, after appropriate transformations, to the final adsorption equation in the following form:

$$p = \frac{\theta}{K_1(1-\theta)} \frac{4}{(\sqrt{4K_n\theta+1}+1)^2} \quad (4)$$

where  $\theta = N/B$  is a dimensionless degree of surface filling of the adsorbent which, in the case of monolayer adsorption, fulfils a double inequality:  $0 \leq \theta < 1$ .

We should begin the assessment analysis of Berezin and Kiselev's concepts by stating that its undisputable value is the fact that its demonstrativeness is particularly close to those who are fluent in chemical statics issues. Demonstrating the possibility of replacing complicated statistical methods with simple formalism based on the concept of constant chemical equilibrium was, probably, the reason for the already mentioned friendly reception of equation (4) by the environment of physicochemists of surface phenomena. However, it is justified to pose the question whether the authors of the model have fully complied with the canons of the method proposed by them. The considerations below will reveal that the answer to this question must be negative.

To this end, let us recall that the chemical equilibrium constant, which is generally dependent on temperature and pressure, is expressed by the equilibrium activity of reagents and that even in the case of the assumed ideal character of these components, the arguments of the considered function are their fractions (molar or molecular) in individual phases. The adsorption phase is a single-component phase, so the fraction of this reagent is equal to 1. On the other hand, the components of the surface phase are unoccupied surface binding sites in the number of B-N and associations of various factors

in the number of  $Y=N_1+N_2+N_3+\dots$ . Hence the corresponding fractions are:

$X_B=(B-N)/(B-N+Y)$  and  $X_{A1}=N_1/(B-N+Y)$ , and the full process equilibrium constant (1),  $K_I$ , is the relation:

$$K_I = \frac{N_1}{(B-N)} \quad (5)$$

Constant  $K_I$  can be presented in the form of the product  $K_I=K_I(T)\chi(p)$ .

For ideal gas, the function  $\chi(p)$  is simply equal to pressure,  $p$ , which under the assumptions of the Langmuir model proves the correctness of equation (1). However, a similar conclusion cannot be formulated with regard to equation (2). As here, according to the findings we have:

$$K_j = \frac{N_j}{N_1 \cdot N_{j-1}} (B - N + Y) \quad (6)$$

A comparison of relationships (2) and (6) clearly shows that the discrepancy between them increases the more the difference  $N-Y$  is comparable to the number of binding sites,  $B$ . This in turn means that the adsorption equation (4) has at most the status of a low-density limit of a solution, which for the model under consideration could be called accurate. The form of this solution is obtained using obvious implications of equation (6). We should note that:

$$N_2 = \frac{K_2}{(B-N+Y)} N_1^2, \quad (7)$$

$$N_3 = \frac{K_2 K_3}{(B-N+Y)^2} N_1^3, \quad (8)$$

$$N_4 = \frac{K_2 K_3 K_4}{(B-N+Y)^3} N_1^4, \quad (9)$$

where

$$N = N_1 + 2N_2 + 3N_3 + \dots \quad (10)$$

and

$$Y = N_1 + N_2 + N_3 + \dots \quad (11)$$

Combining the equations (10) and (11) with relationships (7)-(9) and accepting the assumption (3) we obtain:

$$N = N_1 \left[ 1 + 2 \frac{K_2 N_1}{B-N+Y} + 3 \left( \frac{K_2 N_1}{B-N+Y} \right)^2 + 4 \left( \frac{K_2 N_1}{B-N+Y} \right)^3 + \dots \right] \quad (12)$$

and

$$Y = N_1 \left[ 1 + 2 \frac{K_2 N_1}{B-N+Y} + \left( \frac{K_2 N_1}{B-N+Y} \right)^2 + \left( \frac{K_2 N_1}{B-N+Y} \right)^3 + \dots \right] \quad (13)$$

Treating both of the above series as infinite and assuming the convergence of each of them, we will obtain the following system of equations:

$$N = \frac{N_1}{\left( 1 - \frac{K_2 N_1}{B-N+Y} \right)^2} \quad (14)$$

and

$$Y = \frac{N_1}{1 - \frac{K_2 N_1}{B-N+Y}} \quad (15)$$

The solution of the above series is function  $N_I/N$  in the following form:

$$\frac{N_1}{N} = \frac{4(B-N)^2}{\left[ \sqrt{4K_2 N(B-N) + B^2 + B - 2N} \right]^2} \quad (16)$$

Inserting this solution into equation (1) and taking into account the definition of the degree of occupancy of the surface of the adsorbent,  $\theta$ , ultimately gives:

$$p = \frac{\theta}{K_1(1-\theta)} \frac{4(1-\theta)^2}{\left[ \sqrt{4K_2 \theta(1-\theta) + 1 + 1 - 2\theta} \right]^2} \quad (17)$$

The conclusion that Berezin-Kiselev's equation (4) is the limit to the above expression for  $\theta < 1$  is obvious in this situation but not most important. A more important observation is that equation (17) constitutes a special case of a solution published by Fowler and Guggenheim [4] more than three decades before the publication of Berezin and Kiselev's article. This equation, based on the one-dimensional Ising model [3], is indeed accurate, just as the one-dimensional Ising model is accurate when potential energy is presented as the sum of interactions between pairs of molecules - the closest neighbours.

It is worth mentioning here that the multidimensional variant of the Ising model is a much more serious challenge and that its strict solution given by Onsager [5] concerns only a two-dimensional square-lattice model. The proposal which will be discussed below is the so-called quasi-chemical approximation [4], in which the local correlations between the closest neighbouring molecules are presented as a balance between the three types of pairs of binding sites, i.e. occupied-occupied, empty-empty and occupied-empty.

Equation (17) belongs to the family of solutions based on this approximation, which in turn allows the status of the equation (4) to be objectively assessed. Representing a low density ( $\theta \ll 1$ ) limit of a specific because one-dimensional (the number of closest neighbours of  $c=2$ ) case of quasi-chemical approximation, it is certainly not an original result. An unquestionably original method is the one adopted by its authors, which in the light of the above findings proves to be a complete equivalent to a much less demonstrative statistical method. According to the authors of this paper, this is the lasting contribution of Berezin and Kiselev to the acknowledgement of the phenomenological concept of adsorbate-adsorbate association, as a fully valid alternative to the statistical description of intermolecular interactions in the localised adsorption layer.

Accepting the above opinion as a well-argued one, we will now check the outcome of the assumption limiting the association to at most dimers of adsorbate-adsorbate. With this assumption, instead of equations (12) and (13) we have:

$$N = N_1 \left( 1 + 2K_2 \frac{N_1}{B-N_2} \right) \quad (18)$$

and

$$Y = N_1 \left( 1 + K_2 \frac{N_1}{B-N_2} \right) \quad (19)$$

hence

$$\frac{N_1}{N} = \frac{(2B-N)}{\sqrt{4K_2 N(2B-N) + B^2 + B - 2N}}, \quad (20)$$



which after insertion into equation (1) gives:

$$p = \frac{\theta}{K_1(1-\theta)} \frac{2-\theta}{\sqrt{4K_2\theta(2-\theta)+1+1-2\theta}} \quad (21)$$

The obtained adsorption equation proves to be a more accurate version of a much earlier solution [6] based on the simplified formalism of Kiselev. The relation between the former result and equation (21) is therefore the same as between equations (4) and (17).

The model assuming association of adsorbed molecules also defines the measure of this effect, i.e. the degree of association,  $\gamma$ , expressed in general by the formula:

$$\gamma = \frac{N-Y}{N} \quad (22)$$

Inserting into the above formula equations (14)-(16) and (18)-(20) gives respectively:

$$\gamma_n = \frac{4K_n \theta (1-\theta)}{(\beta_n+1-2\theta)(\beta_n+1)} \quad (23)$$

where

$$\beta_n = \sqrt{4K_n\theta(1-\theta) + 1} \quad (24)$$

and

$$\gamma_2 = \frac{2K_2 \theta (2-\theta)}{(\beta_2+1-\theta)(\beta_2+1)} \quad (25)$$

where

$$\beta_2 = \sqrt{4K_2\theta(2-\theta) + 1} \quad (26)$$

It should be noted that expressions (23) and (25) accurately meet the assumptions of the adsorbate-adsorbate association model, assuming the following limits:

$$\gamma_n = \begin{cases} 0 & \text{dla } K_n = 0 \\ 1 & \text{dla } K_n \rightarrow \infty \end{cases} \quad (27)$$

and

$$\gamma_2 = \begin{cases} 0 & \text{dla } K_2 = 0 \\ \frac{1}{2} & \text{dla } K_2 \rightarrow \infty \end{cases} \quad (28)$$

These expressions also simplify the notation of equations of adsorption giving accordingly:

$$p = \frac{\theta}{K_1(1-\theta)} (1 - \gamma_n)^2 \quad (17)$$

and

$$p = \frac{\theta}{K_1(1-\theta)} (1 - 2\gamma_2) \quad (21)$$

An important aspect of equations (17) and (21) is the identification of their parameters, i.e.  $K_1$ ,  $K_2$  and  $K_n$ . As far as the first of them is concerned, it has been shown that it is a Langmuir isothermal constant, and as a function of temperature it complies with the equation [7]:

$$K_1 = K_1^\circ \left[ \exp\left(\frac{E^\circ}{RT}\right) - 1 \right] \quad (29)$$

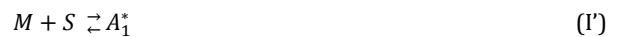
where  $E^\circ$  is an adsorption potential, while the pre-exponential factor  $K_1^\circ$  can, with the right approximation, be treated as temperature independent.

The character of  $K_2$  and  $K_n$  association constants is determined by the Langmuir assumption, preserved in the model, that at most one adsorbate molecule can occupy the binding site of the surface. This means that the adsorbate-adsorbate association does not change the volume of the network gas, which is the adsorption layer. According to the van Laar-Planck equation, both  $K_2$  and  $K_n$  are therefore pressure independent and, like  $K_1$ , are solely isothermal constants. The specific temperature dependence of these constants will be determined together with the statistical justification of the proposed description.

Now, however, let us consider the possibility of generalizing the current description, preserving its phenomenological character and taking into account the non-linear topography of the binding sites of the adsorbent surface.

For this purpose, let us assume that each binding site (excluding, of course, the border site) is surrounded by  $c$  sites closest to it. The surrounding areas define  $c/2$  independent directions that intersect in the centre of a given binding site. Along each of these directions, linear adsorbate-adsorbate associations can form, as described above.

In view of these findings, it is necessary to modify scheme (I) and equation (1) as follows:



and

$$K_1 = \frac{N_1^*}{p(B-N)} \quad (1')$$

where  $A_1^*$  is an adsorption complex that is single simultaneously for all  $c/2$  directions, while  $N_1^*$  is the number of these complexes. In turn,  $A_1$  and  $N_1$  retain their previous meanings for each direction (for example  $A_{1,j}$  and  $N_{1,j}$ , where  $j=1,2,\dots, c/2$ ).

Let us assume that the selected direction, for example  $j$ -th, contain a certain part of the total number of binding sites,  $B_j = \alpha_j B$ , where  $0 < \alpha_j \leq 1$ . This means, by necessity, that in a state of equilibrium it binds the same part of the total number of admolecules, i.e.  $\alpha_j N$ . The probability  $P(A_{1,j})$  that a "randomly" indicated admolecule belonging to this direction is a single adsorption complex  $A_{1,j}$  (it does not have to be for the other directions), i.e. we have the quotient  $N_{1,j}/\alpha_j N$ . On the other hand, in the same state of equilibrium:  $N_{1,j} = \alpha_j N_1$ , where  $N_1$  is the number of  $A_1$  complexes in the entire adsorption layer. It follows that  $P(A_{1,j})$  does not depend on  $j$  and for each individual direction it is  $N_1/N$ . The resulting probability that the indicated admolecule is the  $A_1$  complex for all directions concurrently (i.e. it is the  $A_1^*$  complex) thus takes the form:

$$P(A_1^*) = \left(\frac{N_1}{N}\right)^{\frac{c}{2}} \quad (30)$$

In view of the fact that it is possible to indicate "randomly" any of the  $N$  molecules absorbed, the equation (1) is transformed in the following manner:

$$p = \frac{N \left(\frac{N_1}{N}\right)^{\frac{c}{2}}}{K_1(B-N)} \quad (31)$$

Since in the equilibrium adsorption layer the degree of filling of binding sites in each direction is the same and equal to the total degree of filling of the adsorbent surface  $\theta$ , for the variants of maximum multiplication of adsorbate-adsorbate associations considered in this paper, the correct solution will be substitution in equation (31) expressions (16) and (20) respectively.

We will therefore obtain:

$$p = \frac{\theta}{K_1(1-\theta)} (1 - \gamma_n)^c \quad (32)$$

and

$$p = \frac{\theta}{K_1(1-\theta)} (1 - 2\gamma_2)^{\frac{c}{2}} \quad (33)$$

where  $\gamma_1$  and  $\gamma_2$  given are formulas (23) and (25) respectively.

For  $c=2$  these equations are identical with one-dimensional formulas (17) and (21), while for  $\gamma_n=\gamma_2=0$  ( $K_n=K_2=0$ ) each of them transitions into the Langmuir equation.

Taking into account in the equation (35) the dependence of the constant  $K_n$  on temperature (equation (31)) allows to definitively determine the relation between this expression and the Fowler-Guggenheim [4], based on quasi-chemical approximation. In fact, the latter turns out to be a special case of the first for  $K_n^0=1$ . This condition reflects the essential physical content contained in the functions of the separation of internal degrees of freedom, which form a pre-exponential factor in the expression for the chemical equilibrium constant.

Purely dispersive adsorbate-adsorbate interactions do not change the number of internal degrees of freedom ( $K_n^0=1$ ), while the actual association of admolecules certainly results in the inhibition of part of the rotation and the occurrence of new oscillations, hence  $K_n^0 \neq 1$ . Equation (35) therefore corrects the assumption of the purely non-specific character of adsorbate-adsorbate interactions in the Fowler-Guggenheim equation. Interesting results are obtained with the analysis of equations (35) and (36) in relation to two-dimensional adsorbate condensation. The purpose of this analysis is to determine the coordinates of the saddle point on the so-called critical isotherm. These coordinates, i.e. the critical values of the degree of filling,  $\theta_c$ , and the association constant,  $K_{n,c}$  or  $K_{2,c}$ , are in turn solutions to the system of equations  $\partial p / \partial \theta = 0$  or  $\partial^2 p / \partial \theta^2 = 0$  at  $T = \text{const}$ .

In the case of equation (35), these solutions are known in principle because they correspond to the Fowler-Guggenheim isotherm and amount to  $\theta_c=0.5$  and  $K_{n,c} = 4 \frac{(c-1)}{(c-2)^2}$  respectively, with the value  $\theta_c$  not being dependent on the number  $c$ . Let us add that  $\gamma_{n,c}=2/c$  and for example selected values  $c=4$  and  $c=6$  equal  $\gamma_{n,c}(c=4)=1/2$  and  $\gamma_{n,c}(c=6)=1/3$ , respectively.

The solution for equation (33) is qualitatively different. Here the critical value of the degree of filling of the adsorbent surface depends on the number  $c$  and is given by the formula:

$$\theta_c = \frac{c-4}{2(c-1)} \quad (34)$$

while at the same time

$$K_{2,c} = \frac{4}{c} \left(\frac{c-1}{c-4}\right)^3 \quad (35)$$

and

$$\gamma_{2,c} = \frac{2(c-1)}{c^2-4} \quad (36)$$

Thus, from the equation it follows (35) that two-dimensional adsorbate condensation is also possible when the adsorbate-adsorbate association gives most dimers, but this requires a higher symmetry of the binding sites of the adsorbent surface ( $c>4$ ). For example, for  $c=6$  we have  $\theta_c=0,2$ ,  $K_{2,c}=10,42$  and  $\gamma_{2,c}=0,3125$ .

The above analysis clearly excludes the possibility of the considered phase transition in one dimension ( $c=2$ ).

### STATISTICAL EXPLANATION OF THE DESCRIPTION OF THE ASSOCIATION OF ADMOLECULES IN THE LOCALISED ADSORPTION MONOLAYER

The statistical derivation of the Fowler-Guggenheim equation [4] does not assume, in any way, the formation on the surface of the adsorbent of different as to their multiplicity adsorbate-adsorbate associations. The essence of this derivation, based on the formalism of grand canonical ensemble, lies in the appropriate formulation of the combinatorial element in the partition function and in the determination, on this basis, of the shares of the three previously mentioned pairs of binding sites in the equilibrium. Thus, the physical image of the adsorption layer adopted by the quoted authors is fundamentally different from the one presented in this paper.

Therefore, the derivation based on this image (despite the identity of the solutions, i.e. Fowler-Guggenheim equation and equation 32)) cannot be considered as a statistical equivalent of our phenomenological description. In this situation it seems advisable to undertake an attempt to propose such an explanation of solutions (32) and (33), which, also in its statistical variant, explicitly assumes the presence of various associations constituting an equilibrium adsorption layer. The presentation of this proposal is the aim of the current chapter of this paper.

The canonical ensemble will be chosen as the basis for considerations, bearing in mind the fundamental equivalence of different statistical ensembles within the thermodynamic limit, i.e. for  $N$  and  $B$  moving towards infinity while at the same time  $N/B = \text{const}$ .

First of all, we will determine the general conditions of thermodynamic equilibrium in the adsorption system. Therefore, let the canonical sum of states of the adsorption layer,  $Z_a$ , meet the following dependence:

$$Z_a = Z_a(T, B, N_1, N_2, N_3 \dots), \quad (37)$$

$$\text{with} \\ \sum_{i \geq 1} i N_i = N = \text{const} \quad (38)$$



The symbols used above have exactly the same meaning as in the phenomenological description. Thus  $N_1, N_2, N_3 \dots$  again denote the numbers of single admolecules, dimers, trimmers, etc. respectively, and  $N$  is the total number of adsorbed molecules.

The characteristic function of the canonical syndrome, i.e. free energy,  $F_a = -kT \ln Z_a$ , achieves, as we know, the minimum in the equilibrium state with constants  $T$  and  $B$ . This means, by necessity, the maximum function  $\ln Z_a$ . Due to condition (38) it corresponds to the absolute maximum of the function

$$\chi = \ln Z_a + \alpha \sum_{i \geq 1} i N_i \quad (39)$$

where  $\alpha$  is Lagrange multiplier.

In the sought maximum  $d\chi=0$ , i.e.

$$\left(\frac{\partial \ln Z_a}{\partial N_i}\right)_{T, B, N_{j \neq i}} = -i\alpha \quad (40)$$

and

$$\left(\frac{\partial \ln Z_a}{\partial N}\right)_{T, B} = -\alpha \quad (41)$$

By replacing derivatives in the above equations with appropriate chemical potentials  $\mu_i$  and  $\mu_a$ , we obtain

$$\mu_i = i\mu_1 \quad (42)$$

and

$$\mu_1 = \mu_a \quad (43)$$

At the same time, the condition of equilibrium between the adsorption layer and the non-absorbed gas (adsorptive) induces the equality of chemical potentials of the component in both these phases, i.e.

$$\mu_a = \mu_g \quad (44)$$

The assumption of perfection of the adsorptive (justified due to the drastic difference in density of the phases under consideration) and a combination of equations (43) and (44) gives:

$$\mu_1 = kT \ln \frac{p}{kT f_g t^{-3}} \quad (45)$$

where  $p$  is the equilibrium pressure of the adsorptive, whereas

$$t = \frac{h}{\sqrt{2\pi m k T}} \quad (46)$$

with  $h$  and  $m$  constituting respectively the Planck constant and molecule mass.

The sought, both necessary and sufficient, equilibrium conditions of the adsorption system have therefore the form of equations (42) and (43).

The detailed part of the statistical explanation of the model will begin with the case of linear association ( $c=2$ ). Taking into account the assumption, according to which the components of the adsorption layer are associations in  $Y$  number (equation (11)) and free

adsorption sites in  $B-N$  number ( $N$  defined by equation (10)), we may write down the maximum segment of the canonical sum of states  $Z_a^{max}$  in the following way

$$Z_a^{max} = \frac{[B - \sum_{i \geq 1} (i-1)N_i]!}{(B - \sum_{i \geq 1} iN_i)!} \left( \prod_{i \geq 1} \frac{f_i^{N_i}}{N_i!} \right) \exp \frac{E^\circ \sum_{i \geq 1} iN_i + E^{as} \sum_{i \geq 1} (i-1)N_i}{kT} \quad (47)$$

where  $f_i$  means the internal sum of states of  $i$ -factor association, whereas  $E^{as}$  will be determined through analogy to adsorption potential,  $E^\circ$ , as associative potential.

The transformation

$$\mu_i = -kT \left( \frac{\partial \ln Z_a^{max}}{\partial N_i} \right)_{T, B, N_{j \neq i}} \quad (48)$$

leads to the expression for the chemical potential of  $i$ -factor association written down in the following form:

$$\mu_i = kT \ln \left\{ \frac{1}{f_i} \exp \left[ \frac{(i-1)E^{as}}{kT} \right] \frac{N_i (B-N+Y)^{i-1}}{(B-N)^i} \right\} \quad (49)$$

Hence, under condition (42)

$$N_i = \frac{f_i}{f_1^i} \exp \left[ \frac{(i-1)E^{as}}{kT} \right] \frac{N_1^i}{(B-N+Y)^{i-1}} \quad (50)$$

Equations (47), (49) and (50) respect the obvious fact that in the  $i$ -factor linear association  $i-1$  bonds occur between adjacent segments of the molecule. Taking this fact into account also in relation to the internal sum of states  $f_i$  allows, with a proper approximation, to record this function as follows:

$$f_i = f_1^i f_{osc}^{i-1} \quad (51)$$

where  $f_{osc}$  means the sum of states for vibrations along each bond in the association.

Assuming the harmonicity of these vibrations and assuming the energy of zero vibrations as a conventional zero we will obtain:

$$\frac{f_i}{f_1^i} = \left\{ \frac{1 - \exp \left[ -\left( l_{max} + 1 \right) \frac{\tau}{T} \right]}{1 - \exp \left( -\frac{\tau}{T} \right)} \right\}^{i-1} \quad (52)$$

Where  $\tau$  equal to  $h\nu/k$  has the sense of the characteristic temperature, while  $\gamma$  and  $l_{max}$  indicate, respectively, the frequency of vibrations and the value of the oscillating quantum number, which once exceeded, sees the dissociation of adsorbate-adsorbate bond occurring. This means that  $(l_{max}+1)h\nu = E^{as}$ . Hence the equation (50) can be written in the form of

$$N_i = \left\{ K_2^0 \left[ \exp \left( \frac{E^{as}}{kT} \right) - 1 \right] \right\}^{i-1} \frac{N_1^i}{(B-N+Y)^{i-1}} \quad (53)$$

where:

$$K_2^0 = \frac{e^{\frac{\tau}{T}}}{e^{\frac{\tau}{T}-1}} \quad (54)$$

Equations (53) and (54) also explain the problem of the dependence of the association constant on temperature. For  $i=2$  we can, according to equation (7), write down the following:

$$K_2 = K_2^0 [\exp(E^{\text{as}}/kT) - 1] \quad (55)$$

Currently there is no longer any doubt that a further derivation would give a sequence of equations (10)-(13) and lead, depending on the accepted variant of the maximum factor of adsorbate-adsorbate associations (i.e.  $\infty$  or 2), to equations (17) or (21). It should be stressed that the constants  $K_2$  and  $K_n$  are identical, and the difference in notation indicates only one of the two variants of the model.

Let us now move on to the description of a non-linear association. It should be noted at the beginning that the total number of distributions,  $D(N;B)$ ,  $N$  molecules of the adsorbate on  $B$  binding sites of the adsorbent surface does not depend on the topography of these sites and the assumption: "no more than one molecule at a site" it equals:

$$D(N;B) = \frac{B!}{N!(B-N)!} \quad (56)$$

Hence, the combinatorial factor of the sum of states (47)  $\ell_{c=2}$ , may formally be written down in the form:

$$\varphi_{c=2} = \frac{B!}{N!(B-N)!} X_{c=2} \quad (57)$$

where

$$X_{c=2} = \frac{N!(B-N+Y)!}{B! \prod_i (N_i!)} \quad (58)$$

An argumentation analogous to that presented in the phenomenological variant allows to assume that in general for  $c \geq 2$ :

$$\varphi_{c \geq 2} = \frac{B!}{N!(B-N)!} \left[ \frac{N!(B-N+Y)!}{B! \prod_i (N_i!)} \right]^{c/2} \quad (59)$$

Maintaining the unchanged form of the other factors of the sum of states (47), we obtain the following expression for chemical potential  $\mu_i$ :

$$\mu_i = kT \ln \left\{ \frac{1}{\prod_i f_i^{c(i-1)/2}} \exp \left[ - \frac{iE^0 + \frac{c(i-1)}{2} E^{\text{as}}}{kT} \right] \frac{N_i^{c/2} (B-N+Y)^{\frac{c(i-1)}{2}}}{N^{i(c/2-1)} (B-N)^i} \right\} \quad (60)$$

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The conditions of thermodynamic equilibrium (42)-(44) together with equation (45) lead directly to adsorption equations (32) and (33), respectively, in which the degrees of associations  $\gamma_n$  and  $\gamma_2$  are still defined by equations (23) and (25),  $K_1$  retains the form of equation (29), whereas:

$$K_2 = K_n = \left\{ \frac{e^{\frac{\tau}{T}}}{e^{\frac{\tau}{T}} - 1} \left[ \exp \left( \frac{E^{\text{as}}}{kT} - 1 \right) \right] \right\}^{2/c} \quad (61)$$

Which conclusively confirms the complete equivalence of both methods presented in this paper (i.e. quasi-chemical and statistical) of the description of adsorbate-adsorbate association in a localised adsorption monolayer on homogeneous surfaces.

## CONCLUSIONS

The results of the above considerations allow to formulate the following conclusions:

- The identification of adsorbate-adsorbate interactions in the localised adsorption layer with the formation of linear associations between admolecules, as postulated by Berezin and Kiselev, is an original concept and leads to an uncomplicated adsorption equation.
- It is wrong to see the Berezin-Kiselev equation as an alternative to the former Fowler-Guggenheim isotherm, because the correct application of the rules of chemical statistics proves that it is only a low-density limit of a specific case (the number of closest neighbours  $c=2$ ) of the latter.
- Limiting the factor of associations to no more than dimers results in an adsorption equation allowing for two-dimensional condensation of the adsorption layer with sufficiently high symmetry of binding sites.
- All results obtained by phenomenological method are fully confirmed by statistical data on the basis of the formalism of canonical ensemble.

