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Johannesson, Björn

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Björn F. Johannesson
Lund Institute of Technology, Division of Building Materials
Box 118, SE-221 00 Lund, Sweden

Abstract

Measured adsorption isotherms on porous glass, obtained experimentally at different temperatures, are used to calculate the specific surface area, using two different types of BET-equations. The first is the standard method assuming that the first formed adsorbed layer has a condensation heat different from 'normal' condensation heat. In the second tested approach it is assumed that the two first layers have a special condensation heat. It will be shown that the specific surface differs more among the tested temperatures when using the one-layer method than with the two-layer approach. The use of the two-layer method is, further, motivated by experiments where the global response in terms of adsorption heat is measured with a sorption microcalorimeter. Furthermore, the specific surface areas obtained using the one-layer method, are significantly higher than values obtained by the two-layer method.

The dependency of the material constants $c$ and $b$, introduced in the BET-theory, on the temperature are evaluated. A somewhat high increase of $c$, when increasing test temperature, was observed. This indicates that the energy involved in placing molecules on bare material surfaces is also changed with temperature.

The proposed method of calculating the condensation heats for different adsorption layers, as given by the BET-theory, was shown to differ from the measured values by a factor of approximately 2.5. The calorimetric measurements performed were therefore used to identify
material constants, which in the normal BET-theory are most often explicitly assumed to be equal to unity. The experimentally obtained values of these constants differed very much from unity.

In order to make the evaluation of the calorimetric measurements possible, a prediction of the distribution of molecules present in different layers must be performed. It turns out that equations describing such distributions can be derived directly from the basic assumptions introduced in the BET-theory. This derivation will be explained in detail. Furthermore, the background leading to the so-called Arrhenius factor is discussed. The discussion is conducted using the concept leading to the Boltzmann's distribution law. This is done since the Arrhenius factor is introduced in the main assumptions in the BET-theory. This leads to a concept which allows for the determination of condensation heats of molecules at surfaces once certain material constants have been given proper values.

1 Introduction

The sorption isotherms for porous Vycor glass were measured at four different temperatures, 11, 19, 25 and 37 degrees Celsius. The instrument used for measuring these isotherms was a sorption balance, DVS-1000, which is a symmetrically arranged balance with high precision. The relative humidity in the closed system of this instrument is obtained by mixing dry and saturated air, in desired proportions, using flow regulators. For the tests at 25°C both the sorption balance and a calorimetric approach were used to measure the sorption on porous glass. The method of evaluating the measured data given from the sorption microcalorimeter gives not only the sorption isotherm for the tested material but also the differential heat of sorption as a function of relative humidity. The information about how much heat involved in placing gas molecules on material surfaces becomes important when analyzing certain assumptions used in the well-known BET-theory.

The specific surface areas were calculated from the measured sorption isotherms at 11, 19, 25 and 37 degrees Celsius. These area measures were obtained by using the assumptions included in the BET-theory. As long as the dependency of expansion of material and adsorbed gas is weakly related to temperature, the calculated specific surface areas for different temperatures used in the tests are expected to be almost constant. The obtained sorption isotherms together with the ‘best’ fitted BET-equation, however,
gave a specific surface area at 37°C that was approximately 10% higher than the calculated specific surface area at 11°C. These results were obtained when using only two fitting parameters in the BET-equation, meaning that only molecules being adsorbed directly onto the ‘bare’ material surface have a heat of sorption different from normal condensation heat. This type of BET-equation, with only two fitting parameters, will be referred to as the one-layer method.

Further, an approach referred to as the two-layer method was studied, which is a BET-equation with three fitting parameters. The calculated specific surface areas from this method was found to be significantly smaller than with the one-layer BET-equation. The case was that the surface area calculated at 37°C was approximately 5% higher than for 11°C. The question, therefore, arises whether the prediction of the specific surface area was improved by using one more fitting parameter in the BET-equation or not. This can be examined by noting that certain terms in the BET-equation have a special meaning in terms of the heat involved in creating different discrete adsorption layers on material surfaces. The approach was to measure these heat affects using a calorimeter. The comparisons between the two different BET-equations and the measured data obtained from the calorimeter indicated that the second formed layer of adsorbed gas has a condensation heat different from the normal heat of condensation. Hence, it can be concluded that the two-layer BET-equation is a more adequate approximation than the one-layer approach. Further, one can argue that the specific surface area calculated for this case is more likely to be closer to the ‘true’ specific surface area than the one obtained when using the concept behind the one-layer method.

2 BET-Theory

One of the basic assumptions of the BET-theory is that the net exchange of gas molecules and adsorbed gas between different discrete layers can be described by using an expression similar to the one given by Arrhenius. Since this expression includes heats, which can be associated with mass exchanges, it turns out that the condensation heat involved in creating different adsorbed layers on material surfaces can be predicted by making suitable assumptions. An attempt is made to measure these condensation heats. Therefore, it is important to study the concepts leading to the Arrhenius function which
will give a better understanding of the assumptions introduced in the BET-theory.

The so-called Boltzmann's distribution law, e.g. see [1], which can be used to motivate the structure of the Arrhenius function, can more or less be derived from statistical arguments. A case of an assembly of \(N\) molecules in a gas phase is studied. These molecules are assumed to be assigned to different discrete energy levels. The number of molecules present in each energy level is also of interest. A system of molecules can shift between different states. A state is, in this case, referred to a certain combination of the total number of molecules being distributed in the energy levels. The number of possible combinations \(\Omega\) is called the complexion. It can be shown that the number of complexions is given as: \(\Omega = N!/(\Pi i n_i!))\), where \(N\) is the total number of molecules in assembly and \(n_i\) is the number of molecules in the energy level \(i\). The symbol \(\Pi\) indicates that the term \(\Pi n_i!\) is the product of the \(n_i!\) values for all considered levels. From the expression giving the complexions it can directly be concluded that in a case where all \(N\) molecules are in different energy levels one obtains \(\Omega = N!\), whereas, a case where all molecules except one are in, for example, the lowest energy level gives \(\Omega = N\). That is, when \(N\) is a somewhat large number the number of complexions differs greatly for the two situations examined above. Further, from the above example it can be seen that the number of complexions is large when the distribution of molecules, among all energy levels, is large. Moreover, a state leading to a high number of complexions will be more statistically probable than states with a smaller number of complexions. The derivation leading to Boltzmann's distribution law is based on finding the maximum value of \(\Omega\), since this represents the most probable state. The conclusions from such a derivation lead to an expression of the fraction of molecules present in a certain energy level, which is given as: \(n_i/N = e^{-\beta \varepsilon_i}/(\sum i e^{-\beta \varepsilon_i})\), where \(\beta\) is an arbitrary material constant and \(\varepsilon_i\) is the energy level containing \(n_i\) molecules. The ratio between the numbers of molecules in two different energy levels \(\varepsilon_j\) and \(\varepsilon_i\) can, further, be expressed as: \(n_i/n_j = e^{-\beta(\varepsilon_j - \varepsilon_i)}\). This relation states that the ratio of populations in two different energy levels depends on the energy difference \(\varepsilon_j - \varepsilon_i\), through the material constant \(\beta\). If, for example, the energy levels \(\varepsilon_j\) and \(\varepsilon_i\) are very similar, i.e. \(\varepsilon_j \approx \varepsilon_i\), an approximately equal number of molecules should be present in these levels.

From experimental observations it is seen that many chemical reactions occur at a rate proportional to \(e^{-E_a/(R\theta)}\), where \(E_a\) is the so-called activation energy, \(R\) is the gas constant and \(\theta\) is the (absolute) temperature. The term
\[ e^{-\frac{E_a}{R\theta}} \] can be referred to as the Arrhenius factor. The similarities between the experimentally obtained relation including the term \( e^{-\frac{E_a}{R\theta}} \), describing the influence of temperature on reaction kinetics in a simple system, and the most probable ratio of populations in two different energy levels, given as \( \frac{n_i}{n_j} = e^{-\beta(c_j - c_i)} \), cannot be a coincidence. The analogy between the two relations is that the collision frequency among molecules in a certain volume can be assumed to be proportional to the number of molecules present. Therefore, the fraction of collisions in two different energy states can be represented by the ratio \( \frac{n_i}{n_j} \), given by Boltzmann's distribution. Naturally, the collision frequency between molecules in different energy levels will very much determine the rate of an occurring reaction between the same molecules. The BET-theory to be studied includes the assumption that the evaporation rate of molecules from adsorbed molecules (located in certain discrete layers) is proportional to the Arrhenius factor \( e^{-\frac{E_a}{R\theta}} \).

In the BET-theory, e.g. see [2] and [3], it is assumed that molecules in a vapor phase above a flat material surface can form only discrete layers. The surface area occupied by first layer clusters is denoted \( s_1 \), the area occupied by two layers are denoted by \( s_2 \) an so on. The bare surface area will be denoted \( s_0 \). These areas will be changed when the relative vapor pressure above the surface is changed.

The static condition of having an equal number of molecules entering the bare surface and molecules leaving the material surface is assumed in the BET-theory to be proportional to the surfaces \( s_0 \) and \( s_1 \). The condensation on bare surface and evaporation of molecules located at the surface are the only two processes affecting the area of material with no molecules attached to it. The rate of condensation of molecules onto the bare surface is assumed given as: \( a_1 p s_0 \), where \( a_1 \) is a material constant and \( p \) is the pressure in the gas above material surface. In other words, it is a probable situation that the condensation rate increases when the pressure \( p \) and the area \( s_0 \) are increased. The rate of evaporation of molecules located at the material surface is assumed given as: \( b_1 s_1 e^{-\frac{E_1}{R\theta}} \), where \( b_1 \) is a material constant, \( E_1 \) is the energy associated with the sorption process of molecules located in the first layer, \( R \) is the gas constant and \( \theta \) the absolute temperature. The evaporation rate is, in other words, assumed to increase when the surface area \( s_1 \), i.e. the area occupied by molecules located in first layer (with no other molecules on top of it), increases. Furthermore, this evaporation is assumed to increase with temperature according to the Arrhenius factor \( e^{-\frac{E_1}{R\theta}} \).

An equilibrium condition for the first layer molecules, contributing to a
change of the bare surface area \( s_o \), is defined as a case in which the condensation rate of molecules onto the bare surface, \( a_1ps_o \), and the evaporation rate of molecules located on the surface, \( b_1s_1e^{-E_1/(R\theta)} \), are equal, i.e.

\[
a_1ps_o = b_1s_1e^{-E_1/(R\theta)} \quad (1)
\]

The processes involved in changing the area occupied by the first layer clusters include, (i) condensation on the bare surface, (ii) evaporation from the first layer, (iii) condensation on the first layer (making it belong to the second discrete layer) and (iv) evaporation from the second layer (making it travel back to the first discrete layer). The sum of these four static rate processes must be equal to zero at equilibrium.

Assume the static condensation rate to form second layer clusters on first layers, to be proportional to the area occupied by first layer clusters \( S_1 \) and on the actual surrounding vapor pressure \( p \), as \( a_2ps_1 \), where \( a_2 \) is a constant not necessarily equal to \( a_1 \). The static condensation rate from the second layer is the assumption \( b_2s_2e^{-E_2/(R\theta)} \), where \( s_2 \) is the actual surface area occupied by second layer clusters, \( b_2 \) is a constant and \( E_2 \) is associated with the heat involved in forming the second layer only. The sum of the four static rates involved in the first layer, i.e. involved in changing the value of \( s_1 \), must be equal to zero. The rates as described in equation (1) and the above assumptions therefore give the equilibrium condition

\[
a_2ps_1 + b_1s_1e^{-E_1/(R\theta)} = a_1ps_o + b_2s_2e^{-E_2/(R\theta)} \quad (2)
\]

By combining (1) and (2) one also obtains that

\[
a_2ps_1 = b_2s_2e^{-E_2/(R\theta)} \quad (3)
\]

Proceeding with the same method of constituting static rates, affecting the area measures \( s_{i-1} \), one obtains the equilibrium conditions expressed in a general manner, as

\[
a_is_{i-1} = b_is_i e^{-E_i/(R\theta)} , \quad i = 1, 2, ..., \infty \quad (4)
\]

By summing the surface areas occupied by the different discrete clusters, having different numbers of layers, one obtains the total surface area occupied by the adsorbate, as

\[
A = \sum_{i=0}^{\infty} s_i \quad (5)
\]
Further, the total volume of the adsorbed gas is
\[ v = v_0 \sum_{i=0}^{\infty} i s_i \]  
(6)

where \( v_0 \) represents the volume of adsorbate on the adsorbent surface per unit area of the material when covered by a complete unimolecular layer (this first complete layer is in turn partly covered by more layers).

The ratio \( v / (Av_o) \) is formed as
\[ \frac{v}{Av_o} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} \]  
(7)

where \( v_m = Av_o \) represents the volume of adsorbed gas corresponding to a complete mono-layer.

The standard BET-equation to be derived includes the assumption that only the molecules included in first formed layer have a condensation heat different from normal condensation. Assuming that \( E_2 = E_3 = ... E_i = E_L \), where \( E_L \) is the heat of liquefaction, i.e. the condensation heat involved in creating discrete layers is the same for all layers greater than one, assuming, further, that \( b_2/a_2 = b_3/a_3 = ... b_i/a_i = g \), where \( g \) is a constant, the following can be established
\[ s_1 = y s_o \]  
(8)

where (1) is used and where \( y = (a_1/b_1) p e^{E_1/(RT)} \). Further, by using equation (3) one obtains
\[ s_2 = x s_1 \]  
(9)

where \( x = (p/g) e^{E_L/(RT)} \). Noting also that \( s_i = x s_{i-1} \) holds for all \( i > 1 \), due to expression (4) and the simplifications described above. By combining such equations one can, for example, establish that \( s_3 = x s_2 = x^2 s_1 \). More generally, for \( i > 1 \), one obtains the relations
\[ s_i = x s_{i-1} = x^{i-1} s_1 = y x^{i-1} s_o = cx^i s_o \]  
(10)

where \( c = y/x = a_1/b_1 e^{(E_1-E_L)/(RT)} \). That is, \( s_1, s_2, s_3, ... s_i \) can be expressed in terms of \( s_o \) by the constant \( c \) and different powers of \( x \).
By using $s_i = cx^i s_0$ given from expression (10), equation (7) can be rewritten as

$$\frac{v}{v_m} = \frac{cs_0 \sum_{i=1}^{\infty} ix^i}{s_0 \left(1 + c \sum_{i=1}^{\infty} x_i\right)}$$

(11)

To be able to write the term $v/v_m$ as a function of $x$, one can, for example, assume that an infinite number of layers can be formed. In such a case the sums included in equation (11) converge, as

$$\sum_{i=1}^{\infty} x_i = \frac{x}{1-x}$$

(12)

and

$$\sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2}$$

(13)

That is, when assuming that an infinite number of layers can be formed, the term $v/v_m$ is a function of $x$ given as

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x + cx)}$$

(14)

which was obtained by inserting equation (12) and (13) into (11). Equation (14) is the standard BET-equation. The main assumptions in deriving this equation were that the number of molecules in each layer remains constant at equilibrium and that an infinite number of layers can be formed. It can be concluded, however, that the sums shown in (12) and (13) converge somewhat rapidly, making the assumption of an infinite number of layers formed justified for many materials.

It will be shown later that $x$ can be identified as the relative vapor pressure above the material surface. That is, the BET-equation (14) expresses the total volume of adsorbate $v$ as a function of the relative vapor pressure $x$, and the material parameters $c$ and $v_m$ are used to fit the measured adsorption isotherm.

It can be explicitly assumed that only a maximum number $n$ of discrete adsorbed molecule layers can be formed. The significance of such an assumption can, perhaps, be motivated for some materials. The reason for not obtaining an infinite number of layers can be the shape of the pore system and the properties of the surfaces in the material. The effect of capillary condensation resulting in curved surfaces between air and adsorbed gas cannot
solely be modeled by assuming different \( n \) values, since capillary condensation stems from different ‘forces’ than pure adsorption. The BET-equation stating that only \( n \) layers can be formed is obtained by using the finite sum

\[
\sum_{i=1}^{n} x_i = \frac{x (x^n - 1)}{(x - 1)}
\]  

(15)

and

\[
\sum_{i=1}^{n} ix^i = \frac{x (1 - x^n) - x^{n+1} n (1 - x)}{(1 - x)^2}
\]

(16)

The expression for the sums in (15) and (16) gives together with equation (11) the BET-equation, for a case where only a maximum of \( n \) layers can be formed, i.e.

\[
v = \frac{v_m c x}{1 - (n + 1) x^n + n x^{n+1}}
\]

(17)

This equation includes three fitting parameters, \( c, v_m \) and \( n \), which can be compared to the standard BET-equation (14) which only includes \( c \) and \( v_m \).

By examining equations (14) and (17) it is concluded that when \( v \to 0 \), one must have \( x \to 1 \). Further, it is assumed that \( v \to \infty \) when \( p = p_o \), where \( p_o \) is the saturation pressure of the gas at the examined temperature. This assumption seems to be reasonable for a flat surface being subjected to a gas. However, when considering adsorption in a pore system the value of \( v \) can hardly exceed the value given from the total porosity. Using the definition of \( x \), i.e. \( x = (p / g) e^{E_L/(R T)} \), it is concluded that the relation \( 1 = (p_o / g) e^{E_L/(R T)} \) holds when having \( v \to \infty \) and \( p = p_o \). Furthermore, the term \( e^{E_L/(R T)} / g \) is forced to be constant, since the saturation pressure is forced to be given by \( p_o = g e^{-E_L/(R T)} \). Indeed, this places a restriction on which values \( g \) and \( E_L \) can take. The physical meaning of \( x \) can be obtained by combining the definition \( x = (p / g) e^{E_L/(R T)} \) with the restriction \( p_o = g e^{-E_L/(R T)} \), to yield \( x = p / p_o \). That is, \( x \) is the relative vapor pressure.

It is realized that the basic assumptions leading to the relation \( a_i p s_{i-1} = b_i s_i e^{-E_i/(R T)} \) can be generalized by assuming that the rate of condensation is proportional to \( p^r s_{i-1} \), where \( r \) is a material constant, instead of being proportional to \( p s_{i-1} \). This will mean that the definition of \( x \) will be changed. This new property will be denoted \( x^* \). The property \( x^* \) can easily be shown to be related to the actual pressure \( p \) and the saturation pressure \( p_o \), as \( x^{*1/r} = p / p_o \), which follows directly from a derivation similar to the one.
leading to \( x = p/p_0 \), performed previously. In the following the more general concept leading to the relation \( x^{1/r} = p/p_0 \) will be used. It is observed that the definitions of \( x \) and \( x^* \) are identical when the material constant \( r \) is set equal to unity.

The introduction of a new constant \( r \) when describing the rate of condensation at static equilibrium means that three fitting parameters, \( c, v_m \) and \( r \), are used instead of two in the classical approach, when comparing BET-theory with adsorption measurements.

It is convenient to rewrite the expression of the standard BET-equation in the form

\[
\frac{x^*}{v (1 - x^*)} = \frac{1}{v_mc} + \frac{(c - 1)}{v_mc} x^*
\]

(18)

where the measure \( x^* \) is used instead of \( x \). In expression (18) the term \( 1/(v_mc) \) represents the intercept and \( (c - 1)/v_mc \) represents the slope, when \( x^*/v (1 - x^*) \) is plotted against \( x^* \), for a given pre-defined choice of \( r \). This means that \( c \) and \( v_m \) can be evaluated in a direct manner when using the standard BET-equation (modified in the sense that \( r \) can be allowed to be different from unity).

When it comes to evaluating the measurements of heat of adsorption it is important to find an expression for the development of different adsorbed discrete layers, since the calorimeter cannot distinguish between the same layer but rather only measures the differential heat as a function of relative vapor pressure. The point is that the BET-theory, in the normal case, assumes that the differential heat of condensation is only attributed to the first layer. That is, when examining this condition, the ratio between the volume in first layer \( v_1 \) and the total volume \( v \), is of importance.

The expression for \( v_1 \) is given according to the already described definitions of \( v_o \) and \( s_i \) as

\[
v_1 = v_o \sum_{i=1}^{\infty} s_i
\]

(19)

By inserting the expression for \( s_i \) given by equation (10), i.e. in this case \( s_i = cx^{*i}s_o \), one obtains

\[
v_1 = v_o c s_o \sum_{i=1}^{\infty} x^{*i}
\]

(20)

Hence, the ratio \( v_1/v \) can be established by using equation (20) together with the expression for \( v \), given by (6), the relation \( s_i = cx^{*i}s_o \), and the infinite
sums (12) and (13), i.e.

\[
\frac{v_1}{v} = \frac{\sum_{i=1}^{\infty} x^i}{\sum_{i=1}^{\infty} ix^i} = \frac{x^*}{(1-x^*)} = 1 - x^* 
\]

The volume \(v_1\) can be expressed as a function of \(x^*\) by combining expression (21) with the BET-equation (14), in which \(x^*\) is used instead of \(x\), to obtain

\[
v_1 = \frac{v_m cx^*}{(1 - x^* + cx^*)} \quad (22)
\]

The value of \(v_1\) given as a function of \(x^*\), as described by equation (22), will be used when evaluating the measurements of differential heat during sorption using a newly developed sorption micro-calorimeter.

Another BET-equation, giving the relation of volume adsorbate and the relative vapor pressure, will be derived, in which it is assumed that the two first formed adsorption layers have a condensation heat significantly different from normal condensation. Yet another material constant must be introduced when considering this condition.

The expressions shown in (4) will again be used, now incorporating the possibility that the rate of condensation is proportional to \(p^r s_{i-1}\) through the constant \(a_i\). The rate of evaporation is, again, assumed given by \(b_i s_i e^{-E_i/(R T)}\).

The equilibrium conditions for all different formed layers can, in the same manner as explained earlier, be described by the expression \(a_i p^r s_{i-1} = b_i s_i e^{-E_i/(R T)}\).

For convenience, this condition is written as

\[
s_i = \frac{a_i}{b_i} s_{i-1} p^r e^{E_i/(R T)} \quad (23)
\]

It will be assumed that the differential heat of condensation of molecules in first and second layers, denoted by \(E_1\) and \(E_2\), respectively, are significantly different from the normal heat of liquification, denoted by \(E_L\). The following relation between \(s_i\) and \(s_{i-1}\) values can therefore be defined

\[
\begin{align*}
s_1 &= y^* s_0 \\
s_2 &= x^* s_1 \\
s_3 &= x^* s_2 \\
s_4 &= x^* s_3 \\
... &= ... \\
s_i &= x^* s_{i-1}
\end{align*}
\]

(24)
where $y^*$, $z^*$ and $x^*$ are given as

$$y^* = \frac{a_1}{b_1} p e^{E_1/R\theta}, \quad z^* = \frac{a_2}{b_2} p e^{E_2/R\theta}, \quad x^* = \frac{1}{g} p e^{E_L/R\theta}$$  \hspace{1cm} (25)$$

The property $g$ will in this case have the meaning $g = b_3/a_3 = b_4/a_4 = \ldots = b_4/a_4$. From equation (4) it is, further, concluded that, for example, the relation $s_4 = x^* s_3 = x^* s_2$ can be obtained. More generally, one can express the relations between the actual surface areas occupied by clusters with different molecule layers as

$$s_i = x^* s_{i-1} = x^{*i-2} s_2 = z^* x^{*i-2} s_1 = b x^{*i-1} s_1$$  \hspace{1cm} (26)$$
in which the material constant $b$ is given as

$$b = \frac{z^*}{x^*} = \frac{a_2}{b_2} g e^{(E_2-E_L)/R\theta}$$  \hspace{1cm} (27)$$
The property $s_1$, i.e. the area of material occupied by clusters consisting of mono-layers, can, furthermore, be written as

$$s_1 = c x^* s_o$$  \hspace{1cm} (28)$$
where $c$ according to (24), in this case, takes the form

$$c = \frac{y^*}{x^*} = \frac{a_1}{b_1} g e^{(E_1-E_L)/R\theta}$$  \hspace{1cm} (29)$$
It is also noted that $s_1$ and $s_2$ are related to $x^*$ by the material constant $b$, as

$$s_2 = b x^* s_1$$  \hspace{1cm} (30)$$
where equations (24) and (27) are in use.

The ratio $v/v_m$, for a case in which the two first formed layers have a condensation heat different from $E_L$, is established by using equation (26) and (28), which leads to the expression

$$\frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} = \frac{s_1 + \sum_{i=2}^{\infty} s_i}{s_o + s_1 + \sum_{i=2}^{\infty} s_i} = \frac{c x s_o + b c s_o \sum_{i=2}^{\infty} i x^{*i}}{s_o + c x s_o + b c s_o \sum_{i=2}^{\infty} x^{*i}}$$  \hspace{1cm} (31)$$
Again, \( v \) is calculated from taking the sum of all surface areas \( s_i \), occupied by clusters including molecule layers ranging from zero to infinity, times the 'thickness' of layers in terms of number of molecules, i.e. \( i \). And the total surface area is, again, formed by summing all current values of the \( s_i \) values, e.g. compare the method of establishing relation (7).

The two sums in equation (31) can be expressed as direct functions of \( x^* \) by noting that the series converges according to the formula

\[
\sum_{i=2}^{\infty} ix^i = \frac{x^2(2-x^*)}{(1-x^*)^2}
\]

and

\[
\sum_{i=2}^{\infty} x^i = \frac{x^2}{(1-x^*)^2}
\]

These series can be obtained by adjusting the standard series (12) and (13).

By combining equation (31) with (32) and (33), the BET-equation, valid for a case where two layers contribute to a special condensation heat and where an infinite number of layers can be formed at high relative pressures, will be obtained, as

\[
v = \frac{v_m c x^* (1 + (b - 1)(2x^* - x^{*2}))}{(1 - x^*) (1 + (c - 1)x^* + c(b - 1)x^{*2})}
\]

It is noted that the standard BET-equation (14) is recovered when setting \( b = 1 \) and \( r = 1 \) (note that \( r = 1 \) means that \( x^* = x \), where \( x \) is the relative humidity).

The volume content \( v_1 \) of adsorbate located in the first layer, for this case, will be examined. This volume is obtained by using equation (19) together with (26), (28) and (33), to give

\[
v_1 = v_0 \sum_{i=1}^{\infty} s_i = v_0 c s_o x^* + v_o b c s_o \sum_{i=2}^{\infty} x^i = v_0 c s_o x^* \left( \frac{1 + x^* (b - 1)}{1 - x^*} \right)
\]

The total volume \( v \) of adsorbate is obtained from equations (26) and (28), i.e.

\[
v = v_0 \sum_{i=0}^{\infty} is_i = v_0 \sum_{i=1}^{\infty} is_i = v_0 c x^* s_o + v_o b c s_o \sum_{i=2}^{\infty} ix^i
\]
Using, further, equation (32), one obtain

\[ v = v_o c_s o \frac{x^*}{(1 - x^*)^2 + b x^* (2 - x^*)} \]  \hspace{1cm} (37)

The ratio \( v_1/v \) is obtained by combining equations (35) and (37), i.e.

\[ \frac{v_1}{v} = \frac{(1 - x^*) + x^* (b - 1) (1 - x^*)}{(1 - x^*)^2 + b x^* (2 - x^*)} \]  \hspace{1cm} (38)

where it is noted that for \( b = 1 \), the above expression becomes identical to the same type of expression derived from the assumptions used in the standard BET-theory, i.e. compare with the equation for \( v_1/v \) shown in the equation (21).

When making special assumptions concerning the condensation heat of second layer molecules, the volume content of this layer also becomes important when comparisons with calorimetric experiments are to be performed. The volume of the second layer is obtained as

\[ v_2 = v_o \sum_{i=2}^{\infty} s_i = v_o b c s_o \sum_{i=2}^{\infty} x_i = v_o b c s_o \frac{x^*}{1 - x^*} \]  \hspace{1cm} (39)

where equations (26), (28) and (33) are used. Forming the ratio \( v_2/v \) by the use of expression (37), the result is

\[ \frac{v_2}{v} = \frac{x^* (1 - x^*)}{(1 - x^*)^2 + b x^* (2 - x^*)} \]  \hspace{1cm} (40)

Hence, the expressions for \( v_1 \) are obtained by combining equations (34) and (38), to yield

\[ v_1 = \frac{v_m c x^* (1 + (b - 1) (2 x^* - x^{2*})) ((1 - x^*) + x^* (b - 1) (1 - x^*))}{(1 - x^*) (1 + (c - 1) x^* + (b - 1) x^{2*}) (1 - x^*)^2 + b x^* (2 - x^*)} \]  \hspace{1cm} (41)

and the corresponding expressions for \( v_2 \) are obtained by combining equations (34) and (40) to give the result

\[ v_2 = \frac{v_m c x^{2*} (1 + (b - 1) (2 x^* - x^{2*})) (1 - x^*)}{(1 - x^*) (1 + (c - 1) x^* + (b - 1) x^{2*}) (1 - x^*)^2 + b x^* (2 - x^*)} \]  \hspace{1cm} (42)

The important knowledge about how the different layers are distributed, in terms of volumes, given from the BET-theory, becomes crucial since the
Figure 1: Adsorption of water vapor on unprepared porous glass at different temperatures. Measurements performed using a sorption balance. Circles 11°C, stars 19°C, diamonds 25°C and squares 37°C.
calorimetric measurements cannot distinguish from which layer the heat responses originat.

The method of establishing the equilibrium conditions for all the different layers, as is the approach when deriving the BET-equation, can be questioned. The crux is that the global equilibrium, defined by every point located at the sorption isotherm, can be maintained if the areas $s_i$ area changes in a way that the total volume adsorbate remains constant. A typical case can, for example, be that a molecule is condensed on a layer of three molecules, and at the same time a molecule evaporates from another cluster of three layer molecules. In this case the total adsorbed mass remains constant, the energy remains constant, if also assuming that the involved layers, in this case, have the same condensation/evaporation heats. The areas $s_i$, however, defining the surface area occupied by two, three and four layers, are changed. This dilemma indicates that the surfaces $s_i$, as calculated by using the concept behind the BET-theory, should be interpreted as the most probable distribution in global equilibrium.

3 Experimental procedure

Two types of experiments are used to measure the adsorption isotherms on porous glass. The first is the use of a sorption balance instrument which enables the user to measure both the absorption/desorption isotherm and the kinetics before reaching equilibrium. The second method of measuring is the use of a sorption micro-calorimeter from which the absorption isotherm and the heat of adsorption can be evaluated. This method, which is based on measuring the difference of heat involved when evaporating water from a 'free' water surface and the heat involved in placing vapor molecules on the material surfaces, can be used to check the significance of some of the assumptions included in the BET-theory. The sorption isotherms for porous glass were evaluated at four different temperatures, whereas only one temperature was examined when using the calorimetric approach.

The sorption balance measures changes in sample mass lower than 1 part in 10 million and is therefore suited for measuring sorption. In order to avoid effects caused by vapor being adsorbed on sample holders, a symmetric micro-balance system is used. The instrument is housed in a temperature-controlled incubator. The desired relative humidity at the sample holder is obtained by mixing dry and saturated air in desired proportions using flow
Figure 2: Adsorption of water vapor on unprepared porous glass at different temperatures measured with the sorption balance. Circles 11°C, stars 19°C, diamonds 25°C and squares 37°C.
Figure 3: Comparison between measurements on unprepared porous glass, solid line calorimetric method and stars the DVS method. Measured values on washed sample, diamonds, using the calorimetric method.
Figure 4: Adsorption of water vapor on unprepared porous glass at 11°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the one-layer BET-equation. The stars represent measured values obtained with the sorption balance instrument.
Figure 5: Adsorption of water vapor on unprepared porous glass at 19°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve ‘best’ fit of the one-layer BET-equation. The stars represent measured values obtained with the sorption balance instrument.

regulators. Dry nitrogen is used, and the regulated flow of the gas entering the instrument is divided into two pipes. The proportion of the total flow in the two pipes is controlled by the flow regulators. One of the pipes enters a bottle with distilled water, making the air flow saturated. This saturated flow is reunited with the dry nitrogen gas flow present in the other pipe, making the flow of air passing the sample holder have the desired relative humidity. The flow of gas passing the sample is approximately 1 mm/s.

Even though a certain relative humidity can be obtained by mixing dry and saturated air, humidity probes are situated just below the sample and reference holder to give independent verification of the system performance. The accuracy of the humidity probes is approximately ±0.5%. All measurements presented are based on the relative humidities given by the flow regulators. These values were compared with the measured relative humidities and the difference was found to be small. The temperature is also regis-
Figure 6: Adsorption of water vapor on unprepared porous glass at 25°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve ‘best’ fit of the one-layer BET-equation. The stars represent measured values obtained with the sorption balance instrument.

tered continually, during experiments, from thermo-couples situated below the sample and reference holders.

The equilibrium absorption isotherm can be obtained by letting the system increase the relative humidity in certain steps. The criterion for proceeding from a current value to another can be controlled by the computer, connected to the balance. Different criteria can be used for making a step in relative humidity, one is that a step is performed when an averaged value of several subsequent measured mass changes is close to zero, another is that a step is performed after a certain duration.

It is possible to measure the kinetics of absorption, before reaching equilibrium, using the sorption balance. This because the mass and mass changes are registrated continuously during the experiment. Such considerations will, however, not be included in this work.

The general performance of the instrument was controlled by running ex-
Figure 7: Adsorption of water vapor on unprepared porous glass at 37°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the one-layer BET-equation. The stars represent measured values obtained with the sorption balance instrument.

Experiments on salt solution with known saturation pressures at a given temperature. The calibration procedure performed is first to slowly increase and after that slowly decrease the relative humidity. When the saturation pressure for the tested salt is reached no mass change is registered by the microbalance and the corresponding relative humidity in the instrument will serve as measure of the performance. Tests on sodium chloride showed that the relative humidity given from the flow regulators differed from the saturated humidity value of the salt in use by approximately ±0.5%.

Before starting experiment the balance was calibrated for the reference and sample holder in use. The holders was washed with ethanol and placed symmetrically on the balance. The relative humidity was first set to a high value to avoid statics. After that the relative humidity was set to zero in order to dry the sample holders. When no mass change could be registered the mass was set to zero. After this calibration, the sample holder was taken
The porous glass examined was finely divided using a mortar and pestle. The powder was placed on the dry sample holder which was inserted into the instrument. Approximately 100 mg of sample was used.

The tests at the different temperatures were performed in steps, as for example, shown in Figure 1, from zero up to 60% relative humidity. The criterion for proceeding with a relative humidity step was defined as a case when the mass change was smaller than 0.0008%/minute of dry mass of sample.

In order to avoid components in the air outside the instrument reacting with the surfaces in the finely divided material, the sample was always kept in the instrument during the different tests, using different temperatures. Between runs the new test temperature was adjusted while the relative humidity was set to zero. A stable new temperature was obtained in approximately 3 hours.

A calorimetric method was used in two tests on porous glass. One on a porous glass sample was initially washed in order to remove adsorbed organic vapors from components in air, before being tested, and another was not prepared with regard to organic vapors. By analyzing the results given from this method the absorption isotherm and the differential heat of condensation during absorption can be calculated by making certain approximations, e.g. see [4] and [5]. Therefore, this method can be regarded as an indirect approach to measure absorption, compared to the use of the sorption balance which is a direct method.

The sorption microcalorimeter in use consists of two chambers connected with a thin tube. Heat flow sensors, registering the heat loss or heat gain, are situated on the chamber walls. In one of the chambers liquid water is inserted at the start of the experiment. Evaporation from the 'free' liquid surface is allowed to occur. The vapor molecules evaporated in the chamber travel through the thin tube and into the other chamber where the sample has been inserted. By assuming that the relative humidity in the evaporation chamber always remains saturated and that the heat registered in the same chamber corresponds to the 'normal' heat of vaporization, the flow entering the thin tube can be calculated. Assuming, further, that the diffusion characteristics are quasi-static in the sense that the gradient of the vapor pressure is constant at all spatial locations in the tube during the experiment, that is, the flow entering the thin tube connecting the chambers is equal to the flow entering the sample chamber, at all time levels. By letting the sample chamber be
Figure 8: Adsorption of water vapor on unprepared porous glass at 11°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the two-layer BET-equation. The stars represent measured values obtained with the sorption balance instrument.
Figure 9: Adsorption of water vapor on unprepared porous glass at 19°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve ‘best’ fit of the two-layer BET-equation. The stars represent measured values obtained from the sorption balance instrument.

relatively small compared to the amount of vapor entering chamber and the size of sample, it can be reasonably assumed that all molecules entering the chamber also will be attached to the sample.

One important property remains to be determined in order to measure the absorption, the development of the relative humidity in the sample chamber during the experiment. How to determine this property is described in the following.

By assuming that the thin tube has a certain diffusion resistance, described in terms of a diffusion coefficient, and that, as stated before, the relative humidity always remains constant in the evaporation chamber, i.e. being saturated during the test, the development of the relative humidity surrounding sample can be predicted. The flow, denoted $F$, in the tube is assumed to be given by an expression similar to Fick’s first law, i.e.
\[ F = K (p_{vap}^* - p_{sorp}) \]

where \( K \) is the diffusion coefficient for vapor in the tube connecting chambers, \( p_{vap}^* \) and \( p_{sorp} \) is the constant saturated pressure in the vaporization chamber and the actual pressure in the sample chamber (this pressure will be changed during experiment), respectively. The value of \( K \) can be obtained by making a calibration of the instrument once the length of tube connecting the chambers is known. The only two measured properties in the method are the thermal power registered in the vaporization chamber, \( P_{vap} \), and in the sample chamber \( P_{sorp} \). The flow of vapor in tube is given as: \( F = P_{vap}/\Delta_{vap} h \), where \( \Delta_{vap} h \) is the known vaporization heat of the liquid in use. Having assumed that the vapor pressure in the vaporization chamber, or more correctly, in the connection between the vaporization chamber and the thin tube, is constant and at saturation during experiment, the relative humidity in the sample chamber can be calculated as: \( \phi_{sorp} = p_{sorp}/p_{vap}^* = 1 - F/(Kp_{vap}^*) \). That is, the fact that \( p_{vap}^* \) is the same for both chambers, in isothermal conditions, and that the expression for \( p_{sorp} \) can be established as \( p_{sorp} = p_{vap}^* - F/K \), from Fick’s first law, is used. Further, by inserting the expression for the flow, i.e. \( F = P_{vap}/\Delta_{vap} h \), one obtains \( \phi_{sorp} = 1 - P_{vap}/(\Delta_{vap} h K p_{vap}^*) \). This expression only involves values known in advance, i.e. \( \Delta_{vap} h \), \( K \) and \( p_{vap}^* \), and the measured value \( P_{vap} \). Hence, the development of the relative humidity in the sample chamber \( \phi_{sorp} \) can be calculated whenever the measured function \( P_{vap} \) and the diffusion resistance \( K \) are known.

From the assumption that all molecules entering the sample chamber are directly attached onto surfaces of the tested material, the moisture content \( u \) can be calculated as: \( u(t) = u(0) + 1/(m_o \Delta_{vap} h) \int_0^t P_{vap}(t) \, dt \), where \( u(0) \) is the moisture content at the start of the experiment and \( m_o \) is the dry mass of the sample. Hence, the functions \( \phi_{sorp}(t) \) and \( u(t) \), constituting the sorption isotherm, can be predicted by using the assumptions discussed above in which the constants \( K \) and \( \Delta_{vap} h \) are used together with the measured function \( P_{vap}(t) \).

The thermal power \( P_{sorp} \) in the sample chamber is also measured. The difference between this value and the vaporization heat (measured in the vaporization chamber) can be plotted against \( \phi_{sorp}(t) \) or \( u(t) \), which can be interpreted as the global heat of sorption. The crux is, however, that no experimental measure can be obtained, concerning how the total in flow of vapor entering sample surfaces is distributed among different adsorbed molecule layers. This makes a direct comparison between experimental obtained
Figure 10: Adsorption of water vapor on unprepared porous glass at 25°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve ‘best’ fit of the two-layer BET-equation. The stars represent measured values obtained from the sorption balance instrument.
Figure 11: Adsorption of water vapor on unprepared porous glass at 37°C. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the two-layer BET-equation. The stars represent measured values obtained from the sorption balance instrument.
values of heat of sorption and values proposed from the BET-theory difficult. This is because it is assumed that the heat of sorption is attributed to different formed layers when using the BET-theory. Therefore, the global heat of sorption will be simulated for a given measured isotherm. In such a simulation heats involved in creating different discrete layers will be tested. The distribution, in terms of volume contents of adsorbate in different layers contributing to a heat of condensation different from normal condensation, is calculated using the BET-equation, e.g. see the derived equations in section 2. The heats simulated are then compared to the measured global heats, as registered by the sorption microcalorimeter instrument.
4 Test results

At constant relative humidity the tests on initially ‘unprepared’ porous glass showed that the moisture content decreased with increased temperature, see Figure 1. The word ‘unprepared’ is used to stress that the sample in use was not washed before testing, in order to remove organic vapors being adsorbed onto material surfaces. When plotting the moisture content against the mass density of vapor (which is proportional to absolute vapor pressure) one can see that the moisture content increases when the test temperature is decreased at constant concentration of the mass density of water vapor. That is, when an equal number of gas molecules is present in a representative volume above a material surface of porous glass, more adsorption will occur at low temperatures than at high temperatures, see Figure 2.

The measured adsorption isotherms at 25°C for unprepared and washed porous glass using the sorption microcalorimeter instrument are shown in Figure 3, [6]. In this figure the absorption isotherm for unprepared porous glass measured with the sorption balance instrument is also shown. Higher values of the mass adsorbate per mass adsorbent at medium relative humidities were measured with the sorption balance. No significant difference in the measured absorption isotherms was noticeable for unprepared and washed porous glass. The reason for obtaining lower mass adsorbate per mass adsorbent at medium relative humidities using the calorimetric technique, compared to the sorption balance instrument, can be that the basic assumptions making the evaluation of the obtained isotherms possible are not fully satisfied in the calorimetric method. If the equilibration time during testing in the calorimeter is too slow, the measured absorption isotherm is expected to be lower than the result obtained from the sorption balance, which is the case in the present study.

The values of $c$ and $v_m$, adopting the one-layer method with $r = 1$, was obtained by making a linear regression of the measured data by the use of equation (18). The comparison of fitted adsorption isotherms and measured values, using the one-layer method, can be studied in Figures 4-7. In general a satisfying match was obtained, although it shown to be somewhat less significant at relative humidities higher than 40%. The difference between fitted and measured values was, further, shown to increase at high relative humidities when the test temperature was increased. The development of the volume of adsorbate located in the first layer (and second layer), as predicted by equation (22), is shown in Figures 4-7 with solid lines.
Table 1: Material constants and evaluation of specific surface area for unprepared porous glass, obtained from the one-layer BET-equation.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>c (-)</th>
<th>v_m (-)</th>
<th>S (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>17.60</td>
<td>0.0277</td>
<td>98.05</td>
</tr>
<tr>
<td>19</td>
<td>22.68</td>
<td>0.0289</td>
<td>102.47</td>
</tr>
<tr>
<td>25</td>
<td>25.71</td>
<td>0.0298</td>
<td>105.45</td>
</tr>
<tr>
<td>37</td>
<td>36.85</td>
<td>0.0308</td>
<td>108.98</td>
</tr>
</tbody>
</table>

The corresponding results using the second-layer method are illustrated in Figures 8-11. The same measured data as used in Figures 4-7 are investigated. In Figures 8-11, equations (41) and (42) are used to calculate the volume of adsorbate located in the first and second layers, respectively.

The specific surface areas were calculated using the value of \( v_m \) obtained from fitting the BET-equation to measured data for the different tested temperatures. It is explicitly assumed that the specific surface \( S \) is proportionally related to \( v_m \) as: \( S = k v_m \), where \( k = 3.54 \cdot 10^3 \). The \( k \) value is obtained by assuming that each absorbed water molecule occupies an area of 10.6 Å² on the material surface. The material constant \( k \) is assumed to be independent of temperature.

The obtained values of \( c \) and \( v_m \) corresponding to the results shown in Figures 4-7 are presented in Table 1, in which the calculated values of the specific surface areas are also presented valid for the four different temperatures used in tests. As seen from Figures 4-7, development of first-layer molecules converges towards the \( v_m \) value. It is also observed that the growth of volume occupied by first-layer molecules changes very little when relative humidities about 60% are exceeded. A major difference in the obtained \( v_m \) value is observed among the different examined temperatures, which affects the evaluation of the specific surface area, see Table 1. The surface area evaluated at 11°C and 37°C differed by approximately 10%, which seems to be too large a difference to be attributed to the volume changes of material and adsorbed gas located in the first layer.

The results when using the assumption of having the two first layers formed with an adsorption heat different from normal condensation heat are shown in Table 2. When using the BET-equation corresponding to this situation, see equation (34), three fitting parameters are to be used, i.e. \( c \), \( b \) and \( v_m \). The approach of obtaining \( c \), \( b \) and \( v_m \) was to find an acceptable
match to experimentally obtained data at relative humidities between 20% and 50%.

Comparing the one-layer and two-layer approach, it is concluded that the \( v_m \) values are stabilized, at a somewhat constant value, at lower relative humidities when using the two-layer method, e.g. compare Figures 4-7 with Figures 8-11. It is also seen that the obtained \( v_m \) values from the two layer method are significantly lower than the ones obtained from the one layer approach. The way of matching the experimental data, shown in Figures 8-11, further, resulted in less spreading of the \( v_m \) values among temperatures than when using the one-layer approach.

Results from measurements giving the adsorption isotherm at 25°C for washed porous glass using the sorption microcalorimeter instrument are shown in Figure 12, in which the data have been evaluated with the one-layer method and in Figure 14 where the measured absorption data are analyzed with the two-layer method.

The measured differential heat of sorption as a function of relative humidity corresponding to the simultaneously measured absorption isotherm, see Figure 12 and 14, is shown in Figure 13 and 15. In Figure 13 the simulated development of the differential heat as a function of relative humidity, using the one-layer method, is shown. The material constant \( E_1 - L \) giving the 'best' fitted curve, shown in Figure 13, is presented in Table 4. This table also shows the value of the material constant ratio \( (a_1b_2) / (b_1a_2) \) evaluated from experiment and simulation.

The corresponding simulation using the two-layer method is shown in Figure 15. The material constants used, \( E_1 - L \) and \( E_2 - L \), giving the best fit to the measured data, and the obtained values of the material constant ratios \( (a_1b_3) / (b_1a_3) \) and \( (a_1b_3) / (b_1a_3) \), are presented in Table 4.

A better match between measured differential heat as a function of relative humidity was obtained when allowing for the two first adsorbed layers to have an adsorption heat different from normal condensation heat, i.e. compare Figures 13 and 15.

There is no restriction imposed on the ratio of the material constants \( a_1, a_2, b_1 \) and \( b_2 \), given as \( a_1b_2 / (b_1a_2) \). It can, however, be proposed that this ratio should be approximately equal to unity. The experiments performed, however, indicate that \( a_1b_2 / (b_1a_2) \approx 0.02 \), see Table 4, for the washed porous glass examined at 25°C. This means, in essence, that the static equilibrium rates of exchanging molecules at the first layer are slower that exchanging molecules in the second layer, compare equations (1) and (3), when related
Table 2: Material constants and evaluation of specific surface area obtained from the two-layer BET-equation. Data obtained from measurements on unprepared porous glass obtained with the sorption balance are used.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>c (-)</th>
<th>b (-)</th>
<th>v_m (-)</th>
<th>S (m²/g)</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>26.85</td>
<td>6.00</td>
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<td>75.19</td>
</tr>
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</table>

Table 3: Suggested differential heats using the BET-theory. Data obtained from measurements on unprepared porous glass obtained with the sorption balance are used.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$E^{BET}_1 - L$ (J/kmol)</th>
<th>$E^{BET}_2 - L$ (J/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(One-layer BET)</td>
<td></td>
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<tr>
<td>11</td>
<td>$6.64 \cdot 10^6$</td>
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<td>$7.47 \cdot 10^6$</td>
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<td>25</td>
<td>$7.95 \cdot 10^6$</td>
<td>0</td>
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<td>37</td>
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<td>0</td>
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<tr>
<td>(Two-layer BET)</td>
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<tr>
<td>11</td>
<td>$5.47 \cdot 10^6$</td>
<td>$2.96 \cdot 10^6$</td>
</tr>
<tr>
<td>19</td>
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<td>$3.24 \cdot 10^6$</td>
</tr>
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<tr>
<td>37</td>
<td>$8.39 \cdot 10^6$</td>
<td>$4.15 \cdot 10^6$</td>
</tr>
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</table>

to the actual surface areas $s_0$, $s_1$ and $s_2$ together with the condensation heats $E_1$ and $E_2$. The result was that the term $E_1 - E_L$, calculated from the standard method of setting $a_1 b_2 / (b_1 a_2) = 1$, was 2.5 times lower than the experimentally obtained values for a given value of $c$. That is, in the same manner as the material constants $c$ and $v_m$ are fitted to the measured adsorption isotherm, the material constant $E_1$ is fitted against the global measured heat of condensation, which allows the material ratio $a_1 b_2 / (b_1 a_2)$ to be determined, see Tables 3 and 4.

It should be carefully noted, however, that the distribution of the total volume of adsorbate among different layers must be calculated using the material constants $c$ and $v_m$ (when using the one-layer method), in order to be able to predict heat of condensation of the first layer. That is, any errors
Table 4: Properties obtained from the one- and two-layer BET-theory. Data from the calorimetric measurements on washed porous glass, at 25 degree Celsius are used.

<table>
<thead>
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<th></th>
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<th>Two-layer BET</th>
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<tbody>
<tr>
<td>$c$ (-)</td>
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<td>17.00</td>
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<tr>
<td>$b$ (-)</td>
<td>(1)</td>
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</tr>
<tr>
<td>$v_m$ (-)</td>
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</tr>
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<td>$S$ (m$^2$/g)</td>
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<td>71.68</td>
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<tr>
<td>$E_1 - L$ (J/kmol)</td>
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<td>$17.00 \cdot 10^6$</td>
</tr>
<tr>
<td>$E_2 - L$ (J/kmol)</td>
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</tr>
<tr>
<td>$(a_1b_2)/ (b_1a_2)$ (-)</td>
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<td>(-)</td>
</tr>
<tr>
<td>$(a_1b_3)/ (b_1a_3)$ (-)</td>
<td>(-)</td>
<td>0.01786</td>
</tr>
<tr>
<td>$(a_2b_3)/ (b_2a_3)$ (-)</td>
<td>(-)</td>
<td>0.00420</td>
</tr>
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<td>$E_{1BET}^T - L$ (J/kmol)</td>
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<td>$7.02 \cdot 10^6$</td>
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<tr>
<td>$E_{2BET}^T - L$ (J/kmol)</td>
<td>(-)</td>
<td>$3.43 \cdot 10^6$</td>
</tr>
</tbody>
</table>

in determining this distribution of molecules among different layers will affect the determination of $E_1$ and the value of $a_1b_2/ (b_1a_2)$. This means, further, that the determination of $E_1$ cannot be decoupled from the BET-equation, it is also concluded that it is very difficult to measure the distribution of adsorbed molecules present in different layers in any direct manner.

When setting $a_1b_2/ (b_1a_2) = 1$ it is realized that the heat of condensation $E_1$ can be solely determined by the constant $c$. This actually means, according to the BET-theory, that the shape of the isotherm (corresponding to a given value of $c$ and $v_m$) alone determines the heat of condensation of the first layer. This seems somewhat unrealistic since different adsorbates can most probably have very similar adsorption isotherms but different heat of condensation of first-layer molecules. That is, when assuming $a_1b_2/ (b_1a_2) = 1$, the properties of the studied adsorbent and its effects on the adsorbate are not directly accounted for.

Further, it is noticed that the model predicts that the areas occupied by different clusters, with different number of adsorbed layers, is related as $s_o/ s_1 = 1/(cx)$ and $s_i/ s_{i+1} = 1/(x)$, ($i > 0$), for the method when assigning a special condensation heat only to molecules located in the first layer. When the two-layer method is used the corresponding relations become $s_o/ s_1 = 1/(cx)$, $s_1/ s_2 = 1/(bx)$ and $s_i/ s_{i+1} = 1/(x)$, ($i > 1$). This
Figure 13: Comparison of the measured differential heat of adsorption with predicted values from the one-layer BET-equation. The experiment was performed at 25°C on washed porous glass. The stars represent a few of the points evaluated from the calorimetric measurement.
means that when $c$ is a large number the difference between the distribution of surface area $s_o$ and $s_1$ and higher layers is large for the different relative humidities $x$. It is seen, also, that when $b$ is equal to unity, the two-layer approach is identical with the one-layer approach. This means that the interpretation of the material constants $c$ and $b$ need not necessarily be related to the heat of condensation of the first and second layer molecules. However, the way of introducing the Arrhenius factors $e^{-E_1/(R\theta)}$ and $e^{-E_2/(R\theta)}$ into the basic assumptions, e.g. compare with (4), makes it possible to also interpret the values of $c$ and $b$ to be related to condensation heats. The way the distribution of occupied surface areas and the condensation heats is connected follows directly from the assumptions introduced in the BET-theory. This connection is independent of whether the ratio of material constants $a_1b_2/(b_1a_2)$ is set equal to unity or not.

In Figure 16 the dependence of the material constants $c$ and $b$ on tem-

Figure 14: Adsorption of water vapor on washed porous glass at 25°C, measured with the calorimetric method. Lower curve, mass adsorbate per mass adsorbent located in the second layer. Middle curve, mass adsorbate per mass adsorbent located in the first layer. Upper curve ‘best’ fit of the two-layer BET-equation. The stars represent measured values.
Figure 15: Comparison of the measured differential heat of adsorption with predicted values from the two-layer BET-equation. The measurement was performed at 25°C on washed porous glass. The stars represent a few of the points evaluated from the calorimetric measurement.

Temperature in the range examined is shown. The solid lines in Figure 16 were obtained by using a second-degree polynomial. The dependence of the property \( v_m \) on temperature is presented in Figure 17. This fitted polynomial was used to recalculate the isotherms at different temperatures as shown by the dashed lines in Figure 18. The solid lines in this figure represents expected isotherms at 10, 20, 30 and 40 degrees Celsius.

The influence of the \( v_m \) value on the temperature, shown in Figure 17, again illustrates that the \( v_m \) values become greater when using the one-layer approach than with the two-layer method. The proposed way of fitting the adsorption isotherm in the two-layer approach, further, resulted in less spreading among \( v_m \) values at different temperatures.

The reason for using the second-layer method, i.e. setting the \( b \) value different from unity, is that the results obtained from the calorimetric measurements gave a better match when the material constant \( b \) was set to values around 5.
Figure 16: The dependence of the material parameters $c$ and $b$ (stars and circles, respectively) for unprepared porous glass on temperature, used in the two-layer BET-equation and $c$ (diamonds) in the one-layer BET-equation. Solid line, curve fitting using a second-degree polynomial.
Figure 17: The dependence of the material parameter $v_m$ (stars) for unprepared porous glass on the temperature, used in the two-layer BET-equation and $v_m$ (diamonds) in the one-layer BET-equation. Solid line, curve fitting using a second degree polynomial.
Table 5: Properties obtained from the one- and two-layer BET-theory. Data from the calorimetric measurements on unprepared porous glass, at 25 degree Celsius are used.

<table>
<thead>
<tr>
<th></th>
<th>One-layer BET</th>
<th>Two-layer BET</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$ (-)</td>
<td>19.77</td>
<td>27.00</td>
</tr>
<tr>
<td>$b$ (-)</td>
<td>(1)</td>
<td>6.50</td>
</tr>
<tr>
<td>$v_m$ (-)</td>
<td>0.0281</td>
<td>0.0190</td>
</tr>
<tr>
<td>$S$ (m$^2$/g)</td>
<td>95.50</td>
<td>67.26</td>
</tr>
<tr>
<td>$E_1 - L$ (J/kmol)</td>
<td>$23.00 \cdot 10^6$</td>
<td>$23.00 \cdot 10^6$</td>
</tr>
<tr>
<td>$E_2 - L$ (J/kmol)</td>
<td>0</td>
<td>$23.00 \cdot 10^6$</td>
</tr>
<tr>
<td>$(a_1b_2) / (b_1a_2)$ (-)</td>
<td>0.00184</td>
<td>(-)</td>
</tr>
<tr>
<td>$(a_1b_3) / (b_1a_3)$ (-)</td>
<td>(-)</td>
<td>0.00252</td>
</tr>
<tr>
<td>$(a_2b_3) / (b_2a_3)$ (-)</td>
<td>(-)</td>
<td>0.00061</td>
</tr>
<tr>
<td>$E_1^{BET} - L$ (J/kmol)</td>
<td>$7.40 \cdot 10^6$</td>
<td>$8.17 \cdot 10^6$</td>
</tr>
<tr>
<td>$E_2^{BET} - L$ (J/kmol)</td>
<td>(-)</td>
<td>$4.64 \cdot 10^6$</td>
</tr>
</tbody>
</table>

Results of the absorption isotherm and heat of adsorption on unprepared porous glass at 25°C are shown in Figures 19 and 20. The measured data presented in these figures are evaluated with the one-layer method. In Figures 21 and 22 the same measured adsorption isotherm and heat of adsorption data are shown, in which results from the evaluation using the two-layer method are also presented. The comparison of measured heat of adsorption on washed and unprepared porous glass is also shown in these figures, i.e. see Figure 20 or Figure 22. The obtained material constants from the investigation of the unprepared porous glass are shown in Table 5.

The best fitted values of $E_1$ and $E_2$ for washed and unprepared porous glass differed by a factor of about 0.75, i.e. compare the results shown in Table 4 and Table 5. In turn this will result in the evaluated material constant ratios $a_1b_3 / (b_1a_3)$ and $a_2b_3 / (b_2a_3)$ differing very much between the two tests. The evaluated absorption isotherms given from the measured differential heat of adsorption in the sorption microcalorimetric tests on the washed and unprepared samples were, however, in quite good agreement, see Figure 3.
Figure 18: Expected adsorption isotherms for unprepared porous glass at 10, 20, 30 and 40 degrees Celsius (solid lines, from left to right) in which values given from Figure 15 and 16 were used. Dashed lines obtained using c, b and \( v_m \) values given by Table 2. The circles, stars, diamonds and squares, represent measured values at 11, 19, 25 and 37 degrees Celsius.
Figure 19: Adsorption of water vapor on unprepared porous glass at 25°C. Lower curve, calculated mass adsorbate per mass adsorbent in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve, 'best' fit of the one-layer BET-equation. The stars represent measured values on unprepared porous glass using the calorimetric method.
Figure 20: Comparison of the measured differential heat of adsorption with predicted values from the one-layer BET-equation (dashed line). The measurements were performed at 25°C. The diamonds represent a few of the points evaluated from the calorimetric measurements on washed porous glass. The solid line represents the measured differential heat on unprepared porous glass.
Figure 21: Adsorption of water vapor on unprepared porous glass at 25°C. Lower curve, calculated mass adsorbate per mass adsorbent in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve, 'best' fit of the two-layer BET-equation. The stars represent measured values on unprepared porous glass using the calorimetric method.
Figure 22: Comparison of the measured differential heat of adsorption with predicted values from the two-layer BET-equation (dashed line). The measurements were performed at 25°C. The diamonds represent a few of the points evaluated from the calorimetric measurements on washed porous glass. The solid line represents the measured differential heat on unprepared porous glass.
5 Conclusions

For unprepared porous glass an increased water content was obtained, at constant relative vapor pressure, when increasing the test temperature. As compared with other material, such as wood, the water content decreases when the test temperature is increased (at constant relative vapor pressure). When plotting the measured mass of adsorbate per mass adsorbent against the mass density vapor, which is proportional to the vapor pressure at a given temperature, the water content was seen to increase when the temperature was decreased in the different tests. That is, for a given constant concentration of molecules (or absolute vapor pressure) in the gas phase above a surface in the material tested, more water was adsorbed at equilibrium when low temperatures were examined as compared with a higher temperature.

The theoretically obtained energies of condensation of the first and second layers was observed to increase with increased temperature. These values were obtained by fitting the measured sorption isotherms, at the different test temperatures, against two different BET-equations. An assumption concerning the relation the different material constants $a_1$, $a_2$, $b_1$ and $b_2$ and $a_2$, $a_3$, $b_2$ and $b_3$ must also be assumed in obtaining these condensation heats. The often suggested relations $a_1b_3/(b_1a_3) = 1$ and $a_2b_3/(b_2a_3) = 1$ could not, however, be confirmed by the calorimetric measurements.

A quite satisfying agreement between measured differential heat of sorption, as a function of relative humidity, and simulated values, was obtained, i.e. see Figure 15. In this simulation the BET-theory was used to calculate the distribution of molecules in different layers as a function of relative humidity. It was noted, however, that the assumption leading to the determination of the heat involved in placing molecules in the first and second layer, used in the BET-theory, in which the material constant ratios $a_1b_3/(b_1a_3) = 1$ and $a_2b_3/(b_2a_3) = 1$ was used, differed by a factor of about 2.5 from the ones used to get the best fit to the measured calorimetric data.

The specific surface area obtained when using either the one-layer BET-equation or the two-layer BET-equation, together with assumptions concerning the surface area occupied by one adsorbed molecule on the material surface, was observed to vary with temperature. This effect was smaller when the two-layer method was used as the basis for the evaluations. It is concluded that the difference between the obtained surface areas for the different examined temperatures, using the one-layer approach, was too large to be attributed to volume changes of adsorbent and molecules at material
surfaces due to temperature changes. This result, together with results from the calorimetric measurements, indicates that the distribution of volumes, including different numbers of molecule layers, is not correctly predicted by the BET-theory. One possible improvement to the model can be to relax the requirement of equilibrium for each formed layer by instead controlling that the total volume is constant, i.e. assuming that a change of distribution among layers will be allowed as long the total volume is constant.

With a material with reversed behavior in terms of the influence of test temperature on the isotherms as presented in Figure 1, the BET-theory and the assumption concerning the ratio of material constants will predict that a decreased condensation heat will be obtained when the temperature is increased. This shows that the properties of the material, in terms of condensation heats of different layers, themselves play a very important role in sorption. The only material parameters directly accounting for such effects are the ratios $a_1b_3/(b_1a_3)$ and $a_2b_3/(b_2a_3)$, which are most often ignored by assuming them to be equal to unity for all different types of material.

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References


