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# Multilayer sorption parameters: BET or GAB values?

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## Abstract

The differences between the sets of values for the monolayer capacity and the energy constant obtained by sorption data regressions using two related multilayer sorption isotherms, the two-parameter BET (Brunauer–Emmett–Teller) and the three-parameter GAB (Guggenheim–Andersen–de Boer) isotherms, are analysed. Experimentally, it is found that the GAB monolayer value is always higher than the BET value and the GAB energy constant results always lower than the BET constant. Mathematical and physical reasons are given which explain these differences. The third GAB parameter determines the greater versatility of the GAB equation, which has a quite larger range of applicability than the BET isotherm. It is shown that in terms of the three GAB constants, the two BET parameters are qualitatively and quantitatively reproduced as well as their dependence on the regression interval used in the BET regression, justifying in this way the above-mentioned inequalities. The typical upswing in the BET plots after a (pseudo) linear range at lower activities of the sorbate is also explained. All these findings are exemplified using experimental sorption data of several systems of very distinct chemical nature. A complete regression procedure for sorption data in terms of the GAB isotherm is advanced.

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**Keywords:** Multilayer sorption isotherms; BET equation vs. GAB equation; Inequalities between monolayer and energy constants values; Mathematical and physical foundations; Experimental examples from gas/solid to water/biopolymer and polyelectrolyte sorption systems

## 1. Introduction

In spite of its limitations, the classical BET (Brunauer, Emmett and Teller) multilayer sorption

equation [1] is still used to calculate monolayer values in very different physicochemical fields, and from these data specific area values are obtained. It is certainly used, on one side, because of the simplicity of its application and, on the other, because it has the approval of the International Union of Pure and Applied Chemistry (IUPAC). A report of 1985 of the Commission on Colloid and Surface Chemistry [2] recommends the so-

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called BET plot for a standard evaluation of monolayer values in the following sorbate activity ( $a_0$ )<sup>1</sup> interval:  $0.05 < a_0 < 0.30$ .

Notwithstanding, another equation, the GAB (Guggenheim, Andersen and de Boer) sorption equation [3–5], also provides monolayer sorption values. This equation has become very popular in the field of food technology. The main reason of its use is that the activity range covered by this isotherm is much wider ( $0.05 < a_0 < 0.8–0.9$ ) than that of the BET equation, range which covers almost completely the water sorption range of interest in this field. And so it has been recommended by the European Project Group COST 90 on physical properties of food [6] as the fundamental equation for the characterisation of water sorption by food materials. On the other hand, in other fields the application of the GAB isotherm is still incipient and not yet well established.<sup>2</sup>

The BET and the GAB isotherms are closely related as they follow from the same statistical model [3,8], as we have discussed elsewhere [9]. The GAB model represents a refinement over the BET model and shares with it the two original BET constants ( $v_m$ , the monolayer capacity and  $c_B$ , the energy constant) and owes its major versatility to the introduction of a third constant ( $k$ ).<sup>3</sup> Thus, the regression of an experimental sorption data set by each of these two isotherms will give two sets of values of  $v_m$  and  $c_B$ , besides a single value of  $k$  by the GAB regression. Differences between both sets of values of  $v_m$  and  $c_B$  have been observed (for recent literature, see Refs. [10–12]), which have been also verified for other sorption systems [9,13]. Always the same result is

obtained:

$$\begin{aligned} v_{mB}(\text{BET}) &< v_{mG}(\text{GAB}), \\ c_B(\text{BET}) &> c_B(\text{GAB}). \end{aligned} \quad (1)$$

The  $v_{mB}$  value given by the BET isotherm is always smaller than the monolayer value  $v_{mG}$  corresponding to the GAB isotherm and, reversibly, the BET value of the energy constant  $c_B$  is always higher than the GAB value. Furthermore, both BET values depend markedly on the sorbate activity range used for their determination. As both constants have exactly the same physical meaning for the two isotherms, the following questions arise immediately: which are the correct values? Or, not so absolutely, which of them are physically more realistic?

In this paper, a systematic approach to this problem is performed and it is shown that there exist mathematical and physical reasons for these inequalities and that the GAB values are the more general data. In our paper of 1989 [9], we mentioned the existence of these differences between BET and GAB values, because of an observation of a referee, but we did not make any further consideration because the subject was beyond the scope of that paper. The topic was deferred for a subsequent paper, but it was only partially taken up [13a].

Now, as recent food technology literature [10–12] referred to these differences without offering any plausible explanation, we studied the subject in a systematic way for food materials elsewhere [13] and the inequalities (1) were corroborated for all the analysed systems. But, as objections have been raised [14] to the use of the BET–GAB equations to sorption data of complex materials like food in the present paper we will only refer to simpler physicochemical systems. It will be shown that the problem at hand is intrinsic to the mathematical nature of the two equations discussed here and does not depend on the physical or physicochemical characteristics of the sorption systems to which they may be applied.

Moreover, it would be fair to point out that the inequalities (1) have been observed already by Brunauer himself in a paper of 1969 [15]. Brunauer et al. discuss Anderson's [4] and de Boer's [5] ideas

<sup>1</sup> The sorbate activity  $a_0$  is taken equal to the (partial) relative vapour pressure of the sorbate, i.e.  $a_0 = p/p_0$ , where  $p$  is the experimental (partial) vapour pressure of the sorbate and  $p_0$  its value at saturation.

<sup>2</sup> Well-known textbooks of physical chemistry of surfaces [7] do not consign this equation, although they state criticisms at the BET model, a number of which point directly to the GAB improvement. Among these, de Boer's general arguments [5] are mentioned throughout, but Anderson's modification [4] to the BET equation is only cited and commented in Ref. [7a] while Guggenheim's approach is not quoted [7b].

<sup>3</sup> The symbolism in use in food technology is applied, which is slightly different than that used in Ref. [9].

about the modifications of the BET equation and derive on their own the equation known today as the GAB equation. They analyse the effect of the new constant  $k$  upon the values of  $v_{mB}$  and  $c_B$  and conclude that with decreasing values of  $k$  ( $< 1$ ) the inequalities (1) are observed (see Table 1 of Ref. [15]). But they only point out these consequences in a qualitative way and do not fix or evaluate definitive values of  $k$  for the experimental cases they consider. Certainly these authors do not recognise the GAB equation as a true alternative to the BET isotherm and did not perform any further quantitative analysis. In consequence, this paper by Brunauer et al. can only be considered as a valuable qualitative antecedent for the problem at hand.

## 2. BET regression vs. GAB regression

### 2.1. BET regression

Multilayer sorption isotherms show usually a sigmoid or S-shaped form and the first theoretical equation to interpret these shapes was the well-known BET relation [1]:

$$\text{BET: } v(a_0) = \frac{v_{mB}c_B a_0}{(1 - a_0)(1 + (c_B - 1)a_0)}, \quad (2)$$

where  $v(a_0)$  is the amount of sorbate sorbed by a gram of sorbent at sorbate activity  $a_0$ ,  $v_{mB}$  the monolayer value in the same units as  $v$  and  $c_B$  the energy constant, related to the difference of free enthalpy (standard chemical potential) of the sorbate molecules in the pure liquid state and in the monolayer (first sorbed state [9]).

To obtain the two characteristic constants, the BET equation is linearised by the following function [1,7,9]:

$$F(\text{BET}) \equiv \frac{a_0}{(1 - a_0)v(a_0)} = \frac{1}{c_B v_{mB}} + \frac{c_B - 1}{c_B v_{mB}} a_0, \quad (3)$$

which should result linear in  $a_0$  if the BET postulates apply. The so-called BET plots, i.e.,  $F(\text{BET})$  vs.  $a_0$ , give usually a apparently linear part at low activities ( $0.05 < a_0 < 0.3\text{--}0.5$ ) after which always an upward curvature is observed. This

deviation shows that, at higher activities, less gas or vapour is sorbed than that indicated by the BET equation using the values of the constants corresponding to the low activity range.

Fig. 1 shows typical plots of this type. Three special cases have been chosen to illustrate this behaviour. The first two cases correspond to the sorption systems taken by Guggenheim [3a] and by Anderson [4a], respectively, to exemplify their proposals to improve the original BET formulation, proposals, which were identical and later become to be known as the GAB equation [6]. Guggenheim analysed the sorption of nitrogen on the catalyst  $\text{Fe}/\text{Al}_2\text{O}_3$  studied by Brunauer et al. [3b], while Anderson [4a] considered, among others, the nitrogen sorption on glass spheres. The third case examines the water sorption by a biopolymer, namely wheat starch, studied by van der Berg [16], author who introduced the acronym GAB. While Guggenheim's data set does not cover the whole activity range, the other two examples present points at much higher activities, points, which deserve special consideration (see below). The three BET plots present the typical upswing at  $a_0 \approx 0.3\text{--}0.4$ , although they correspond to systems of very different physicochemical nature.

### 2.2. GAB regression

On the other hand, the GAB equation is [3–5]:

$$\text{GAB: } v(a_0) = \frac{v_{mG}c_G k a_0}{(1 - k a_0)(1 + (c_G - 1)k a_0)}, \quad (4)$$

where

$$c_{B(G)} \equiv c_G k. \quad (5)$$

Here  $v_{mG}$  is the GAB monolayer capacity and  $c_{B(G)}$  the analogue of this formulation to the BET energy constant  $c_B$ . Moreover, the extra assumption of the GAB model over the BET formulation, stating that the sorption state of the sorbate molecules in the layers beyond the first is the same but different to the pure liquid state, demands the introduction of the additional constant  $k$ . This constant is just the measure of the difference of free enthalpy (standard chemical potential) of the sorbate molecules in these two

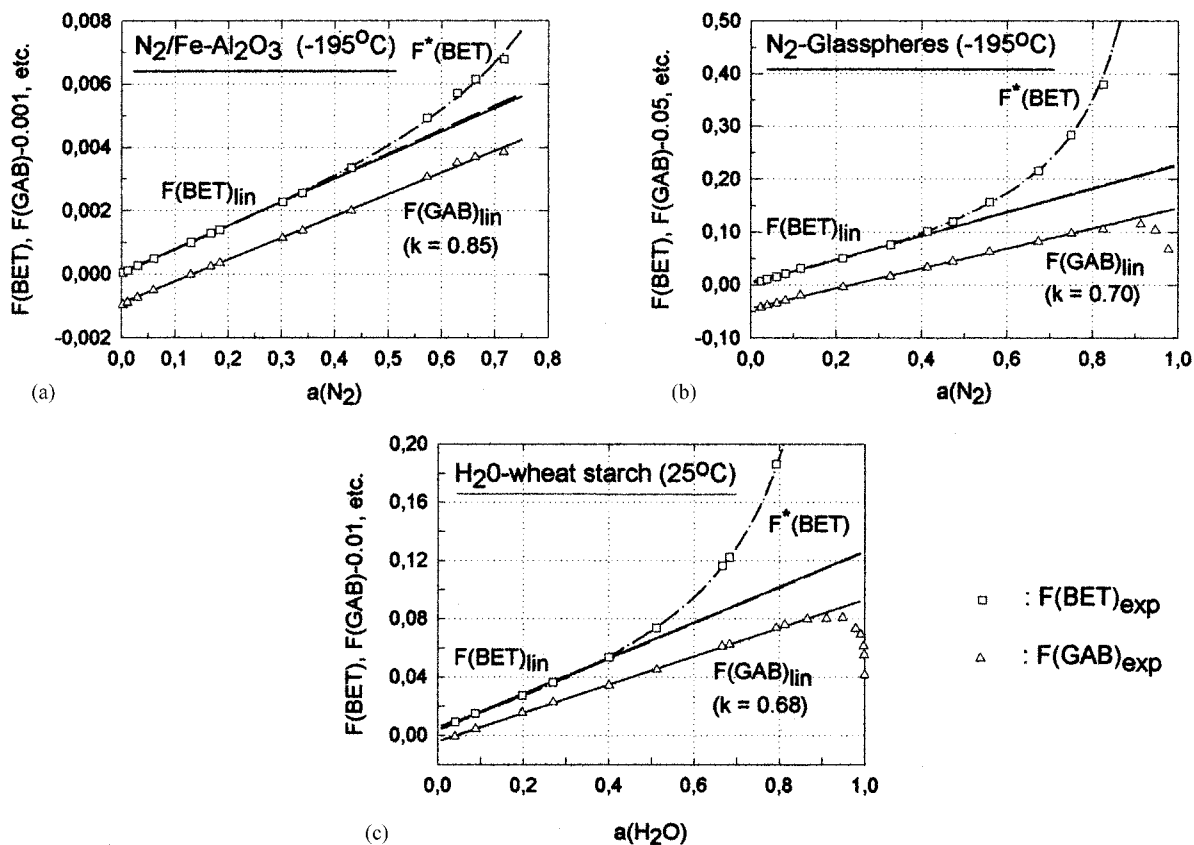


Fig. 1. BET and GAB plots for (a)  $\text{N}_2/\text{Fe}-\text{Al}_2\text{O}_3$  ( $-195^\circ\text{C}$ ) (Guggenheim's system [3a,3b]), (b)  $\text{N}_2/\text{glasspheres}$  ( $-195^\circ\text{C}$ ) (Anderson's system [4]), (c)  $\text{H}_2\text{O}/\text{wheat starch}$  ( $25^\circ\text{C}$ ) (data by van der Berg [16]). See text. The BET plots include  $F(\text{BET})_{\text{exp}}$  (squares),  $F(\text{BET})_{\text{lin}}$  by experimental linear regression (full lines) and by calculation (Eqs. (18a) and (18b)) (dashed lines) and  $F^*(\text{BET})$  (Eqs. (8), (9), (10a), (10b) and (10c)) (dotted-dashed lines). The GAB plots include  $F(\text{GAB})_{\text{exp}}$  (triangles) using the indicated  $k$ -values and  $F(\text{GAB})_{\text{lin}}$  (Eq. (6)) (full lines); for a better view, these plots are displaced downwards by a constant value indicated in each case.

states, the pure liquid and this second sorption stage [9], the layers above the monolayer. It is always found that  $k < 1$  [9] and especially for water sorption it takes characteristic values for different types of biopolymers [17]. Likewise the other GAB energy constant  $c_G$  measures the difference of the chemical potentials of the sorbate molecule in the upper sorption layers and in the monolayer and the three energy constants are related by Eq. (5) [9]. Finally, with  $k = 1$  the GAB isotherm reduces to the original BET equation ( $v_{\text{mB}} = v_{\text{mG}}$ ;  $c_{\text{B}} = c_{\text{B(G)}}$ ).

To determine the three constants of the GAB equation, several methods are employed. In the present context, the linearisation method of the

GAB isotherm analogue to that of the BET model (Eq. (3)) is the most adequate; the other methods will be examined in Section 4. To linearise the GAB isotherm, the following function  $F(\text{GAB})$  applies:

$$F(\text{GAB}) \equiv \frac{a_0}{(1 - ka_0)v(a_0)} = \frac{1}{c_G k v_{\text{mG}}} + \frac{c_G - 1}{c_G v_{\text{mG}}} a_0, \quad (6)$$

The so-called GAB plots [9], i.e.,  $F(\text{GAB})$  vs.  $a_0$ , should be linear in  $a_0$  if the correct  $k$ -value is used for the experimental  $F(\text{GAB})$ . In practice, one looks for the  $k$ -value which best linearises  $F(\text{GAB})$

vs.  $a_0$ .<sup>4</sup> Then, from the two linear regression coefficients, the other constants— $v_{mG}$  and  $c_G$ —are obtained. In general, it is found that the linearisation by Eq. (6) of experimental data is possible within the range  $0.05 < a_0 < 0.8$ .

Fig. 1 shows these plots for the three systems. The values of the  $k$ -constant used are given in Tables 1 and 2. Again the behaviour of the three cases is similar. The GAB plot of Guggenheim's system is linear over the complete activity range covered by the data, while for the other two systems the plots are linear up to  $a_0 \approx 0.8$ – $0.9$ . The much more extended range of application of the GAB equation over to the BET equation is evident [6,9].

### 2.3. Comparison of both types of regressions

As already stated, the results of both regressions for the same set of experimental data give the inequalities (1). The dilemma not solved so far of which values resemble better physical reality may be envisaged in the following way.  $F(\text{GAB})$  is related to  $F(\text{BET})$  by

$$F(\text{BET}) = \frac{a_0}{(1 - a_0)v(a_0)} = \frac{1 - ka_0}{1 - a_0} F(\text{GAB}). \quad (7)$$

By introducing here the expression (6) of  $F(\text{GAB})$  and multiplying out the resulting expression a second relationship for  $F(\text{BET})$ , named  $F^*(\text{BET})$ , is obtained, now in terms of the three constants of the GAB isotherm:

$$\begin{aligned} F^*(\text{BET}) &\equiv \left( \frac{1}{kc_G v_{mG}} + \frac{c_G - 1}{c_G v_{mG}} a_0 \right) \frac{1 - ka_0}{1 - a_0} \\ &= \frac{1}{c_{B(G)} v_{mG}} + \frac{c_{B(G)} - 1 + 2(1 - k)}{c_{B(G)} v_{mG}} a_0 \\ &\quad + \frac{(1 - k)(c_{B(G)} + 1 - k)}{c_{B(G)} v_{mG}} \frac{a_0}{1 - a_0}, \quad (8) \end{aligned}$$

<sup>4</sup> A too high  $k$ -value determines an upward curvature in the GAB plots as in the BET plots and a too low  $k$ -value determines a downward curvature [4a,18]. Analytically, the minimum of the sum of the least-squares of the linear regression of Eq. (6) in terms of the variable  $k$  determines the best  $k$ -value.

where Eq. (5) has been used to introduce  $c_{B(G)}$ . This second expression for  $F(\text{BET})$  shows that, if  $k < 1$ ,  $F(\text{BET})$  will not be linear in  $a_0$  but will present a *hyperbolic* behaviour:

$$\begin{aligned} F^*(\text{BET}) &= A + Ba_0 + \frac{Ca_0}{1 - a_0} \\ &= (A - C) + (B - C)a_0 + \frac{C}{1 - a_0}, \quad (9) \end{aligned}$$

where

$$A \equiv \frac{1}{c_{B(G)} v_{mG}}, \quad (10a)$$

$$B \equiv \frac{c_{B(G)} - 1 + 2(1 - k)}{c_{B(G)} v_{mG}}, \quad (10b)$$

$$C \equiv \frac{(1 - k)(c_{B(G)} + 1 - k)}{c_{B(G)} v_{mG}}. \quad (10c)$$

Conversely, if  $k = 1$  Eqs. (3), (8) and (9) become identical as  $C(k = 1) = 0$ .

Eq. (9) readily explains qualitatively and quantitatively (Eqs. (10a), (10b) and (10c)) the usually observed upswing in the BET plots at  $a_0 > 0.3$ – $0.4$ , if the constants of the GAB isotherm are known ( $k < 1$ ). In the graphs of Fig. 1,  $F^*(\text{BET})$  has been represented in terms of the corresponding GAB constants given in Tables 1 and 2. It can be observed that this nonlinear function reproduces  $F(\text{BET})_{\text{exp}}$  in the three cases over the whole range of applicability of the GAB equation, i.e., far beyond the linear range usually used for the BET evaluation using  $F(\text{BET})$ .

Furthermore, it is evident that, if  $F(\text{BET})$  responds to Eq. (9) but it is analysed using Eq. (3), the so obtained  $v_{mB}$  and  $c_B$  values associated to the BET isotherm will be certainly functions of the three GAB constants  $v_{mG}$ ,  $c_G$  and  $k$  through Eqs. (8), (9), (10a), (10b) and (10c) and of the  $a_0$ -interval over which the regression is performed. And this functional dependence determines the difference between the BET and the GAB sets for  $v_m$  and  $c_B$  and the inequalities stated by Eq. (1). In the following sections, the quantitative relations are derived and evaluated.

### 3. Quantitative expressions of inequalities (1)

#### 3.1. Classical least-squares analysis of $F(\text{BET})$ of Eq. (3)

This method is well known. In synthesis, the experimental values of  $F(\text{BET})$  are adjusted by the linear polynomial

$$P(\text{BET})_i = \alpha_0 + \alpha_1 x_i \quad (11)$$

by minimising the sum over the  $n$  experimental points (index  $i$ ):

$$\sum_{i=1}^n [F(\text{BET})_i - (\alpha_0 + \alpha_1 x_i)]^2 = \text{minimum}, \quad (12)$$

where  $x_i$  stands for  $a_0$  at the point  $i$ . The coefficients  $\alpha_0$  and  $\alpha_1$  are given by the solutions of the system of normal equations associated to the extremum condition (13a) and (13b) (see Appendices A and B). By Eqs. (3) and (11), the least-squares estimates of  $\alpha_0$  and  $\alpha_1$ ,  $\hat{\alpha}_0$  and  $\hat{\alpha}_1$ , are given directly by the BET constants,

$$\text{BET: } \hat{\alpha}_0 \equiv \frac{1}{c_B v_{\text{mB}}}, \quad (13a)$$

$$\text{BET: } \hat{\alpha}_1 \equiv \frac{c_B - 1}{c_B v_{\text{mB}}}, \quad (13b)$$

and hereafter

$$v_{\text{mB}} = \frac{1}{\hat{\alpha}_0 + \hat{\alpha}_1}, \quad (14a)$$

$$c_B = \frac{\hat{\alpha}_0 + \hat{\alpha}_1}{\hat{\alpha}_0}, \quad (14b)$$

relations by which the BET constants are usually calculated.

It must be observed that the energy constant  $c_B$  is, by Eq. (14b), inversely proportional to  $\hat{\alpha}_0$ , the intercept of the linear regression polynomial  $P(\text{BET})$  of Eq. (11). Thus the estimate of  $c_B$  is a much more sensitive quantity to the value of  $\hat{\alpha}_0$  than the estimate of  $v_{\text{mB}}$ . Because of the upswing of the experimental  $F(\text{BET})$  (see Fig. 1) at increasing sorbate activity the linear correlation  $P(\text{BET})$  of  $F(\text{BET})$  tends to increase the slope  $\hat{\alpha}_1$  and to decrease the intercept  $\hat{\alpha}_0$  as the regression range is extended. This causes, on one hand, the

well-known dependency of the experimental values of the BET constants obtained by Eqs. (14a) and (14b) on the regression range of  $a_0$  used. On the other hand, this decrease of the intercept  $\hat{\alpha}_0$  may cause that this quantity passes through the origin and thereafter becoming negative, and, consequently,  $c_B$  rapidly acquires very high values, then diverges and hereafter results negative, a behaviour which is physically completely unsound.

In the literature, this problem is ‘overcome’ by simply restricting the BET evaluation to the so-called ‘linear’ range and paying much more attention to the estimate of  $v_{\text{mB}}$ , than to the estimate of  $c_B$ , obviously because the former has much more concrete practical applications than the latter. It is accepted that, with very large values of  $c_B$ , the intercept of the linear BET plot becomes so small that it cannot be determined very accurately, and little error is introduced if the best straight line is drawn through the origin and the slope taken to be equal to  $1/v_{\text{mB}}$ . But the essence of the problem remained unsolved.

#### 3.2. Least-squares analysis of $F^*(\text{BET})$ of Eq. (9)

The second expression  $F^*(\text{BET})$  may also be adjusted by the same linear polynomial (11), but now using an analytical formulation, as  $F^*(\text{BET})$  is known as a function of  $a_0$  and not by a set of numerical data. The calculation implies the adjustment of a function of a known functional dependence of a higher degree than one to a straight line. This regression of  $F^*(\text{BET})$  can be made either in a discrete form or in a continuous form. The discrete form will be discussed below, while the continuous form is described in Appendices A and B.

In the discrete procedure  $F^*(\text{BET})$ , given by Eq. (9), is explicated in condition (12), which become:

$$\sum_{i=1}^n \left[ A - C + (B + C)x_i + \frac{C}{1 - x_i} - (\alpha_0 + \alpha_1 x_i) \right]^2 = \text{minimum}, \quad (15)$$

and this expression can now be solved analytically for  $\alpha_0$  and  $\alpha_1$  in the usual way of least-squares. The details are given in Appendices A and B and the result is that  $\alpha_0$  and  $\alpha_1$  become functions of the constants  $A$ ,  $B$  and  $C$  of Eq. (9), on one side, and

of regression sums over the values of the independent variable  $x_i$ , on the other. These results are given by Eqs. (B.4a) and (B.4b):

$$\alpha_0^* = A + CS_0^*, \quad (16a)$$

$$\alpha_1^* = B + CS_1^*, \quad (16b)$$

where  $\alpha_0^*$  and  $\alpha_1^*$  are the minimum squares estimates in terms of  $F^*(\text{BET})$ . The functions  $S_0^*$  and  $S_1^*$ , defined by Eqs. (B.6a) and (B.6b), contain only the regression sums of  $a_0$  over the employed regression interval, with the following signs:  $S_0^* < 0$ ,  $S_1^* > 0$  and  $S_0^* + S_1^* > 0$  for  $a_0 < 1$ . As Eqs. (13a), (13b), (14a) and (14b) remain valid, the BET constants are given as

$$v_{\text{mB}} = \frac{1}{\alpha_0^* + \alpha_1^*} = \frac{1}{A + B + C(S_0^* + S_1^*)}, \quad (17a)$$

$$c_{\text{B}} = \frac{\alpha_0^* + \alpha_1^*}{\alpha_0^*} = \frac{A + B + C(S_0^* + S_1^*)}{A + CS_0^*}. \quad (17b)$$

By Eqs. (10a), (10b) and (10c),  $A$ ,  $B$ ,  $C = f(v_{\text{mG}}, c_{\text{G}}, k)$  and after some algebra explicit expressions for  $v_{\text{mB}}$  and  $c_{\text{B}}$  in terms of the three GAB constants are obtained:

$$v_{\text{mB}} = \frac{v_{\text{mG}}}{[1 + 2(1 - k)/c_{\text{B(G)}}]R_{\text{m}}^*}, \quad (18a)$$

$$c_{\text{B}} = c_{\text{B(G)}} \left[ 1 + \frac{2(1 - k)}{c_{\text{B(G)}}} \right] R_{\text{c}}^*, \quad (18b)$$

where  $R_{\text{m}}^*$  and  $R_{\text{c}}^*$  are functions containing the  $a_0$ -regression sums given by

$$R_{\text{m}}^* \equiv 1 + (1 - k) \left[ \frac{c_{\text{B(G)}} + (1 + k)}{c_{\text{B(G)}} + 2(1 - k)} \right] \times (S_0^* + S_1^*), \quad (19a)$$

$$R_{\text{c}}^* \equiv \frac{R_{\text{m}}^*}{1 + (1 - k)(c_{\text{B(G)}} + 1 - k)S_0^*}. \quad (19b)$$

These functions are always greater than unity. Hence, Eqs. (18a) and (18b) reproduce the inequalities (1) if  $k < 1$ .

As already stated above, a continuous regression procedure is also at hand. Taking  $F^*(\text{BET})$  as continuous, i.e., as given by infinite points, a continuous regression form can be developed in which the sums of the discrete procedure are

replaced by defined integrals which depend only on the limits  $a_0'$  and  $a_0''$  of the regression interval. This procedure is described in Appendix B (see section B.1 and Eqs. (B.28a) and (B.28b)) and the corresponding expressions resemble those of the discrete method being similar functions of the constants  $A$ ,  $B$  and  $C$  of Eq. (9).

Eqs. (18a) and (18b) as well as Eqs. (B.28a) and (B.28b) of the continuous method explicit and quantify the differences between  $v_{\text{mB}} - c_{\text{B}}$  and  $v_{\text{mG}} - c_{\text{B(G)}}$ . These are directly related to  $k < 1$  through the factor  $(1 - k)$  present in these equations and hence explain inequalities (1). On the other hand, if  $k = 1$  [ $C(k = 1) = 0$ ], all these expressions coincide with the classical results of Section B.1.

These differences are analysed graphically in Fig. 2 where  $v_{\text{mB}}$  and  $c_{\text{B}}$  are plotted in terms of Eqs. (B.28a) and (B.28b) for different values of  $k$  and in function of the upper limit  $a_0''$  of the regression interval, with arbitrarily fixed values of  $v_{\text{mG}} = 1$  and  $c_{\text{B(G)}} = 20$ . The lower limit  $a_0'$  is taken as usually as  $a_0' = 0.05$ , a value which has some theoretical and practical foundations [1,7]. In these calculations, the continuous equations (B.28a) and (B.28b) have been used to obviate any dependence on a specific discrete data distribution. Henceforth these graphs represent upper limits of the differences between the BET and GAB parameters.

Fig. 2 clearly explicit both inequalities (1).  $v_{\text{mB}}$  underestimates the monolayer capacity and  $c_{\text{B}}$  overestimates the energy constant. The deviations become more important with decreasing values of  $k$  and with an increase of the regression interval (increasing  $a_0''$ ) and the effect is much more pronounced for  $c_{\text{B}}$  than for  $v_{\text{mB}}$ . In particular, the special behaviour of the energy constant already mentioned at the end of Section 3.1 is explained, i.e., the marked tendency of  $c_{\text{B}}$  to increase, to diverge and then to become negative in terms of the upper limit of the regression interval, as it is shown by Fig. 2(b). As stated, these properties are due to the fact that  $c_{\text{B}}$  is inversely proportional to  $\alpha_0$  (see Eqs. (14a), (14b), (17a) and (17b)). Now, as  $F^*(\text{BET})$  explains the upswing of the experimental  $F(\text{BET})$  in the BET plots and thereby also the increase of the slope  $\alpha_1$  and the decrease of the intercept  $\alpha_0$  of the linear



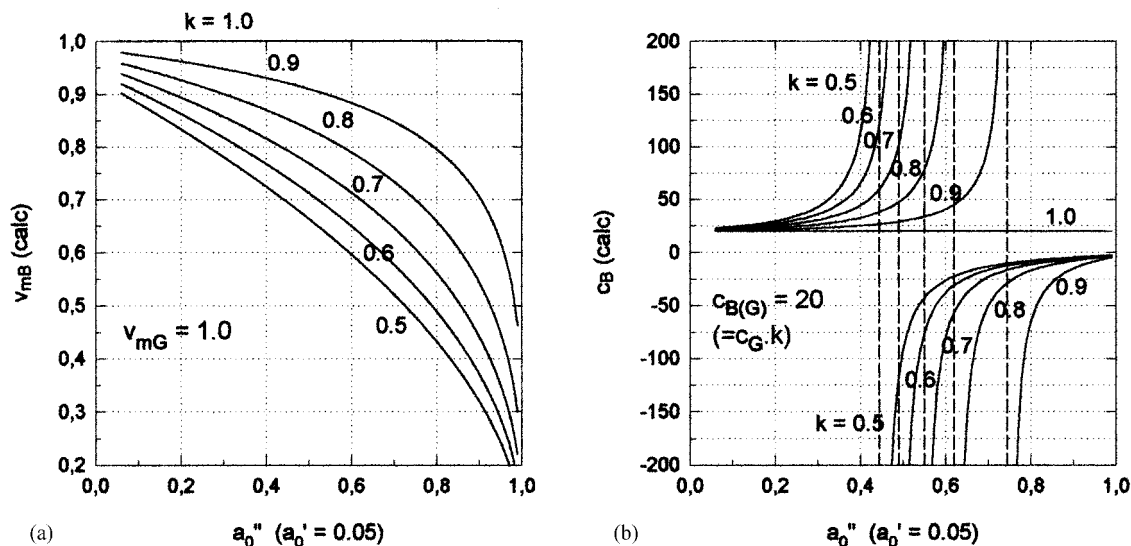


Fig. 2.  $v_{mB}$  (BET) (a) and  $c_B$  (BET) (b) calculated by Eqs. (B.28a) and (B.28b), for different values of the third GAB constant  $k$  at fixed values of other two GAB constants,  $v_{mG}$  (GAB) ( $= 1$ ) and  $c_{B(G)}$  (GAB) ( $= 20$ ), in terms of the upper limit  $a_0''$  of the BET regression interval (lower limit  $a_0' = \text{const.} = 0.05$ ).

regression polynomial  $P(\text{BET})$  (Eq. (11)) as the regression interval is enlarged it is to be concluded that this behaviour of  $c_B$  is certainly inherent to the original BET description and determines its limited ability to reproduce the experimental sorption data. In fact, the deviations of both  $c_B$  and  $v_{mB}$  in terms of  $k$  and of the extent of the regression range go hand in hand and have to be considered together. Only the much less marked effect on the monolayer capacity value may sustain the position usually found in the literature to consider only the  $v_{mB}$  value and to discard or ignore the  $c_B$  value.

Finally, it is also to be pointed out that it becomes evident from the drawings that even at the limit of  $a_0'', a_0' \rightarrow 0$  the BET constants do not return the correct values of  $v_{mG}$  ( $= 1$ ) and of  $c_{B(G)}$  ( $= 20$ ). At this limit, the auxiliary functions  $R_m^*$  and  $R_c^*$  (Eqs. (19a) and (19b)) as well as  $\tilde{R}_m$  and  $\tilde{R}_c$  (Eqs. (B.29a) and (B.29b)) become unitary and the limiting values are:

$$\lim_{a_0'', a_0' \rightarrow 0} v_{mB} \equiv v_{mB}^0(\text{BET}) = \frac{1}{A + B} = \frac{v_{mG}}{1 + 2(1 - k)/c_{B(G)}} < v_{mB}, \quad (20a)$$

$$\lim_{a_0'', a_0' \rightarrow 0} c_B \equiv c_B^0(\text{BET}) = \frac{A + B}{A} = c_{B(G)} \left[ 1 + \frac{2(1 - k)}{c_{B(G)}} \right] > c_{B(G)}. \quad (20b)$$

## 4. Experimental examples

### 4.1. Experimental systems

To show the general applicability of the theoretical equations derived in the preceding sections, experimental cases of diverse physicochemical nature will be discussed. The experimental cases are mainly those considered in Ref. [9], i.e., systems of sorption of (a) gas on solids, (b) water by biopolymers and (c) water by electrolytes and polyelectrolytes. The corresponding sorption data are represented graphically in Fig. 3.

It is shown that in all cases inequalities (1) are found and that the relations presented in the previous section quantitatively reproduce the BET values. Tables 1–3 summarise the results. In the group of gas sorption on solids, the system

analysed by Guggenheim [3a], i.e.,  $N_2$  on  $Fe/Al_2O_3$  (data by Brunauer et al. [3b]), the first case of Fig. 1, has been included. In the cases of sorption of nitrogen gas and of water vapour on crystalline anatase, several data sets due to Harkins and Jura [19a] are considered together ( $N_2/TiO_2$ : three data sets [19a,19b];  $H_2O/TiO_2$ : two data sets [19c,19d,19e]). It is observed that these sets correspond statistically to the same universe and can be combined for the regression calculus, allowing to

consider a much more numerous data collection than in all other cases. In the same way, in the group of biopolymers the sorption of water by wheat starch [16] has been incorporated because of its more abundant data set than the data collections for proteins.

Tables 1–3 give the numerical values for the three groups. The number of points ( $n_B$ (BET),  $n_G$ (GAB)) used and the regression intervals are indicated in each case. The first two columns give

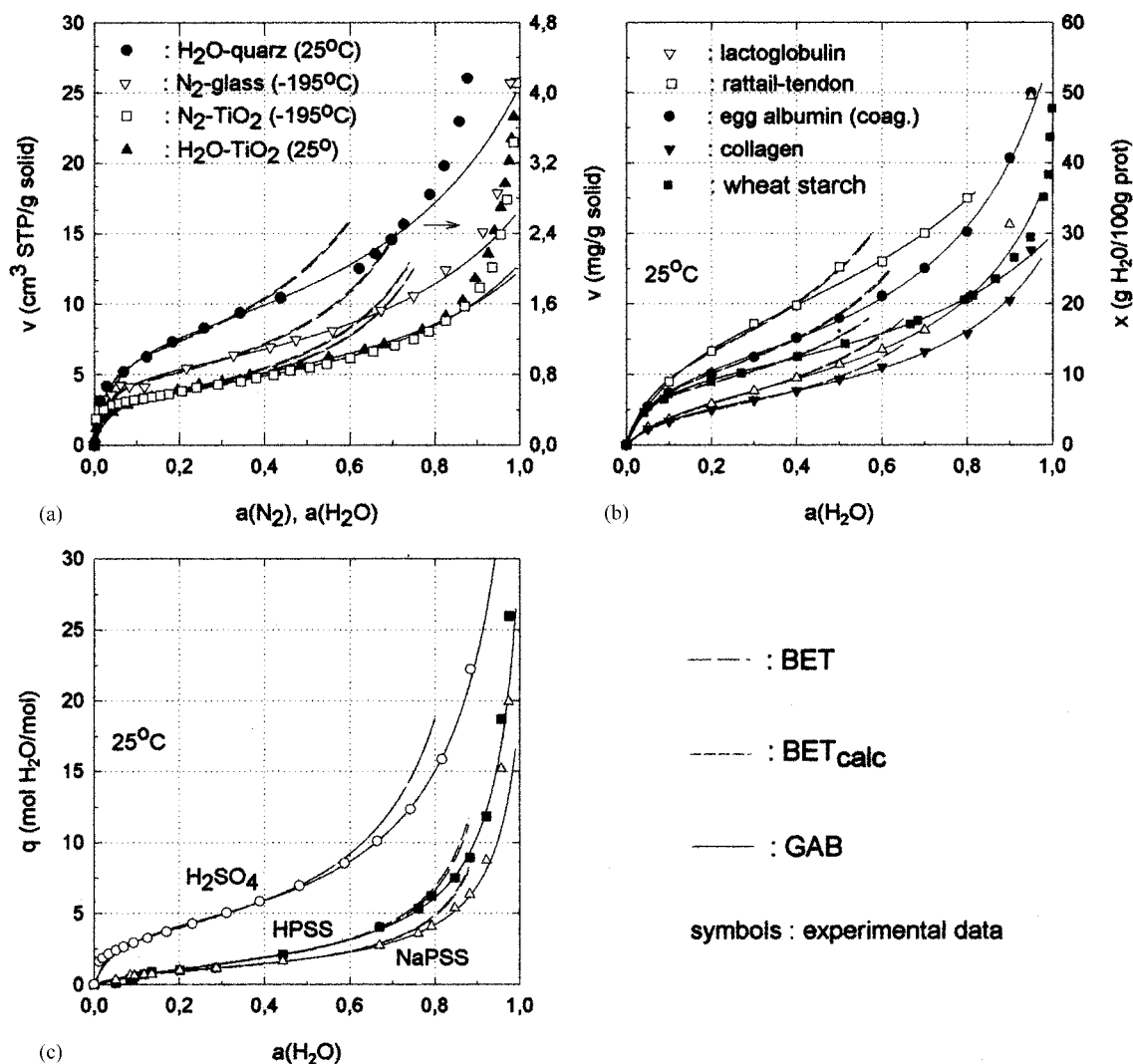


Fig. 3. Sorption isotherms of (a) gas/solid systems, (b) water by biopolymers, (c) water by electrolytes and polyelectrolytes. References and details in Tables 1–3. Symbols: experimental points. Lines: isotherms calculated by BET equation (experimental linear regression (long dashes) and by calculated BET constants (short dashes)) and by GAB equation (full lines).

Table 1  
Gas/solids (unit:  $v_m$ ,  $\text{cm}^3 \text{STP g}^{-1}$ )

BET <sub>exp</sub>		BET <sub>calc</sub>				GAB <sub>exp</sub>			
$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mG}$	$c_G$	$k$	$c_{B(G)}$
Range; $n_B$		Discrete (Eqs. (18a) and (18b))		Continuous (Eqs. (B.28a) and (B.28b))		Range; $n_G$			
N <sub>2</sub> /Fe–Al <sub>2</sub> O <sub>3</sub> (–195 °C) ([3b] $v_{mB} = 133.0$ , $c_B = 156.7$ ; [3] $v_{mG} = 144$ , $c_G = 130$ , $k = 0.83$ )									
0.030 < $a_0$ < 0.339; $n_B = 7$									
134.1 ± 0.4	171.4 ± 15.5	132.2 ± 1.7	285.6 ± 182.5	132.7 ± 3.5	324.3 ± 471.8	143.2 ± 3.7	119.8 ± 56.0	0.85 ± 0.05	101.8 ± 53.5
NEF = 0.68		3.57				3.30			
N <sub>2</sub> /glasspheres (–195 °C) ([4] $v_{mB} = 4.8$ , $c_B = 72.2$ ; $v_{mG} = 5.1$ , $c_G = 55.1$ , $k = 0.715$ )									
0.061 < $a_0$ < 0.327; $n_B = 5$									
4.42 ± 0.2	70.2 ± 37.6	4.38 ± 0.11	80.3 ± 26.2	4.40 ± 0.19	96.2 ± 70.5	5.18 ± 0.22	51.2 ± 20.2	0.70 ± 0.08	35.5 ± 18.2
NEF: 5.77		2.48				4.43			
N <sub>2</sub> /TiO <sub>2</sub> (–195 °C) ([19a,19b]: $v_{mB} (= 13.8 \text{ m}^2 \text{ g}^{-1}) = 3.17$ ; [4]: $v_{mG} = 3.72$ , $c_G = 64.4$ , $k = 0.70$ )									
0.053 < $a_0$ < 0.336; $n_B = 35$									
3.14 ± 0.02	139.6 ± 13.9	3.15 ± 0.02	139.1 ± 21.1	3.13 ± 0.13	159.2 ± 192.6	3.63 ± 0.04	64.0 ± 6.8	0.72 ± 0.02	45.9 ± 6.1
NEF: 1.21		2.45				2.46			
H <sub>2</sub> O/TiO <sub>2</sub> (25 °C) ([19c,19d,19e]: $v_{mB} (= 9.8 \text{ m}^2 \text{ g}^{-1}) = 3.47$ )									
0.064 < $a_0$ < 0.310; $n_B = 10$									
3.39 ± 0.06	48.5 ± 6.9	3.38 ± 0.05	50.0 ± 6.8	3.38 ± 0.14	51.5 ± 19.2	4.02 ± 0.05	38.4 ± 4.3	0.68 ± 0.03	26.0 ± 3.9
NEF: 1.88		2.02				1.41			
H <sub>2</sub> O-quartz (25 °C) ([20])									
0.068 < $a_0$ < 0.342; $n_B = 5$									
1.04 ± 0.02	41.9 ± 6.6	1.03 ± 0.03	47.6 ± 13.7	1.03 ± 0.05	49.7 ± 21.3	1.24 ± 0.05	33.9 ± 9.8	0.70 ± 0.07	24.8 ± 9.4
NEF: 1.41		2.51				2.21			

Table 2  
H<sub>2</sub>O/biopolymers (25 °C) (unit:  $v_m$ , g per 100 g dry weight)

BET <sub>exp</sub>		BET <sub>calc</sub>		GAB <sub>exp</sub>					
$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mG}$	$c_G$	$k$	$c_{B(G)}$
Range; $n_B$		Discrete (Eqs. (18a) and (18b))		Continuous (Eqs. (B.28a) and (B.28b))		Range; $n_G$			
0.05 < $a_0$ < 0.40; $n_B = 5$						0.05 < $a_0$ < 0.8; $n_G = 9$			
Collagen ([21]: $v_{mB} = 9.52$ ; $c_B = 17.8$ )									
9.72 ± 0.11	20.3 ± 1.0	9.85 ± 0.28	19.6 ± 2.5	9.90 ± 0.45	20.3 ± 4.2	11.5 ± 0.5	17.3 ± 4.4	0.80 ± 0.09	13.8 ± 5.0
NEF: 0.99		2.13				3.01			
β-Lactoglobulin ([21]: $v_{mB} = 6.67$ ; $c_B = 8.6$ )									
0.05 < $a_0$ < 0.40; $n_B = 5$						0.05 < $a_0$ < 0.8; $n_G = 9$			
6.60 ± 0.24	9.7 ± 0.9	6.54 ± 0.17	10.0 ± 0.7	6.57 ± 0.28	10.2 ± 1.1	7.72 ± 0.45	9.5 ± 2.4	0.81 ± 0.11	7.7 ± 2.9
NEF: 1.72		1.45				1.93			
Eggalbumin (coag.) ([21]: $v_{mB} = 4.97$ ; $c_B = 13.6$ )									
0.05 < $a_0$ < 0.40; $n_B = 5$						0.05 < $a_0$ < 0.8; $n_G = 9$			
5.14 ± 0.78	13.5 ± 0.7	5.26 ± 0.16	13.7 ± 1.2	5.29 ± 0.25	13.0 ± 2.0	6.29 ± 0.26	11.8 ± 2.3	0.78 ± 0.07	9.2 ± 2.6
NEF: 1.00		1.83				2.70			
Rattail-tendon [22]: $v_{mG} = 19.6$ , $c_G = 11.6$ , $k = 1/1.65$ )									
0.1 < $a_0$ < 0.4; $n_B = 4$						0.1 < $a_0$ < 0.8; $n_G = 7$			
13.3 ± 1.0	15.3 ± 4.2	13.2 ± 0.7	15.8 ± 3.4	13.3 ± 0.9	16.1 ± 4.2	18.0 ± 0.8	13.7 ± 2.6	0.65 ± 0.07	8.2 ± 2.5
NEF: 3.27		2.59				1.06			
Native wheat starch [16] ( $v_{mG} = 9.82$ , $c_G = 27.3$ , $k = 0.68$ ; $n_G = 11$ )									
0.0404 < $a_0$ < 0.401; $n_B = 5$						0.0404 < $a_0$ < 0.8663; $n_G = 11$			
7.93 ± 0.17	32.8 ± 4.7	7.92 ± 0.37	33.8 ± 11.2	7.98 ± 0.55	37.2 ± 20.4	9.89 ± 0.21	26.7 ± 3.8	0.68 ± 0.04	17.6 ± 3.8
NEF: 1.99		4.48				1.65			

Table 3  
H<sub>2</sub>O/polyelectrolytes and electrolytes (25 °C) (unit:  $v_m$ , mol H<sub>2</sub>O per mol)

BET <sub>exp</sub>		BET <sub>calc</sub>				GAB <sub>exp</sub>			
$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mB}$	$c_B$	$v_{mG}$	$c_G$	$k$	$c_{B(G)}$
Range; $n_B$		Discrete (Eqs. (18a) and (18b))		Continuous (Eqs. (B.28a) and (B.28b))		Range; $n_G$			
SO <sub>4</sub> H <sub>2</sub> [23]									
0.0506 < $a_0$ < 0.481; $n_B = 18$									
3.78 ± 0.03	24.8 ± 0.9	3.76 ± 0.03	24.7 ± 1.00	3.76 ± 0.11	26.0 ± 5.1	4.04 ± 0.06	21.4 ± 2.0	0.92 ± 0.03	19.7 ± 2.5
NEF: 1.84		1.42				2.48			
PSSNa [24]									
0.085 < $a_0$ < 0.443; $n_B = 7$									
1.00 ± 0.04	13.0 ± 1.6	0.99 ± 0.01	13.7 ± 0.3	0.99 ± 0.01	13.8 ± 0.7	1.03 ± 0.05	13.9 ± 2.9	0.95 ± 0.09	13.3 ± 3.9
NEF: 3.46		5.14				4.88			
PSSH [24]									
0.177 < $a_0$ < 0.443; $n_B = 4$									
1.38 ± 0.17	6.6 ± 1.6	1.45 ± 0.01	5.9 ± 0.7	1.46 ± 0.02	5.9 ± 0.2	1.54 ± 0.24	5.7 ± 2.9	0.95 ± 0.25	5.4 ± 4.2
NEF: 4.25		0.20				14.6 (!)			
PSSNa [25]									
0.05 < $a_0$ < 0.4									
–	–	–	–	1.37 ± 0.03	13.62 ± 0.84	1.05 ± 0.20	13.0 ± 9.5	0.91 ± 0.21	10.9 ± 11.2
–	–	–	–			NEF: 2.24			

the experimental BET constants and their errors, then columns 3–6 give the BET constants and their errors calculated by the discrete (Eqs. (18a) and (18b); columns 3 and 4) and continuous methods (Eqs. (B.29a) and (B.29b); columns 5 and 6) in terms of the experimental GAB constants stated in columns 7–10. For the discrete method, the experimental values of the independent variable ( $a_0$ ) have been used (see Appendices A and B). The respective errors are calculated by the error propagation formulae in terms of the standard deviations of the least-squares parameters. Finally, complements each set of constants a normalised error function (NEF), defined as

$$\text{NEF} \equiv 100 \frac{\left( \sum_{i=1}^n (v_{\text{exp}} - v_{\text{calc}})_i^2 / n \right)^{1/2}}{v_m}. \quad (21)$$

This function is related to, but simpler than the relative percentage root mean square value often used in the literature.

In Fig. 3, the direct and calculated BET curves as well as the GAB curve are drawn. In each case both BET curves are practically identical. The different applicability ranges of the BET and the GAB isotherms are clearly noticed. In all cases, the approach given in the present paper is verified, without exception.

#### 4.2. Determination of the GAB parameters

It is evident that to perform the proposed analysis reliable values of the constants of the GAB isotherm are required. In order to obtain these values, the applicability range of the GAB equation must be established as one should only work with experimental points, which lay within this range of activities. For this, the data set over the complete range of activities must be examined and the points corresponding to the third sorption stage described in Ref. [9] should be separated from the set of points to work with. These points can be identified by using the inverse plot, as indicated in Refs. [9,26], and, in general, one observes that at  $a_0 \approx 0.80$ – $0.85$  the third sorption stage becomes evident and, henceforth, points at these and higher activities should not be used for

the evaluation of the GAB constants. In Fig. 3, it can be observed that practically in all cases the points of highest activities ( $a_0 > 0.85$ – $0.9$ ) are beyond the GAB range, presenting a higher sorption than that predicted by this equation and indicating the presence of the third (BET-like) sorption stage [9].

The GAB constants can be determined using the  $F(\text{GAB})$ -function method discussed in Section 2.2 (Eq. (6)), but two other methods are more straightforward. Here the so-called method of the transformed form of the GAB isotherm [6] is applied. The transformed GAB relation<sup>5</sup> is the following parabolic expression, which is easily derived from Eq. (3):

$$\frac{a_0}{v(a_0)} = \alpha + \beta a_0 + \gamma a_0^2, \quad (22)$$

where

$$\alpha \equiv \frac{1}{kc_G v_{mG}}, \quad (23a)$$

$$\beta \equiv \frac{c_G - 2}{c_G v_{mG}}, \quad (23b)$$

$$\gamma \equiv -\frac{(c_G - 1)k}{c_G v_{mG}}. \quad (23c)$$

The constants  $\alpha$ ,  $\beta$  and  $\gamma$  are readily determined by a least-squares regression of this second-degree polynomial and from these the GAB constants are calculated by

$$k = \frac{\beta + \sqrt{f}}{2\alpha}, \quad (24a)$$

$$c_G = 2 + \frac{\beta}{\alpha k} = 1 - \frac{\gamma}{\alpha k^2} = \frac{\sqrt{f}}{\alpha k}, \quad (24b)$$

<sup>5</sup> Originally the parabolic regression was used [27a] to determine the parameters of a three-parameter isotherm due to Hailwood and Horrobin [27b], based on a solution-hydration model. The versatile behaviour and good ability to fit experimental water sorption data for foods led to consider this isotherm as a sort of “universal” isotherm [27c], but later on its equivalency with the GAB equation was shown [27d] and this latter isotherm becomes predominant and popular in food technology [6,28].

$$v_{\text{mG}} = \frac{1}{\sqrt{f}} = \frac{1}{2\alpha k + \beta^2}, \quad [f \equiv \beta^2 - 4\alpha\gamma]. \quad (24c)$$

On the other hand, the other method to obtain the three GAB constants consists directly in a nonlinear least-squares regression of Eq. (3), a calculus procedure which is today usually included in modern software packages. It has been claimed [29] that this method and that of the parabolic transform give different results, but if the points corresponding to the third sorption stage are not included both regressions give identical results [30]. The points of the third stage behave as outliers for these regressions and affect them, because of the different mathematical nature of both methods, with different strength (weights). Moreover, it is observed that a root mean square deviation function such as NEF (Eq. (21)) increases sharply if these points at highest activities are included in the regression. In this paper, we will use throughout the parabolic regression (the constants stated in Tables 1–3 were all obtained by this method) and the stated differences, the discussion of which goes beyond the scope of this paper, will be treated in a separate work [30].

#### 4.3. General *modus operandi*

The complete calculation procedure is illustrated graphically in Fig. 4 at hand of one experimental data set of  $\text{N}_2/\text{TiO}_2$  due to Harkins and Jura [19a,19b]. Table 1 states the corresponding regression constants.

The calculation process starts with the inverse plot (Fig. 4(a)) by which the GAB applicability range is identified, as it is recommended in Ref. [9]. At high  $a_0$ , for strongly sorbing substances ( $c_G \gg 1$ ), both isotherms become very simple for the inverse of  $v(a_0)$ :

$$\text{BET: } \frac{1}{v} = \frac{1}{v_{\text{mB}}}(1 - a_0), \quad (25a)$$

$$\text{GAB: } \frac{1}{v} = \frac{1}{v_{\text{mG}}}(1 - ka_0). \quad (25b)$$

These relations indicate that  $1/v$  is linear at high enough  $a_0$  for both isotherms and that the limits for  $1/v = 0$  ( $v \rightarrow \infty$ ) are at the points ( $a_0 = 1$ ,  $1/v =$

0; BET) and ( $a_0 = 1/k$  ( $> 1$ ),  $1/v = 0$ ; GAB), respectively. Thus, if the linear part at higher  $a_0$  of the inverse plot  $1/v$  vs.  $a_0$  do not extrapolate to  $a_0 = 1$  for  $1/v = 0$  (BET condition) it is indicative that  $k < 1$  (see Eqs. (25a) and (25b)) and that the GAB equation applies. The extrapolation to  $1/v = 0$  gives  $1/k$  directly as the intercept with the  $a_0$ -axis [9]. Hence, these plots readily visualise which isotherm applies. Furthermore, if after the linear part the graph become curved downward (usually at  $a_0 \approx 0.85$ – $0.9$ ) this is a direct evidence of the presence of the third sorption stage [9]26. These points must be discarded for the parabolic GAB regression (Eq. (22)) and so the upper limit for this regression can be directly read off from the graph.

In Fig. 4(a), the calculated BET and GAB isotherms are drawn and the upper limits of both equations are shown by arrows. On the other hand, dashed arrows indicate the lower limit of the regression intervals, limit which is the same for both isotherms ( $a_0 = 0.05$ ). The limiting linear relation of GAB isotherm at high sorbate activities (Eqs. (25a) and (25b)) is also drawn, by which two of the GAB constants,  $v_{\text{mG}}$  and  $k$ , can be obtained by rapid and direct graphical extrapolations [9]. In this figure, this limiting line has been drawn using the correct values of  $v_{\text{mG}}$  and  $k$  of Table 1, and the plot attests the properness of this extrapolation.

Once the GAB range is known, the GAB constants are determined by the parabolic regression indicated by Eqs. (22), (23a), (23b), (24a) and (24b). Fig. 4(b) gives the parabolic representation of the sorption data and the regression curve of the GAB equation as well as parabolic plots of the BET equation using the experimental and calculated constants. Again, the different applicability intervals of the two equations are evident. The BET range coincides with that recommended by IUPAC,  $0.05 < a_0 < 0.3$ .

Complementary is the next step consisting in the BET and GAB plots, which play a central role in this paper. They were already analysed in Fig. 1. In the present case, they are given in Fig. 4(c) and the same picture is obtained. The observations made about Fig. 1 in the previous sections also apply here.

The BET plot in Fig. 4(c) includes  $F(\text{BET})_{\text{exp}}$  (open symbols) calculated from the experimental

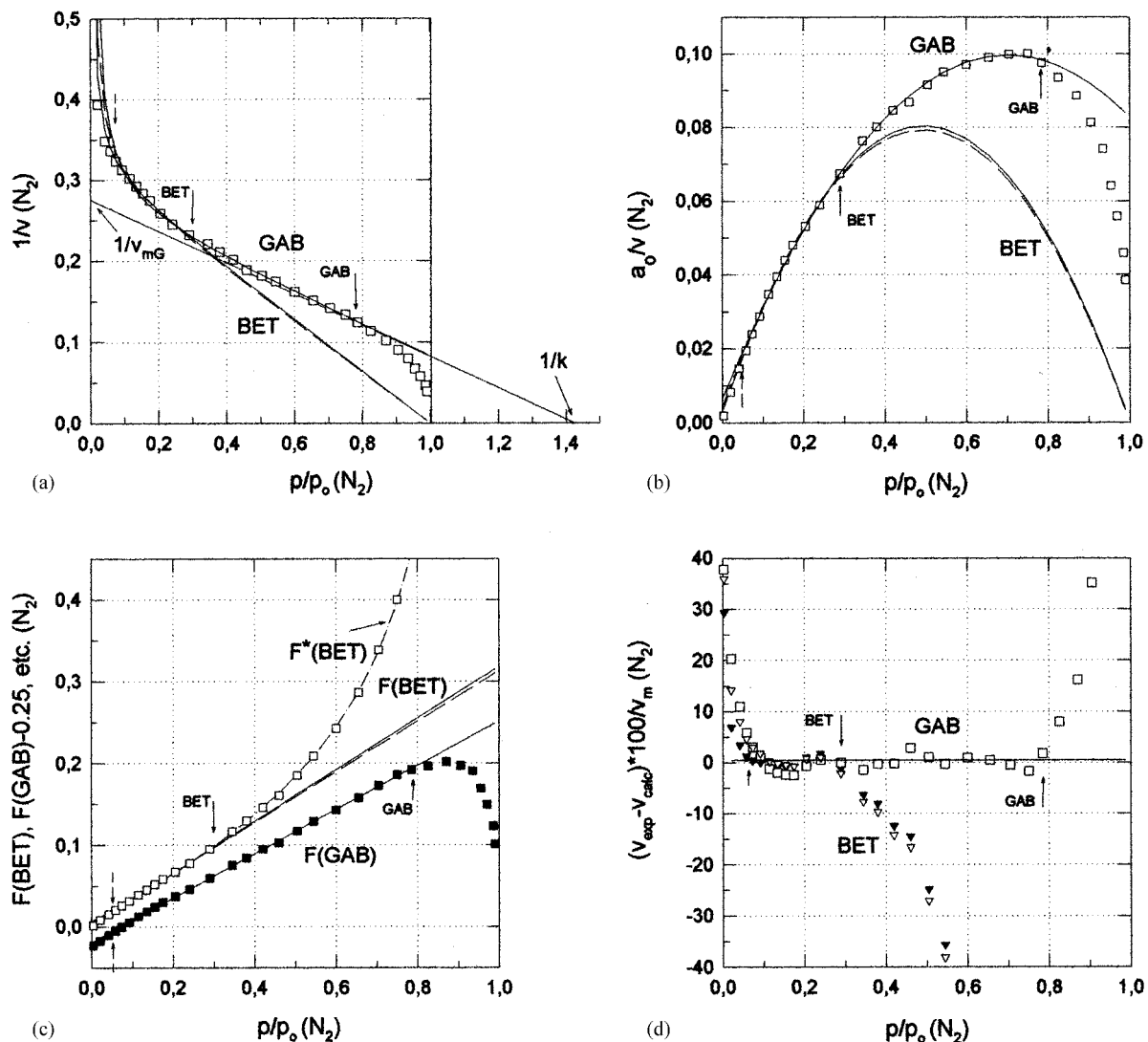


Fig. 4. Graphical illustration of the calculation procedure. System:  $N_2/TiO_2$  of Fig. 3(a). Symbols: experimental points; full lines: functions calculated by the experimental BET and GAB regressions, respectively; dashed line: BET function using the BET constants calculated in terms of the GAB constants; full arrows: upper limit of application range, dashed arrow: lower limit. (a) Inverse plots; also shown the asymptotic GAB line for first estimations of  $v_{mG}$  (GAB) and of  $k$ ; (b) parabolic representation; (c) BET plot (open symbols) and GAB plot (filled symbols; displaced 0.025 units downwards); point-dash line:  $F^*(BET)$  (Eqs. (9), (10a), (10b) and (10c)); (d) relative errors; GAB (squares), BET (open triangles), calculated BET (filled triangles). For further details, see text.

data by Eq. (3) (1st expression) as well as the linear  $F(BET)$  (full line) drawn by Eq. (3) (2nd expression) using the BET constants obtained by the linear regression of  $F(BET)_{exp}$  over the apparent 'linear' range  $0.05 < a_0 < 0.3$  and the coincident

calculated linear  $F(BET)$  (dashed line) based on the GAB constants (Eqs. (18a) and (18b)). Moreover, the dashed-dotted line represents the alternative  $F^*(BET)$  function (Eqs. (8), (9), (10a), (10b) and (10c)) calculated with the GAB constants



obtained by the parabolic regression, function which reproduces completely the upswing of  $F(\text{BET})_{\text{exp}}$  up to the upper limit of the GAB range.

For the GAB plot in Fig. 4(c), the experimental  $F(\text{GAB})_{\text{exp}}$  Eq. (6) (1st expression) (filled points, displaced 0.25 units downwards) is calculated with the experimental sorption data using the  $k$ -value obtained by the parabolic regression of Fig. 4(b)). The full line represents  $F(\text{GAB})_{\text{calc}}$  Eq. (6) (2nd expression) calculated using the GAB constants of the same regression (Table 1), which reproduces  $F(\text{GAB})_{\text{exp}}$  within the range of regression. Furthermore, the drawing is interesting as it illustrates the fall-off of the points beyond the upper limit of the GAB range corresponding to the third sorption stage (see also Fig. 1).

Finally, Fig. 4(d) offers the error plots of  $[v_{\text{exp}} - v_{\text{calc}}] \times 100/v_{\text{m}}$  for the BET and GAB calculations. The normalisation of the differences  $[v_{\text{exp}} - v_{\text{calc}}]$  with respect to  $v_{\text{m}}$ , the only parameter of direct proportionality of all these isotherm equations, allows that all these equations can be compared on the same footing. (The same argument assists the introduction of the error function NEF defined by Eq. (21)).

Fig. 4(d) shows that within its regression range the errors of the GAB regression (squares) are of the order of 2–3% of  $v_{\text{m}}$  and beyond the lower and upper limits of this range marked positive deviations are observed, pointing out that there the GAB equation do not apply. On the other hand, the errors of the BET regressions (open and filled triangles) present similar order of magnitude within their validity interval and large positive deviations below the lower limit, but large negative deviations beyond the upper limit as this isotherm predicts here a too large sorption.

This general modus operandi has been applied to all experimental cases studied in this paper and the results are condensed in Tables 1–3 and in Fig. 3.

## 5. Discussion

### 5.1. General considerations

We can now go over to review all the data given in Tables 1–3. In the cases in which the original

authors of the analysed sorption systems stated values of the BET and GAB constants these are reproduced in the corresponding headings.

Inequalities (1) are systematically verified, inequalities that are graphically reproduced in Fig. 5(a). This figure presents the experimental values of the two BET constants ( $v_{\text{mB}}$ : open symbols,  $c_{\text{B}}$ : filled symbols) against the corresponding GAB constants. It is seen that the GAB monolayer values (column 7 of Tables 1–3) are about 10–20 to 40% higher than the experimental BET values (column 1), while the GAB energy constant  $c_{\text{B(G)}}$  (column 10) is much lower (30–50% and even more) than the experimental BET values (column 2). Thus, the difference between the BET and the GAB values is much more pronounced for the energy constant than for the monolayer capacity. In the same way the errors of the energy constant values are much stronger (15–25 to 50–60% and more, see p.ex.  $\text{N}_2$  on glasspheres) than that of the monolayer (2–8%). Moreover, the error of the third GAB constant  $k$  is always of the order of 10–15% and, therefore, the value of this constant should only be given with two significant figures.

On the other hand, the tables show that the BET constants are well reproduced by both methods of calculation, being best the results of the discrete method (columns 3 and 4) using the experimental activity values. The differences with the results of the continuous method (columns 5 and 6) are certainly due to the infinite number of data implied by the integration and the values calculated by the latter method represent the ‘theoretical’ limiting figures for the BET constants in the regression interval considered. The larger errors are also due the same effect and it is readily verified that they are related to those of the discrete method by a factor  $1/\sqrt{n}$  ( $n$  is the number of points used in the discrete method; see Appendices A and B).

Good examples are the first two systems of the gas/solid group, cases which were used as experimental examples as the first versions of the GAB equations were presented [3,4]. The original values of the constants stated by Guggenheim ([3a], GAB values) and Brunauer ([3b], BET values) for  $\text{N}_2/\text{Fe}-\text{Al}_2\text{O}_3$  and by Anderson ([4], BET and GAB values) for  $\text{N}_2/\text{glasspheres}$ , respectively, are well

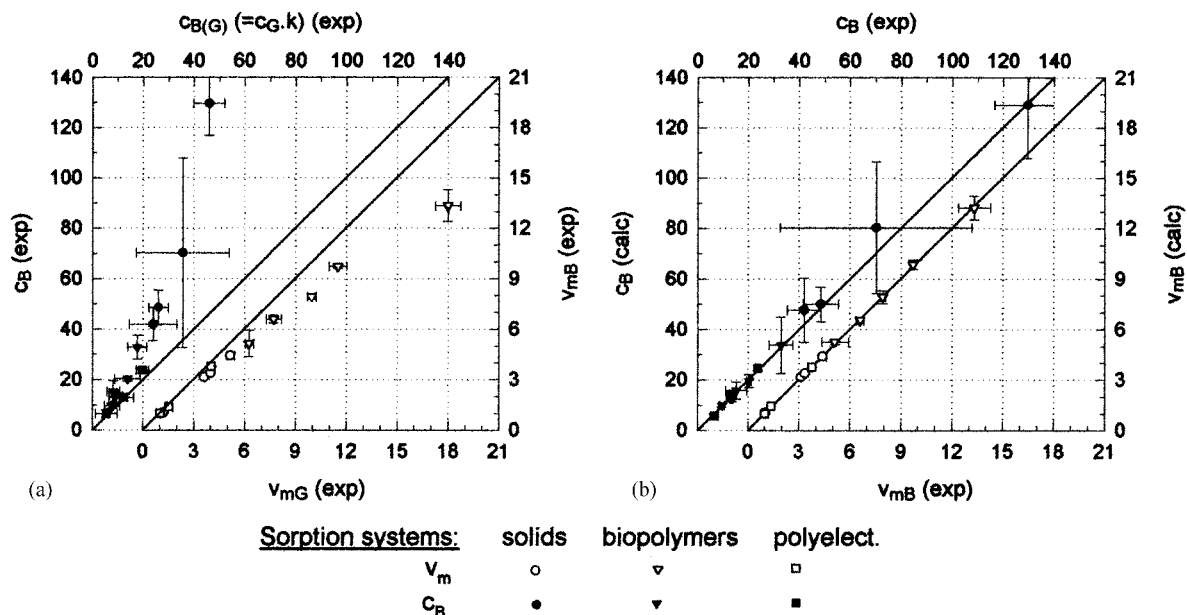


Fig. 5. (a) Illustration of inequalities (1): experimental BET values (Tables 1–3), the monolayer capacity  $v_{mB}$  (BET) (open symbols) and the monolayer energy constant  $c_B$  (BET) (filled symbols), for the sorption systems of Fig. 3 represented against the corresponding GAB values (Tables 1–3), the monolayer capacity  $v_{mG}$  (GAB) and the monolayer energy constant  $c_{B(G)}$  (GAB) ( $= c_G k$ ), respectively. (b) Illustration of the applicability of Eqs. (18a) and (18b): Calculated values of  $v_{mB}$  (BET) (open symbols) and of  $c_B$  (BET) (filled symbols) (Eqs. (18a) and (18b)) using the GAB constants) represented against the experimental  $v_{mB}$  (BET) and of  $c_B$  (BET) (Tables 1–3) for the sorption systems of Fig. 3.

reproduced by direct evaluation as well as by calculus. It is noteworthy to state that Anderson [4] also analysed, among others, the data of  $N_2/TiO_2$  by Harkins and Jura ([19b], Part XIII, Fig. 2) and his results (see headings of this system) are completely coincident with our results, although this author only used a reduced set of points and not the complete data collection. Moreover, Harkins and Jura [19] stated only BET monolayer values in their studies of  $N_2/TiO_2$  and  $H_2O/TiO_2$ . For proteins the BET values stated originally by Bull [21] correspond to the mean of the values at 25 °C and at 40 °C and the regression intervals were not specifically indicated, facts which explain the differences with our results. On the other hand, our GAB values for wheat starch are coincident with those presented originally by van der Berg [16].

Furthermore, the tables show that the BET monolayer  $v_m$  is much better reproduced than the BET energy constant  $c_B$ , in terms of the GAB constants. The constant  $c_B$  is, as already stated,

much more regression interval-dependent and therefore physically much more unreliable. Fig. 5(b) illustrates graphically these facts. The experimental values of the two ‘experimental’ BET constants are plotted against the calculated values (discrete method) of these constants in terms of the GAB constants. The calculated ones reproduce exactly the experimental BET monolayer values (open symbols), while the BET energy constant values (filled symbols) are well reproduced within the error ranges. The different orders of magnitude of the errors are to be pointed out. The errors of the  $v_{mB}$  values fall within the used sizes of the symbols, while that of  $c_B$  are at least one order of magnitude higher (15–25%).

For the GAB constant  $k$  only less than unity values are obtained, confirming the findings and figures observed in previous papers [4a,9]. Values of  $k$  less than unity are typical for the GAB isotherm; cases of  $k > 1$  are not found. Moreover, the values of  $k$  given in Table 1 of ca. 0.7 can be considered as characteristic of solid non-porous

sorbants [4a,9]. For the other sorption systems, although always with water as a unique sorbate, other values of  $k$  nearer to unity are observed. For proteins one finds  $k \approx 0.8$  (in coincidence with values found [17] for proteic foods ( $k \approx 0.8$  (range: 0.78–0.85))) and for wheat starch  $k = 0.68$  (coincident with starchy foods ( $k \approx 0.7$  (range: 0.65–0.75) [17])), and for electrolytes and polyelectrolytes ( $k \approx 0.92$ ), values which also can be taken as characteristic of all these sorbants.

Finally, there are some words about NEF.<sup>6</sup> In the mean good values of NEF are in the order of 2–5%. In principle this function is a measure of the experimental dispersion of the sorption data. If this dispersion is homogeneous over the whole GAB range, NEF has coincident values for the BET as well as for the GAB regressions indicating the much better ability of the GAB equation to represent the data as it embraces a much broader range of the sorbate activity. Especially good examples for this are  $N_2/TiO_2$ ,  $H_2O/TiO_2$  and  $H_2O$ /wheat starch sorption data systems, systems which present a much higher number of experimental points than the usual number of data given in the literature. But if this dispersion is different at low sorbate activities (BET region) than at higher activities (GAB region), then NEF will oscillate about the same values, being in some cases the BET values lower than the GAB values and in others the opposite is observed, but always within the range 2–5%. Examples of this are, among others, eggalbumin and rattail tendon data systems, respectively. A case markedly beyond this range is the  $H_2O/PSSH$  system (NEF(GAB)  $\approx 15$  (!)).

Moreover, the NEF values of the BET parameters calculated by Eqs. (18a) and (18b) using the GAB constants are due to the intrinsic hyperbolic curvature of  $F^*(BET)$  (Eqs. (8), (9), (10a), (10b) and (10c)) over the BET range of activities. The experimental NEF values of the BET regression include this effect and the experimental dispersion of the data determines that these NEF values

oscillate (upwards or downwards) about the ‘theoretical’ values indicated by the former.

Concluding this analysis, all results show that it is straightforward to conclude that the GAB constants are to be taken as the representative parameters of the multilayer sorption. It is also evident that a much more precise description of the multilayer sorption phenomenon can be achieved if the analysis is made with a set of experimental data which spans over the complete sorbate activity range and the values of all parameters should be considered and/or analysed.

### 5.2. Constant $k$ and complementary energy considerations

Although preferred or exclusive attention is paid to the monolayer capacity values, because of its importance for the determination of specific areas and for food stability, the values of the energy constants should not be overlooked or ignored. First simply because they are simultaneous outputs of the regression processes and the whole sets of constants should be considered. Then because the energy constants determine the details of the sigmoidal shape of the isotherms, i.e., the form of the normalised  $v/v_m$  vs.  $a_0$  plots. So  $c_B$  and  $c_G$  determine the more or less pronounced form of the ‘knee’ at the lower activity range. On the other hand, the constant  $k$  determines the profile at the higher activity range, regulating the upswing after the plateau following the ‘knee’ at the medium activity range. Higher values of  $k$  establish a more pronounced upswing. This can be readily observed in Fig. 3. Electrolytic systems ( $k \approx 0.92$ ) as well as proteins ( $k \approx 0.8$ ) present a much more noticeable upswing than the gas/solid systems as well as wheat starch ( $k \approx 0.7$ ). The isotherms of the latter are much plainer at the higher activity range. Finally, these upswings determined by constant  $k$  should not be confused with the upswing due to the third sorption stage which appears at the highest sorbate activities ( $a_0 > 0.85$ –0.9).

As already stated in Ref. [9], each group presents characteristic values for the energy constants and certain trends in the variations of these values can be recognised from one group to another. On one hand, we have the gas/solid

<sup>6</sup> NEF, defined by Eq. [21], is directly related to the correlation coefficient  $r^2$  by the following relation:  $r^2 = 1 - (NEF/100)^2 (v_m/S_v)^2$ , where  $S_v = [(\sum v_{exp}^2/n) - (\sum v_{exp}/n)^2]^{1/2}$ .

group, which presents high values of  $c_G$  (40–70) and low values of  $k$  ( $\approx 0.7$ ). On the other hand, within the other groups, always for water sorption,  $c_G$  has much lower values (15–25) and  $k$  varies from  $\approx 0.7$  for wheat starch through  $\approx 0.8$  for proteins to  $\approx 0.92$  for electrolytic systems. The extent of the second (GAB) sorption stage also increases in the same sequence [9].

This behaviour of the constant  $k$  deserves some comments, as this constant has never been analysed in detail in the literature. An interesting interpretation of  $k < 1$ , and indeed a justification of the introduction of this constant, is forwarded by de Boer himself [5a]. A molecule of a second layer situated on top of a (isolated) molecule sorbed directly on the solid (thus building up the BET pile) would hardly “be bounded strongly enough to show a heat of desorption of the order of magnitude of the heat of evaporation” of a molecule from the pure liquid sorbate. Thus, it is quite logical to expect that the sorbate molecules are easier to desorb from these layers than from the pure liquid, or, otherwise speaking, free energy-wise, that the molecules in these upper (GAB) layers (GL) will have a higher standard vapour pressure  $p_{GL}$  than that of the liquid ( $p_0$ ). Hence, we have  $k = p_0/p_{GL}$  ( $< 1$ ), relation which acts as an definition of  $k$ , although originally Guggenheim [3a] as well as de Boer [5] worked directly with  $p_{GL}$  as the third GAB constant [9b]. Thus, lower than unity values of  $k$  indicates a less structured state of the sorbate in the GAB layers following the monolayer than in the sorbate’s pure liquid state.

It is evident that the fact that  $k$  is different (and less) than unity cancels Brunauer’s original assumption that the state of all these molecules is already liquid-like. If the physicochemical nature of the experimental systems is taken into account, the trends mentioned above correspond to an increase of the strength and extent of the interactions between sorbate and sorbant in the sequence stated and indicates that the sorption potential of the solid extends beyond the first layer. The potential certainly diminish progressively with the increase of the distance from the surface and dies out at some upper sorbate layer and hence compensates in part the missing lateral (liquid-

like) interactions, neglected by the model, in the sorption pile. The GAB equation takes all this into account in an averaged form through the constant  $k$ , which increases with stronger interactions between sorbate and sorbant. It also explains that the applicability of this equation is limited to  $h$  layers, after which the third sorption stage [9] starts up with now liquid like (BET-like) sorbed molecules. So in the case of the strong electrostatic interactions of the electrolytic and polyelectrolytic systems both, the constant  $k$  ( $\approx 0.92$ ) and the extension of the GAB sorption stage ( $h \approx 25$  [9]), are highest and are evidently interrelated.

On the other hand, the interpretation of the other energy constants  $c_B$  and  $c_G$  is less straightforward and still so controversial in the literature that these magnitudes are not seriously taken into consideration. It is habitual to interpret these constants energy-wise by relating them directly to the differences of the molar heats ( $Q$ ) of desorption of the sorbate molecules from the different sorption stages (monolayer, ML and GAB layers, GL) with respect to the molar heat of evaporation (EV) from the pure sorbate liquid, in both cases the final state being the pure gas/vapour at standard pressure. So it is usually written that

$$RT \ln c_B \approx Q_{ML} - Q_{EV} \quad (c_B > 1), \quad (26a)$$

$$RT \ln c_G \approx Q_{ML} - Q_{GL} \quad (c_G > 1), \quad (26b)$$

$$RT \ln k \approx Q_{GL} - Q_{EV} \quad (k < 1). \quad (26c)$$

The second and third expressions have been written down by analogy with the first one by taking into account the physical meaning of the GAB constants  $c_G$  and  $k$  (see also Eq. (5)). By using these equations to relate these constants, specifically  $c_B$ (BET) via Eq. (26a), with experimental values of heat of desorption in general no agreement is found [7]. The net heat value calculated from  $c_B$ (BET) is usually less than the experimental one. Moreover, the BET model predicts that this magnitude is constant in the monolayer region and zero thereafter, while experimentally a decreasing dependence in terms of the amount sorbed is observed which levels off only smoothly in the multilayer region. So it is accepted that  $c_B$ (BET) gives only a very rough measure of the net heat of sorption [7]. If now the

conclusion of the present paper is introduced, i.e., that the values of this energy constant  $c_{B(G)}$  ( $= c_G k$ ) reduces drastically ( $\approx 35$ – $40\%$  or more) in terms of the GAB isotherm with respect to the values of  $c_B$  by BET, the situation becomes even worse and the energy-wise interpretation of these constants yet more doubtful. Notwithstanding, all the sorption steps can be considered as endothermic ( $> 0$ ) and consequently  $Q_{ML} > Q_{EV} > Q_{GL} > 0$ .

The alternative is to interpret these constants more strictly free energy-wise in terms of the statistical model [9]. Then these constants measure (logarithmically) differences of the standard value ( $^\circ$ ) of the chemical potential  $\mu^\circ$  of the sorbate molecules in the pure liquid state (L) with respect to its values in the different sorption stages (in the rational scale):

in the monolayer (ML) ( $c_B > 1$ ):

$$RT \ln c_B = \mu_L^\circ - \mu_{ML}^\circ$$

$$[= (Q_{ML} - Q_{EV}) - T(S_L^\circ - S_{ML}^\circ)], \quad (27a)$$

in the GAB layers (GL) ( $k < 1$ ):

$$RT \ln k = \mu_L^\circ - \mu_{GL}^\circ$$

$$[= (Q_{GL} - Q_{EV}) - T(S_L^\circ - S_{GL}^\circ)], \quad (27b)$$

and between sorption stages ( $c_G > 1$ ):

$$RT \ln c_G = \mu_{GL}^\circ - \mu_{ML}^\circ$$

$$[= (Q_{ML} - Q_{GL}) - T(S_{GL}^\circ - S_{ML}^\circ)]. \quad (27c)$$

The differences of (standard) entropies ( $S^\circ$ ) of sorption, neglected in the energy-wise formulation, cover the discrepancies between both approaches. This entropic contribution is particularly important for  $k$ , contribution, which is determined by the effects, discussed above in the analysis of this parameter.

As  $c_B > 1$ , the sorbate in the monolayer is more stable (lower standard chemical potential, i.e., negative thermodynamic deviation from ideality in the rational scale) than in the pure liquid

sorbate. As it is found that  $c_B > c_{B(G)}$  ( $> 1$ ), the GAB monolayer is also stable, but not so stable as the BET monolayer. Further, as  $k < 1$ , the sorbate in the GAB layers is less stable (higher standard chemical potential, i.e., positive thermodynamic deviation) than in the pure liquid of the sorbate, as Guggenheim and de Boer postulated. This less-favourable situation determines that the amount sorbed is less than in the ‘idealised’ (BET) case, situation which finally conduces to a state of saturation at  $a_0 = 1$  [9]. Again, if this latter situation is relaxed at higher layers a subsequent increment in the amount of sorption is observed (the third sorption stage [9]), and consequently the GAB equation becomes not applicable over the complete range of activities.

As a special example, let us consider in detail the sorption of nitrogen and of water on rutile (systems 3 and 4 of Table 1). The numerical energy values (in  $\text{cal mol}^{-1}$ ) are as follows:

	N <sub>2</sub> /TiO <sub>2</sub> (77 K)	de Boer (90 K) <sup>a</sup>	H <sub>2</sub> O/TiO <sub>2</sub> (298 K)
$RT \ln c_B$	750		2400
$RT \ln c_G$	600	820	1950
$RT \ln k$	–50	–25	–240
$\mu_L^\circ (= \mu_v^\circ)^b$	–4330		–56560
$Q_{EV}^c$	1300	1500	10500

In this table, <sup>a</sup> $c_G = 100$ ,  $k = 1/1.15 = 0.869$  [5b]; <sup>b</sup>R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, 58th Ed., 1977–1978; and <sup>c</sup>Ch.E. Hodgman (Ed.), Handbook of Chemistry and Physics, Chemical Rubber Publ. Co., 30th Ed., 1946. One observes that, for both systems, the distinction of the sorbed states with respect to the liquid reference state are much less pronounced in terms of free energy (chemical potentials) than in terms of heat exchange, a fact that indicates that the entropy differences are not neglectable. However, the differences between both systems for all these quantities are notable, although the energy constants of the sorption isotherms are quite similar. The differences reflect different physical

situations (sorption temperature), through the factor  $RT$ , as well as the different chemical nature of the sorbates.

Finally, column 3 states interesting values, which are surprisingly close to those of  $N_2/TiO_2$ . They correspond to a theoretical example given by de Boer [5b] illustrating the sorption behaviour at 90 K in terms of his (now GAB) isotherm of an hypothetical nitrogen-like gas (molecular weight of 30, boiling point of 80 K, heat of evaporation of  $1500 \text{ cal mol}^{-1}$  [5b]). de Boer chooses intuitively these values taking as reference BET results for nitrogen sorption given in Brunauer's book [1], but never verified them against experimental data. The coincidence with the values found in this paper is certainly remarkable.

## 6. Final remarks

Inequalities (1), the motives of this paper, have been explained in terms of the GAB isotherm. The superiority of this equation has been shown, based on a quite larger range of applicability and the ability to reproduce the results of the BET equation.

The marked differences between the BET and the GAB constants are noteworthy; the GAB monolayer capacity  $v_{mG}$  is about 15% higher than the BET value and the energy constant  $c_{B(G)}$  ( $=c_G k$ ) reduces drastically ( $\approx 35\text{--}40\%$  or more) in terms of the GAB isotherm respect to the BET values, differences which have been explained. Moreover, the GAB isotherm, as an improved version of the sorption isotherm of the multilayer sorption model originally formulated by Brunauer et al. by the introduction of the third parameter,  $k$ , characterising the state of the sorbed molecules beyond the first layer, allows to explain the upswing systematically found in the BET plots after the initial (pseudo) linear range. Unfortunately behind this substantial affirmation there lays another which is not so pleasant considering the status of seniority of the BET isotherm and its undoubtful merits and contributions to the understanding of multilayer sorption. This affirmation indicates that, strictly speaking, the BET isotherm

is really never valid, unless it is verified experimentally that  $k$  is certainly equal to unity.

The direct consequence of these conclusions is that the GAB constants have to be taken as being the representative parameters of the multilayer sorption. In particular this means that it is the GAB monolayer parameter, which has to be used to estimate surface areas of the sorbant, and consequently the recommendations of IUPAC concerning this item are to be revised. On the other hand, in food technology a detailed knowledge of water sorption isotherms is fundamental in concentrating, dehydrating and drying of food-stuffs, as well as in determining the quality, stability and shelf life of foods. Also the rate of the food deterioration reactions such as enzymatic hydrolysis, maillard browning and non-enzymatic oxidation as well as microbial growth depend markedly on moisture content and these rates decrease as the moisture is reduced. A critical minimum moisture content corresponds to the monolayer sorption value [31–33], beyond which a loss of organoleptic properties on rehydration is found. Because of all these, the knowledge of this parameter is so important in this field and its GAB value seems to be is a much more adequate value to work with, although, as already stated, some objections have been raised to the use of the monolayer concept to complex materials like food [14]. Finally, there remains as a challenge to be solved the drawback of all these isotherms about their inability to explain and represent the sorption at very low activities ( $a_0 < 0.1$ ).

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## Appendix A: Classical least-squares regression

The linear regression model function  $F(x)$ , as  $F_i = \alpha_0 + \alpha_1 x_i + \varepsilon_i$ , where  $\varepsilon_i$  is the error of the adjustment, and the least-squares method estimates  $\alpha_0$  and  $\alpha_1$  from  $n$  data of  $F(x)$  observed at values  $x_i$  of the independent variable  $x$  through the minimum condition

$$Q(\alpha_0, \alpha_1) = \sum_{i=1}^n \varepsilon_i^2 = \sum_{i=1}^n (F(x_i) - (\alpha_0 + \alpha_1 x_i))^2$$

$$= \text{minimum}, \quad (\text{A.1})$$

where  $\alpha_0$  and  $\alpha_1$  are the coefficients of the proposed linear polynomial

$$P(x_i) = \alpha_0 + \alpha_1 x_i. \quad (\text{A.2})$$

The normal equations are obtained by derivation of Eq. (A.1) with respect to the parameters  $\alpha_0$  and  $\alpha_1$ :

$$-2 \sum_{i=1}^n (F_i - (\alpha_0 + \alpha_1 x_i)) = 0, \quad (\text{A.3a})$$

$$-2 \sum_{i=1}^n x_i (F_i - (\alpha_0 + \alpha_1 x_i)) = 0. \quad (\text{A.3b})$$

Solving these equations for  $\alpha_0$  and  $\alpha_1$ , we obtain the minimum estimates:

$$\hat{\alpha}_0 = \frac{[x^2][F] - [x][Fx]}{D}, \quad (\text{A.4a})$$

$$\hat{\alpha}_1 = \frac{n[Fx] - [x][F]}{D}, \quad (\text{A.4b})$$

where  $[Y]$  are the Gaussian brackets

$$\left( [Y] \equiv \sum_{i=1}^n Y_i \right) \quad \text{and} \quad D \equiv n[x^2] - [x]^2. \quad (\text{A.5})$$

The errors of variance  $\sigma^2$  is given by

$$\hat{\sigma}^2 \equiv \frac{Q(\hat{\alpha}_0, \hat{\alpha}_1)}{n-2} = \frac{[F^2] - [F]^2/n - \hat{\alpha}_1^2 D/n}{n-2}$$

$$= \frac{[F^2] - [F]\hat{\alpha}_0 - [Fx]\hat{\alpha}_1}{n-2}, \quad (\text{A.6})$$

and the variances of the parameters are

$$\sigma^2(\hat{\alpha}_0) = \frac{[x^2]}{D} \hat{\sigma}^2, \quad (\text{A.7a})$$

$$\sigma^2(\hat{\alpha}_1) = \frac{n}{D} \hat{\sigma}^2. \quad (\text{A.7b})$$

## Appendix B: Regression with a known analytical expression $F^*(x)$

### B.1. Discrete least-squares regression

If analytical expressions  $F^*(x)$  such as Eq. (9) are known, we can replace them directly in the minimum condition. Using the second expression of Eq. (9), i.e.

$$F^*(x_i) = (A - C) + (B - C)x_i + \frac{C}{1 - x_i}, \quad (\text{B.1})$$

we have:

$$Q(\alpha_0, \alpha_1) = \sum_{i=1}^n \varepsilon_i^2 = \sum_{i=1}^n \left[ (A - C) + (B - C)x_i + \frac{C}{1 - x_i} - (\alpha_0 + \alpha_1 x_i) \right]^2 = \text{minimum}. \quad (\text{B.2})$$

The corresponding least-squares normal equations, obtained again by derivation with respect to the parameters  $\alpha_0$  and  $\alpha_1$ , are now more explicit and read, using Gaussian brackets:

$$(A - C)n + (B - C)[x] + C \left[ \frac{1}{1 - x} \right]$$

$$= \alpha_0 n + \alpha_1 [x], \quad (\text{B.3a})$$

$$(A - C)[x] + (B - C)[x^2] + C \left[ \frac{x}{1 - x} \right]$$

$$= \alpha_0 [x] + \alpha_1 [x^2]. \quad (\text{B.3b})$$

Solving these equations for  $\alpha_0$  and  $\alpha_1$ , we obtain the minimum estimates:

$$\alpha_0^* = (A - C) + \frac{CD_0^*}{D} = A + CS_0^*, \quad (\text{B.4a})$$

$$\alpha_1^* = (B - C) + \frac{CD_1^*}{D} = B + CS_1^*. \quad (\text{B.4b})$$

The functions  $D_0^*$ ,  $D_1^*$ ,  $S_0^*$  and  $S_1^*$  contain the regression sums over the independent variable  $x_i$ :

$$D_0^* \equiv \left[ \frac{1}{1-x} \right] [x^2] - \left[ \frac{x}{1-x} \right] [x], \quad (\text{B.5a})$$

$$D_1^* \equiv \left[ \frac{x}{1-x} \right] n - \left[ \frac{1}{1-x} \right] [x], \quad (\text{B.5b})$$

and

$$S_0^* \equiv \frac{D_0^*}{D} - 1, \quad (\text{B.6a})$$

$$S_1^* \equiv \frac{D_1^*}{D} - 1 \quad (\text{B.6b})$$

with  $D$  given by Eq. (A.5). Eqs. (B.4a), (B.4b), (B.5a), (B.5b), (B.6a) and (B.6b) are the basis of Eqs. (16a), (16b), (17a), (17b), (18a), (18b), (19a) and (19b).

The equations for the error variances resemble those of the former case, Eqs. (A.6), (A.7a) and (A.7b). They are:

$$\sigma^{*2} \equiv \frac{Q(\alpha_0^*, \alpha_1^*)}{n-2} = \frac{[F^{*2}] - [F^*]\alpha_0^* - [xF^*]\alpha_1^*}{n-2}, \quad (\text{B.7a})$$

$$\sigma^2(\alpha_0^*) = \frac{[x^2]}{D} \sigma^{*2}, \quad (\text{B.7b})$$

$$\sigma^2(\alpha_1^*) = \frac{n}{D} \sigma^{*2}. \quad (\text{B.7c})$$

Eq. (B.7a) can be written more explicitly taking Eqs. (B.1), (B.4a) and (B.4b) into account. After some algebra we find:

$$\sigma^{*2} = \frac{C\{[F^*/(1-x)] - (D_0^*/D)[F^*] - (D_1^*/D)[F^*x]\}}{n-2} \quad (\text{B.8})$$

with

$$\left[ \frac{F^*}{1-x} \right] = (A-C) \left[ \frac{1}{1-x} \right] + (B-C) \left[ \frac{x}{1-x} \right] + C \left[ \frac{1}{(1-x)^2} \right], \quad (\text{B.9a})$$

$$[F^*x] = (A-C)[x] + (B-C)[x^2] + C \left[ \frac{x}{1-x} \right], \quad (\text{B.9b})$$

$$[F^*] = (A-C)n + (B-C)[x] + C \left[ \frac{1}{1-x} \right]. \quad (\text{B.9c})$$

Eqs. (B.4a), (B.4b), (B.8), (B.9a), (B.9b) and (B.9c) are particularly expressive. They show the decisive importance of the term of constant  $C$  of  $F^*$ (BET) for this adjustment. As it is to be expected, with  $C=0$  the regression is exact, i.e.,  $\alpha_0^* = A$ ,  $\alpha_1^* = B$ ,  $\sigma^{*2} = 0$ .

Finally, it is to be stated that the values to be taken for the independent variable  $x_i$  are a matter of convenience or taste. They can be those of the experimental data set and a direct comparison with the classical method (Appendix A) can be made; they can be equal in number ( $n = n_{\text{exp}}$ ) but equally spaced, and also their number can be increased at will. In this latter case, if the number becomes very large it goes over to the continuous regression process, which is described in the following section.

## B.2. Continuous least-squares regression

For the regression of a continuous process of  $F(x)$  ( $= P(x) + e(x)$ ) by a lineal expression  $P(x)$  like Eq. (A.2), the minimum condition is to be transformed into an integral:

$$Q = \int_{x'}^{x''} \varepsilon(x) dx = \int_{x'}^{x''} (F(x) - (\alpha_0 + \alpha_1 x))^2 dx = \text{minimum}, \quad (\text{B.10})$$

where  $x''$  and  $x'$  are the limits of the regression interval. The normal equations are again obtained by derivation with respect to the parameters  $\alpha_0$  and  $\alpha_1$  and read now

$$-2 \int_{x'}^{x''} [F(x) - (\alpha_0 + \alpha_1 x)] dx = 0, \quad (\text{B.11a})$$

$$-2 \int_{x'}^{x''} x[F(x) - (\alpha_0 + \alpha_1 x)] dx = 0. \quad (\text{B.11b})$$

Solving the integrals involved and then the equations themselves for  $\alpha_0$  and  $\alpha_1$ , we obtain the estimates



$$\tilde{\alpha}_0 = \frac{(\Delta x^3/3)I_0 - (\Delta x^2/2)I_1}{\Delta}, \quad (\text{B.12a})$$

$$\tilde{\alpha}_1 = \frac{(\Delta x)I_1 - (\Delta x^2/2)I_0}{\Delta}, \quad (\text{B.12b})$$

where

$$\Delta x^k \equiv x^{nk} - x'^k, \quad k = 1, 2, 3. \quad (\text{B.13})$$

$I_0$  and  $I_1$  are the integrals:

$$I_k \equiv \int_{x'}^{x''} F(x)x^k dx, \quad k = 0, 1, \quad (\text{B.14})$$

and  $\Delta$  stands for

$$\Delta \equiv \Delta x \left( \frac{1}{3} \Delta x^3 \right) - \left( \frac{1}{2} \Delta x^2 \right)^2. \quad (\text{B.15})$$

The error variance  $\sigma^2$  is now estimated by

$$\tilde{\sigma}^2 \equiv \frac{Q(\alpha_0^*, \alpha_1^*)}{\Delta x} = \frac{I_2 - I_0 \tilde{\alpha}_0 - I_1 \tilde{\alpha}_1}{\Delta x}, \quad (\text{B.16})$$

where

$$I_2 \equiv \int_{x'}^{x''} F(x)^2 dx, \quad (\text{B.17})$$

and the variances of the parameters become

$$\sigma^2(\tilde{\alpha}_0) = \frac{\Delta x \Delta x^3}{3\Delta} \tilde{\sigma}^2, \quad (\text{B.18a})$$

$$\sigma^2(\tilde{\alpha}_1) = \frac{(\Delta x)^2}{\Delta} \tilde{\sigma}^2. \quad (\text{B.18b})$$

All these equations are completely general and may be specialised for any specific function  $F(x)$ . But before doing this for the problem at hand it is convenient to show that the expressions of both procedures are directly related. When the observed values  $x_i$  are equally spaced, i.e.,  $x_i - x_{i-1} = \Delta x/n$ , the averages converge to mean value integrals as  $n$  increases:

$$\frac{[G]}{n} \Rightarrow \frac{1}{\Delta x} \int_{x'}^{x''} G(x) dx, \quad (\text{B.19})$$

where  $G$  in the present case stands for  $1, x, x^2, F^*, xF^*, F^{*2}, 1/(1-x), x/(1-x), 1/(1-x)^2, F^*/(1-x)$ , etc. Therefore, since  $\alpha_0^*, \alpha_1^*$  and  $\sigma^{*2}$  converge to  $\tilde{\alpha}_0, \tilde{\alpha}_1$  and  $\tilde{\sigma}^2$ , respectively, we have that

$$n\sigma^2(\alpha_0^*) \Rightarrow \frac{\Delta x \Delta x^3}{3\Delta} \tilde{\sigma}^2, \quad (\text{B.20a})$$

$$n\sigma^2(\alpha_1^*) \Rightarrow \frac{(\Delta x)^2}{\Delta} \tilde{\sigma}^2, \quad (\text{B.20b})$$

which allow us to define the variances in the continuous case as in Eqs. (B.18a) and (B.18b). These relations relate the discrete and continuous cases and correspond to the experimental fact that when the number of observations increases the standard deviations of the parameters decrease to 0 at an  $\sqrt{n}$ -rate.

Specialising  $F(x)$  by  $F^*$ (BET) given by Eq. (B.1) and using directly the variable  $a_0$  the integrals (B.14) and (B.17) take the following expressions, being now  $a_0'$  and  $a_0''$  the limits of the regression interval:

$$I_0 = (A - C)\Delta a_0 + (B - C) \frac{\Delta a_0^2}{2} - C \ln \left( \frac{1 - a_0''}{1 - a_0'} \right), \quad (\text{B.21a})$$

$$I_1 = (A - C) \frac{\Delta a_0^2}{2} + (B - C) \frac{\Delta a_0^3}{3} - C (\Delta a_0 + \ln \left( \frac{1 - a_0''}{1 - a_0'} \right)), \quad (\text{B.21b})$$

$$I_2 = (A - C)I_0 + (B - C)I_1 - CI_2', \quad (\text{B.21c})$$

$$I_2' \equiv \int_{a_0'}^{a_0''} \left( \frac{F(a_0)}{1 - a_0} \right) da_0 = -(A - C) \ln \left( \frac{1 - a_0''}{1 - a_0'} \right) - (B - C) \times (\Delta a_0 + \ln \left( \frac{1 - a_0''}{1 - a_0'} \right)) + C \left( \frac{1}{1 - a_0''} - \frac{1}{1 - a_0'} \right). \quad (\text{B.21d})$$

With Eqs. (B.21a) and (B.21b), Eqs. (B.12a) and (B.12b) become:

$$\tilde{\alpha}_0 = (A - C)\tilde{S}_0, \quad (\text{B.22a})$$

$$\tilde{\alpha}_1 = (B - C)\tilde{S}_1, \quad (\text{B.22b})$$

where

$$\tilde{S}_0 \equiv \frac{A_0}{A} - 1, \quad (\text{B.23a})$$

$$\tilde{S}_1 \equiv \frac{A_1}{A} - 1, \quad (\text{B.23b})$$

and

$$A_0 \equiv \left( \frac{\Delta a_0^2}{2} - \frac{\Delta a_0^3}{3} \right) \ln \left( \frac{1 - a_0''}{1 - a_0'} \right) + \frac{\Delta a_0 \Delta a_0^2}{2}, \quad (\text{B.24a})$$

$$A_1 \equiv \left( \frac{\Delta a_0^2}{2} - \Delta a_0 \right) \ln \left( \frac{1 - a_0''}{1 - a_0'} \right) - \Delta a_0 \Delta a_0, \quad (\text{B.24b})$$

$$A \equiv \frac{\Delta a_0 \Delta a_0^3}{3} - \left( \frac{\Delta a_0^2}{2} \right)^2, \quad (\text{B.24c})$$

$$\Delta a_0^k \equiv a_0''^k - a_0'^k, \quad k = 1, 2, 3. \quad (\text{B.24d})$$

The regression interval determines exclusively the functions  $A_0$ ,  $A_1$  and  $A$  as  $f(a_0'', a_0')$  and the attributes of the GAB equation enter only through the constants  $A$ ,  $B$  and  $C$  as  $f(v_m, c, f)$ . Furthermore, the error variances read now:

$$\tilde{\sigma}^2 = C \frac{I_2 - (A_0/A)I_0 - (A_1/A)I_1}{\Delta a_0} \quad (\text{B.25})$$

$$\sigma^2(\tilde{x}_0) = \frac{\Delta a_0 \Delta a_0^3}{3A} \tilde{\sigma}^2, \quad (\text{B.26a})$$

$$\sigma^2(\tilde{x}_1) = \frac{(\Delta a_0)^2}{A} \tilde{\sigma}^2. \quad (\text{B.26b})$$

Eqs. (B.22a), (B.22b), (B.23a), (B.23b), (B.24a), (B.24b), (B.24c), (B.24d), (B.25), (B.26a) and (B.26b) are the principal results in this case and are similar to Eqs. (B.4a), (B.4b), (B.5a), (B.5b), (B.6a), (B.6b), (B.7a), (B.7b) and (B.7c) and the role of the nonlinear term of constant  $C$  is evident. With  $C=0$  the exact result comes out:  $\tilde{x}_0 = A$ ,  $\tilde{x}_1 = B$ ,  $\tilde{\sigma}^2 = 0$ .

By substitution of Eqs. (B.22a) and (B.22b) into Eqs. (14a) and (14b), the following expressions for the BET constants,  $v_{mB}$  and  $c_B$ , are derived:

$$v_{mB} = \frac{1}{A + B + C(\tilde{S}_0 + \tilde{S}_1)}, \quad (\text{B.27a})$$

$$c_B = \frac{A + B + C(\tilde{S}_0 + \tilde{S}_1)}{(A + C)\tilde{S}_0}, \quad (\text{B.27b})$$

expressions which are analogous to that of Eqs. (17a) and (17b) and are now only functions of the limits of the integration interval.

Direct expressions for  $v_{mB}$  and  $c_B$  in terms of the GAB constants result by substituting  $A$ ,  $B$  and  $C$  (Eqs. (10a), (10b) and (10c)) into Eqs. (B.27a) and (B.27b). After some algebra we find:

$$v_{mB} = \frac{v_{mG}}{[1 + 2(1 - k)/c_{B(G)}]\tilde{R}_m(\Delta a_0)}, \quad (\text{B.28a})$$

$$c_B = c_{B(G)} \left[ 1 + \frac{2(1 - k)}{c_{B(G)}} \right] \tilde{R}_c(\Delta a_0), \quad (\text{B.28b})$$

where the auxiliary functions  $\tilde{R}_m$  and  $\tilde{R}_c$  are now

$$\tilde{R}_m(\Delta a_0) \equiv 1 + (1 - k) \frac{c_{B(G)} + (1 - k)}{c_{B(G)} + 2(1 - k)} \times (\tilde{S}_0 + \tilde{S}_1), \quad (\text{B.29a})$$

$$\tilde{R}_c(\Delta a_0) \equiv \frac{\tilde{R}_m(\Delta a_0)}{1 + (1 - k)(c_{B(G)} + (1 - k)\tilde{S}_0)}. \quad (\text{B.29b})$$

Eqs. (B.28a), (B.28b), (B.29a) and (B.29b) closely resemble Eqs. (18a), (18b), (19a) and (19b) of the discrete method, but are independent of the discrete distribution of experimental points. They represent upper limits of the differences between BET and GAB parameters and these equations have been used to calculate the curves of Fig. 1.

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