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2000

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Abstract

A sorption micro-calorimeter and a sorption balance were used to obtain sorption isotherms for two different materials, porous Vycor glass and micro-crystalline cellulose, MCC, at room temperature. The results from these measurements are compared with the predictions given by the BET-equation.

The results from measurements together with simulations of sorption on porous glass indicate that not only molecules adsorbed onto the solid surface have an adsorption heat significantly different from normal condensation heat. By assuming adsorption of molecules forming the second discrete layer having a condensation heat that differs from that of bulk water, a better match between measurements of adsorption and global heat of condensation was obtained than with the one-layer method. The experimentally obtained values of adsorption heat of molecules on a 'bare' material surface differed by about a factor 2.5 from the one suggested by the BET-theory. This indicates that one of the assumptions leading to a theoretical expression for the adsorption heat involved in adsorbing water molecules onto the material surface may be incorrect.

A very poor match was observed between experimentally obtained values, for micro-crystalline cellulose MCC regarding the heat of adsorption, and values predicted on basis of physical sorption models. This indicates that other mechanisms than molecule adsorption (on flat surfaces) are active for this material.

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The assumptions in the BET-theory are carefully studied. The Boltzmann distribution law is examined in order to justify some of the assumptions. Further, a detailed study is included leading to an expression for the relation between the pressure in vapor above adsorbate and in adsorbed layers. These considerations are based on thermodynamics as defined in the so-called mixture theory, which is a continuum approach.

1 Summary

The BET-theory can be used to establish how different adsorbed layers are distributed among the total volume of adsorbate at different relative humidities. According to the BET-theory each layer can be assigned a special adsorption heat which, normally, is assumed to be different from the normal condensation heat. The differential condensation heat measured for a material adsorbing vapor is only the global response, i.e. heat effect from all developed layers. Therefore, it is of interest to check whether the volume of adsorbate in different adsorbed layers, calculated by the BET-theory, can be compatible with assigned condensation heats for the same layers when comparing with experiments using a sorption micro-calorimeter. It will be shown that for porous glass a quite good match between theory and experiment can be obtained when assigning a special heat of condensation for only the two first layers. For micro-crystalline cellulose no satisfying match could be obtained using the BET-theory together with assumptions concerning different heat of adsorption in different layers.

The expressions for the fraction of total adsorbed water in material located in different assumed discrete layers will be written down explicitly, as a function of the relative humidity, by using some of the basic equations in the BET-theory. These expressions will be used when converting the measured global heat of adsorption, given from the sorption micro-calorimeter, to heat of sorption values assigned to different discrete layers. The crux is, as mentioned above, that the calorimetric measurements do not include any measure of how the adsorbed molecule layers are distributed among the total volume. That is, only a portion of vapor molecules entering the sample chamber, will be located at sites in the material resulting in a heat response different from normal heat of condensation. Therefore, the assumptions leading to the prediction of the formation of layers on material surfaces are analyzed

carefully. Certain possible generalizations of the classical BET-theory are also discussed in this context.

The sorption micro-calorimeter used for determining sorption isotherms consists of two connected chambers, a vaporization chamber and a sample chamber. Heat flow sensors are placed at the two chambers. At the start of the experiment water is added to the vaporization chamber and a dry, finely divided, material is inserted into the sample chamber. By assuming that the air in the vaporization chamber is always saturated together with an assumption stating that the gradient of the relative humidity in the thin tube connecting the chambers is always constant, it becomes possible to calculate the development of the relative humidity of air surrounding the tested material in the sample chamber. This can be done since the measured heat of vaporization in the water-filled chamber easily can be converted to a mass flow of water molecules in the tube connecting the chambers. The mass gain of sample is, further, calculated by integrating the mass flow of vapor molecules entering the sample chamber. One drawback with the described calorimetric test method is that the diffusion resistance in the thin tube connecting the chambers must be adjusted in such a way that the underlying assumptions becomes relevant. One consequence is that the sorption kinetics must be shown to be quite rapid, otherwise the significance of the measurements fails (see paper, *Restrictions on the Rate of Adsorption when Evaluating Sorption Isotherms from Measurements Using a Micro-calorimetric Technique*).

In order to compare the relevance of the sorption isotherms obtained from the sorption micro-calorimeter, measurements are also performed with a more direct method. The instrument used is a sorption balance (DVS-1000). This instrument consists of a closed system in which dry and saturated air are mixed in desired proportions, using flow regulators, obtaining different relative humidities. The system is placed in a climate chamber. A balance is placed in the system, a reference pan and a sample pan are connected symmetrically to this balance. The construction is used to avoid effects caused by sorption on the sample holder. Different pre-defined relative humidities can be set with an accuracy of about ±0.5%. The mass of samples in use is typically around 100 mg and the balance measures changes in sample mass lower than 1 part per 10 million. Relative humidity probes are placed near the sample and reference holders. The registered measures from these probes are only used to check the general performance during experiments since the flow regulators are used to obtain the desired relative humidity. The performance of the flow regulators can be tested by running calibration measurements

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using saturated salt solutions.

One of the main assumptions included in the BET-theory is the introduction of an Arrhenius factor describing the evaporation from different adsorbed layers. By introducing this factor it becomes possible to predict the energy required to form the few first layers by setting the ratio of some material constants included in BET-theory equal to unity, see section 3. It will, however, be shown that this type of assumption is in conflict with the results obtained from the experiments, which suggests that the ratio of material constants in use should be in the order of 0.02 instead of unity. Using the classical BET-theory the difference in terms of heat of condensation, forming adsorbed molecules at surfaces became a factor 2.5 smaller than using the experimentally obtained ratio of material constants for porous glass.

Since the Arrhenius factor, see section 2, is very important in the BET-theory, the arguments for introducing it will be discussed. It turns out that statistical arguments can be used to establish the so-called Bolzmann's distribution law. This 'law' implies that the ratio of populations, in terms of the number of molecules present in different energy levels at equilibrium, is proportional to a factor very similar to the Arrhenius factor. From experimentally obtained data it has, further, been concluded that many types of chemical reaction rates are proportional to the Arrhenius factor, i.e. when using the Arrhenius factor, when constituting chemical reactions, the temperature dependence can be incorporated in a stringent manner.

A section is devoted to restrictions, in the model describing sorption, imposed by the second axiom of thermodynamics. It is assumed that the vapor and adsorbed gas can be described in terms of the Helmholtz free energy which, for the two constituents considered, is assumed to depend solely on the temperature and its corresponding mass density concentrations. In isothermal conditions it is shown that a differential expression can be established connecting the pressure in gas and in the adsorbate. Some classical results concerning, for example, the thermodynamical definition of partial pressures and the relation for the chemical potentials at equilibrium are derived. It is concluded, however, that explicit expressions for the Helmholtz free energies for the constituents are difficult to establish. One issue is that the energy equations as described with the Helmholtz free energies must give a reasonable prediction of the temperature while simultaneously satisfying all derived thermodynamic relations.

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2 The Boltzmann distribution law

The BET-theory contains constitutive equations describing the mass exchange between adsorbed molecules and molecules in the gas phase above the material surface. An equilibrium state is defined when the rate of condensation is equal to the evaporation rate for different discrete adsorbed layers considered. These rates are described by using an expression very similar to the Arrhenius equation. The Arrhenius equation was originally based on experimental observations for chemical reaction kinetics. It turns out, however, that a deeper theoretical justification for the reliability of the Arrhenius factor can be obtained by studying the concepts established within statistical mechanics. The similarities between the so-called Boltzmann distribution law, which is one of the most central results given from statistical mechanics, and the Arrhenius factor will be pointed out. This subject becomes important since the motivation of using an Arrhenius equation in the BET-theory cannot directly be motivated by experimental proofs but rather by statistical methods.

Consider an assembly of N molecules in the gas phase. It is assumed that these molecules can appear in different discrete energy levels denoted by $\varepsilon_o, \varepsilon_1, \varepsilon_2, ...\varepsilon_h$, where ε_o is the lowest discrete energy level and ε_h is the highest level. The number of molecules in each level is presented as $n_o, n_1, n_2, ...n_h$. A system of molecules can shift between different states, where a state is referred to a certain combination of the total number of molecules being distributed in the different energy levels. The number of possible combinations is referred to as complexions, denoted by Ω. It can be confirmed that the number of complexions is given as

$$\Omega = \frac{N!}{\Pi_i n_i!} \tag{1}$$

e.g. see [1], where $\Pi_i n_i!$ is the product of the $n_i!$ values for all the considered levels. The important point that can be made from (1) is that for a large number of molecules a certain state will dominate. This can, for example, be illustrated by considering that all N molecules are in different energy levels, which gives $\Omega = N!/(1!1!..) = N!$; this value can be compared with the situation when all the molecules except one are in the lowest level, which gives $\Omega = N!/((N-1)!1!..) = N$. This example indicates that the number of complexions is large when considering a broad distribution of the molecules over all energy levels. Further, a state leading to a high complexion will be

more probable than states having a smaller complexion.

Before proceeding, two restrictions will be introduced. The first is that the sum of the number of molecules present in the different energy levels is equal to the total number of molecules, i.e.

$$\sum_i n_i = N \tag{2}$$

The second restriction is that the total energy density is fixed, i.e.

$$\sum_i n_i \varepsilon_i = E \tag{3}$$

where E denotes the total energy of the assembly.

From the above discussion it is clear that the combination of the values $n_o, n_1, n_2, ...n_i$ among its corresponding energy levels leading to the highest Ω is the most probable one. It is therefore of interest to find the maximum of Ω by using the equation

$$\delta\Omega = \sum_i \frac{\partial\Omega}{\partial n_i}\delta n_i = 0 \tag{4}$$

Since N and E are constant, i.e. $\delta N = 0$ and $\delta E = 0$, equations (2) and (3) can be written as

$$\alpha\sum_i \delta n_i = 0 \tag{5}$$

$$\beta\sum_i \varepsilon_i\delta n_i = 0 \tag{6}$$

where α and β are arbitrary constants.

Taking the total sum of (4), (5) and (6), one obtains

$$\sum_i \left(\frac{\partial\Omega}{\partial n_i} + \alpha - \beta\varepsilon_i\right)\delta n_i = 0 \tag{7}$$

For choices of δn_i values not violating the equation (2) one can make the choice that for all i values one should have

$$\frac{\partial\Omega}{\partial n_i} + \alpha - \beta\varepsilon_i = 0 \tag{8}$$

where it is noted that Ω is a function of n_i as defined by the expression (1).

The (approximative) solution to equation (8) can be written as

$$n_i = e^{\alpha} e^{-\beta \varepsilon_i} \tag{9}$$

The total number of molecules must further be related to the energy level ε_i, as

$$N = \sum_i n_i = e^{\alpha} \sum_i e^{-\beta \varepsilon_i} \tag{10}$$

The fundamental equation of the Boltzmann distribution is obtained by establish the ratio n_i/N using (9) and (10) to obtain

$$\frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} \tag{11}$$

This equation gives the fraction of molecules that are in a specified energy state ε_i. The ratio between the numbers of molecules in two different levels of energy can be obtained in the same manner, i.e.

$$\frac{n_i}{n_j} = e^{\beta(\varepsilon_j - \varepsilon_i)} \tag{12}$$

The conclusion drawn from this relation is that the ratio of populations in the two energy states depends on the energy difference $\varepsilon_j - \varepsilon_i$, through the material constant β. Within the kinetic gas theory it can, further, be shown that $\beta = 1/(k_b \theta)$, where k_b is the Boltzmann constant and θ is the absolute temperature.

From experimental evidence it is shown that the rate of many chemical reactions involving two constituents is proportional to the factor $e^{-E_a/(R\theta)}$. This term may be referred to as the Arrhenius factor.

Summing up, the conclusion drawn from experiments is in essence the same conclusion drawn from the Boltzmann distribution or equation (12). The analogy is that the number of molecules in a certain volume can be assumed proportional to the collision frequency among molecules in the same volume. Therefore, the fraction of collisions in two different energy states can be presented by the same formula. That is, the fraction of collisions in which the energy is in excess of a particular value E_a is $e^{-E_a/(R\theta)}$. Furthermore, the collision frequency is very much a controlling factor for the rate of reaction among molecules with different energy levels. It can also be noted that R is related to k_b as $k_b = R/N_a$, where N_a is the Avogadre constant. The property E_a is often referred to as the activation energy.

In the BET-theory different discrete energy levels will be assigned to discrete layers formed on a flat surface. The static equilibrium condition in which an equal number of molecules enters and leaves a certain layer will be constituted by using the Arrhenius factor.

3 The BET-theory

The BET-theory gives, among other things, an estimate of the volume of gas required to form a unimolecular layer on an adsorbent, and further, it is possible to yield the heat of adsorption to form this layer. From the information regarding the area on a material surface occupied by one molecule it is also possible to predict the specific surface area of the material, from the properties given from the BET-equation. The basic assumption in the BET-theory is that only discrete molecule layers can be formed on the bare material surface. Equilibrium conditions concerning the different layers are introduced by constituting the net condensation and evaporation rates in the system to be equal, e.g. see [2] and [3]. Different types of BET-equations to be used express the relation of total volume of gas adsorbed in relation to the relative vapor pressure, i.e. the BET-equation gives a theoretically derived adsorption isotherm. The equation is derived in a way that makes the materials constants have a clear physical meaning. When considering, for example, the standard BET-equation, two material constants are used, one related to the energy required to place molecules on bare surfaces and the other related to the specific surface area of material.

The area on a material surface, occupied by molecules present in the first layer, can be changed in two ways, either by condensation on the bare surface or by evaporation from the first layer. At equilibrium it is stated that an equal number must enter and leave the first layer. By assuming that the static rate of condensation, forming first layer clusters, is related to the vapor pressure p above the adsorbent surface and the area of the bare material surface s_o, as $a_1 p s_o$, where a_1 is a material constant related to the nature of the adsorbate and adsorbent. Assuming, further, that the static rate of evaporation contributing to a reduction of clusters, including one layer, is only related to the surface area s_1 occupied by these clusters and to the temperature according to $b_1 s_1 e^{-E_1/(R\theta)}$, where b_1 and E_1 are constants. The temperature is denoted θ and R is gas constant. The constant E_1 is a measure of the heat of adsorption of molecules in the first layer. At the static

equilibrium condition considered the rate of evaporation and condensation related to the first layer must be equal, i.e.

$$a_1 p s_o = b_1 s_1 e^{-E_1/(R\theta)} \tag{13}$$

where s_o is the current area of bare material surface and s_1 is the current area occupied by molecules present in the first layer.

The process involved in the first layer clusters affecting the area s_1 includes: (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 will be assumed to be zero, which defines an equilibrium condition for the area s_1. Assuming 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 $a_2 p s_1$, where a_2 is a constant not necessarily equal to a_1. The static evaporation rate from second layer is the assumption $b_2 s_2 e^{-E_2/(R\theta)}$, 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 establishing the first layer is assumed to be equal to zero. The equation (13) and the above assumptions therefore give

$$a_2 p s_1 + b_1 s_1 e^{-E_1/(R\theta)} = a_1 p s_o + b_2 s_2 e^{-E_2/(R\theta)} \tag{14}$$

By combining (13) and (14) one also obtain that

$$a_2 p s_1 = b_2 s_2 e^{-E_2/(R\theta)} \tag{15}$$

Proceeding with the same method of constituting static rates at higher formed layers one obtains

$$\begin{aligned} a_3 p s_2 &= b_3 s_3 e^{-E_3/(R\theta)} \\ a_4 p s_3 &= b_4 s_4 e^{-E_4/(R\theta)} \\ \ldots &= \ldots \ldots \\ a_i p s_{i-1} &= b_i s_i e^{-E_i/(R\theta)} \end{aligned} \tag{16}$$

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

$$A = \sum_{i=0}^{\infty} s_i \tag{17}$$

Further, the total volume v of the adsorbed gas is

$$v = v_o \sum_{i=0}^{\infty} i s_i \tag{18}$$

where v_o 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).

By forming the ratio $v/(Av_o)$ as

$$\frac{v}{Av_o} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} \tag{19}$$

and defining v_m as the volume of adsorbed gas corresponding to a complete mono-layer, i.e. $v_m = Av_o$, an expression for v is obtained. Considering the value v_m to be constant, the total volume of adsorbate can be determined solely by i and s_i.

First the standard BET-equation will be examined. The derivation leading to this equation includes the assumption 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 the material constant ratios $b_2/a_2 = b_3/a_3 = ... b_i/a_i = g$, where g is a constant, the following can be established

$$s_1 = y s_o \tag{20}$$

where (13) is used and where the property y is defined as $y = (a_1/b_1) p e^{E_1/(R\theta)}$. Further, by using (15) one obtains

$$s_2 = x s_1 \tag{21}$$

where $x = (p/g) e^{E_L/(R\theta)}$. Note also that $s_i = x s_{i-1}$ holds for all $i > 1$, due to (16) and the above described simplifications. By combining such equations

one can, for example, establish that $s_3 = xs_2 = x^2 s_1$. More generally, for $i > 1$, one obtains the relations

$$s_i = xs_{i-1} = x^{i-1} s_1 = yx^{i-1} s_o = cx^i s_o \tag{22}$$

where the property c is defined as $c = y/x = \frac{a_1 g}{b_1} e^{(E_1 - E_L)/(R\theta)}$. That is, the areas occupied by i molecule layers, i.e. 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 $s_i = cx^i s_o$ given from (22), the equation (19) can be written as

$$\frac{v}{v_m} = \frac{cs_o \sum\limits_{i=1}^{\infty} ix^i}{s_o \left(1 + c \sum\limits_{i=1}^{\infty} x_i\right)} \tag{23}$$

To be able to write the term v/v_m as a function of x only, one can, for example, assume that an infinite number of layers can be formed. In such a case the sums included in equation (23) converge, as

$$\sum\limits_{i=1}^{\infty} x_i = \frac{x}{(1-x)} \tag{24}$$

and

$$\sum\limits_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2} \tag{25}$$

That is, when assuming that an infinite number of layers can be formed on a ('flat') material surface, the term v/v_m is a function of x, including the material constants v_m and c, given as

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{26}$$

which was obtained by inserting (24) and (25) into (23). The expression (26) can be referred to as the (one-layer) standard BET-equation.

Assuming, instead, that a maximum finite number n molecule layers can be formed, the two sums in (23) can be expressed as

$$\sum\limits_{i=1}^{n} x_i = \frac{x(x^n - 1)}{(x-1)} \tag{27}$$

and

$$\sum_{i=1}^{n} i x^i = \frac{x\left(1 - x^n\right) - x^{n+1} n\left(1 - x\right)}{\left(1 - x\right)^2} \tag{28}$$

By substituting (27) and (28) into (23), an alternative version of (26) is obtained as

$$v = \frac{v_m c x}{(1 - x)}\left(\frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c - 1)x - cx^{n+1}}\right) \tag{29}$$

As will be shown later, x is a number between zero and unity, therefore the terms $(n + 1)x^n$, nx^{n+1} and cx^{n+1} become small when n is a large number. Hence, when x not is to close unity, the expression (29) becomes identical with (26). A choice of a maximum infinite number n layers formed can be motivated by considering the available space in the pore system. It should be noted, however, that wetting of material surfaces contributing to a curved liquid surface being in contact with the vapor is not included in the BET-theory. Therefore, the use of an infinite n value, in the expression (29), is somewhat questionable.

By examining the equations (26) and (29) it is concluded that when $v \rightarrow \infty$, one must have $x \rightarrow 1$. Further, it is assumed that $v \rightarrow \infty$ 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. $x = (p/g)\,e^{E_L/(R\theta)}$, it is concluded that the relation $1 = (p_o/g)\,e^{E_L/(R\theta)}$ holds when having $v \rightarrow \infty$ and $p = p_o$. Furthermore, the term $e^{E_L/(R\theta)}/g$ is forced to be constant, since the saturation pressure is forced to be given by $p_o = g e^{-E_L/(R\theta)}$. Indeed, this places a restriction on the values that g and E_L can take. The physical meaning of x can be obtained by combining the definition $x = (p/g)\,e^{E_L/(R\theta)}$ with the restriction $p_o = g e^{-E_L/(R\theta)}$, to yield $x = p/p_o$. That is, x is the relative vapor pressure.

Another type of assumption concerning the static condensation rates will be tested. Assuming that the static rate of evaporation, forming the first layer clusters, is related to the surrounding vapor pressure p and the surface area of the bare surface s_o, as $a_1 p^r s_o$, instead of $a_1 p s_o$ as used before, where a_1 is a material constant related to the nature of the adsorbate and adsorbent and r is a material constant being restricted to be greater than zero. Assuming, again, that the static rate of evaporation contributing to a reduction of clusters, including one layer only, is related to the surface area

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occupied by these clusters and to the temperature according to $b_1 s_1 e^{-E_1/(R\theta)}$, where b_1 and E_1 are the same constants as used in the normal BET-theory. In this case, the equation corresponding to (13), is

$$a_1 p^r s_o = b_1 s_1 e^{-E_1/(R\theta)} \tag{30}$$

In the same way and with the same motivations as used before one obtains

$$a_2 p^r s_1 + b_1 s_1 e^{-E_1/(R\theta)} = a_1 p^r s_o + b_2 s_2 e^{-E_2/(R\theta)} \tag{31}$$

By combining (30) and (31) one also obtains the general expression valid for the different formed layers, i.e.

$$a_i p^r s_{i-1} = b_i s_i e^{-E_i/(R\theta)}; \qquad i = 1, 2, ..., \infty \tag{32}$$

The area occupied by mono-layers, i.e. s_1, can be related to s_2 as $s_1 = y^* s_o$, by defining y^* as $y^* = (a_1/b_1) p^r e^{E_1/(R\theta)}$. Assuming, again, that all condensation heats involved in forming layers including more than one molecule are equal to the normal condensation heat E_L, i.e. $E_2 = E_3 = ... E_i = E_L$, and that $b_2/a_2 = b_3/a_3 = ... b_i/a_i = g$, where g is a constant. This means that $s_2 = x^* s_1$ can be established by (32) and by using $x^* = (p^r/g) e^{E_L/(R\theta)}$.

Defining c in the same manner as before, i.e. $c = y^*/x^* = (a_1/b_1) g e^{(E_1 - E_L)/(R\theta)}$, it is straightforward to obtained a generalized version of (26), as

$$\frac{v}{v_m} = \frac{c x^*}{(1 - x^*)(1 - x^* + c x^*)} \tag{33}$$

and the generalized version of (29) becomes

$$v = \frac{v_m c x^*}{(1 - x^*)} \left(\frac{1 - (n+1) x^{*n} + n x^{*n+1}}{1 + (c-1) x^* - c x^{*n+1}} \right) \tag{34}$$

where x^* is related to the relative vapor pressure as $x^{*1/r} = p/p_o$. When using the generalized (one-layer) BET-equation (33), three material constants must be searched for, i.e. c, v_m and r. When using (34), four material constants are used, i.e. c, v_m, r and n.

When it comes to comparing measurements with the BET-theory it is convenient to plot the property $x^*/(v(1 - x^*))$ against x^*, as shown in equation (35). By doing this, the intercept becomes $1/(v_m c)$ and the slope is $(c-1)/(v_m c)$. From this information the value of c and v_m can be predicted.

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$$\frac{x^*}{v(1-x^*)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c} x^* \tag{35}$$

This type of method evaluating the material constants c and v_m can only be used in the standard BET-equation (26). The result from this type of method can, however, be used as an indication regarding the range in which values c and v_m vary, when also incorporating the material constants r and n.

In order to compare the measured heat due to adsorption with the values given from the BET-theory it is of interest to find an expression of the amount of adsorbate located in different layers. Considering, first, the standard BET-equation in which it is assumed that only the first layer has a condensation heat different from the normal condensation E_L. The volume of adsorbate in the first layer can be expressed as

$$v_1 = v_o \sum_{i=1}^{\infty} s_i \tag{36}$$

Combining, further, this expression with (22), i.e. $s_i = cx^{*i}s_o$, one obtains

$$v_1 = v_o c s_o \sum_{i=1}^{\infty} x^{*i} \tag{37}$$

The total volume of adsorbate is given by the following expression

$$v = v_o c s_o \sum_{i=1}^{\infty} i x^{*i} \tag{38}$$

where (18) and (22) are in use. The ratio between the volume in first layer v_1 and the total volume v is

$$\frac{v_1}{v} = \frac{\displaystyle\sum_{i=1}^{\infty} x^{*i}}{\displaystyle\sum_{i=1}^{\infty} i x^{*i}} = \frac{\frac{x^*}{(1-x^*)}}{\frac{x^*}{(1-x^*)^2}} = 1 - x^* \tag{39}$$

in which the equations (24) and (25) are used. Hence the volume v_1 can be expressed as a function of x^* by combining (39) with the BET-equation (33), to obtain

$$v_1 = \frac{v_m c x^*}{(1 - x^* + cx^*)} \tag{40}$$

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Now the interest will be turned to the derivation of the BET-equation when assuming that the two first layers have an energy of condensation which significantly differs from the normal condensation heat E_L. The expression of the volume content in these two layers will also be established.

In the same manner as obtaining the expressions shown in (16), one can again conclude that s_i can be written as

$$s_i = \frac{a_i}{b_i} s_{i-1} p^r e^{E_i/R\theta} \tag{41}$$

The difference of (41) compared to the expression (16) is the power of r on the pressure p. The following relation between s_i and s_{i-1} values can, in this case, be defined

$$
\begin{aligned}
s_1 &= y^* s_o \\
s_2 &= z^* s_1 \\
s_3 &= x^* s_2 \\
s_4 &= x^* s_3 \\
... &= ... \\
s_i &= x^* s_{i-1}
\end{aligned}
\tag{42}
$$

where y^*, z^* and x^*, according to (42), must be given as

$$y^* = \frac{a_1}{b_1} p^r e^{E_1/R\theta}; \quad z^* = \frac{a_2}{b_2} p^r e^{E_2/R\theta}; \quad x^* = \frac{p^r}{g} e^{E_L/R\theta} \tag{43}$$

The property g will in this case have the meaning $g = b_3/a_3 = b_4/a_4 = ... = b_i/a_i$. From (32) and (42) it is, further, concluded that, for example, the relation $s_4 = xs_3 = x^2 s_2$ can be obtained. More generally one can express this as

$$s_i = x^* s_{i-1} = x^{*i-2} s_2 = z x^{*i-2} s_1 = b x^{*i-1} s_1 \tag{44}$$

where b is defined as

$$b = \frac{z^*}{x^*} = \frac{a_2}{b_2} g e^{(E_2 - E_L)/R\theta} \tag{45}$$

The property s_1, defining the area occupied by mono-layers can, furthermore, be written as

$$s_1 = c x^* s_o \tag{46}$$

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where c, in this case, takes the form

$$c = \frac{y^*}{x^*} = \frac{a_1}{b_1} g e^{(E_1 - E_L)/R\theta} \tag{47}$$

The ratio v/v_m is established by using (19), (44) and (46), which leads to the equation

$$\frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} = \frac{s_1 + \sum_{i=2}^{\infty} s_i}{s_o + s_1 + \sum_{i=2}^{\infty} s_i} = \frac{c x s_o + b c s_o \sum_{i=2}^{\infty} i x^{*i}}{s_o + c x s_o + b c s_o \sum_{i=2}^{\infty} x^{*i}} \tag{48}$$

The two sums in equation (48) can be expressed as direct functions of x^*, as

$$\sum_{i=2}^{\infty} i x^{*i} = \frac{x^{*2} (2 - x^*)}{(1 - x^*)^2} \tag{49}$$

and

$$\sum_{i=2}^{\infty} x^{*i} = \frac{x^{*2}}{(1 - x^*)^2} \tag{50}$$

in which the standard series (24) and (25) where used.

By combining (48) with (49) and (50) the BET-equation for a case where the two first layers contribute to a special condensation heat will be obtained, as

$$v = \frac{v_m c x^* (1 + (b - 1) (2 x^* - x^{*2}))}{(1 - x^*) (1 + (c - 1) x^* + (b - 1) x^{*2} c)} \tag{51}$$

This equation expressing the relation between the total adsorbed volume v and the property x^*, which is related to the relative vapor pressure as $x^{*1/r} = p/p_o$, can be referred to as a modified two-layer BET-equation. Expression (51) includes four material constants, i.e. c, v_m, r and b. When setting $b = 1$ the above relation is identical to the BET-equation (33) valid for the first-layer molecules having a condensation heat different from normal condensation heat.

Again, it will be of interest to establish the expressions for the volume content v_1 in the first layer. This volume is obtained by using (36) together with (44), (46) and (50), to give

$$v_1 = v_o \sum_{i=1}^{\infty} s_i = v_o c s_o x^* + v_o b c s_o \sum_{i=2}^{\infty} x^{*i} = v_o c s_o x^* \left(\frac{1 + x^* (b - 1)}{(1 - x^*)} \right) \tag{52}$$

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The total volume v of adsorbate is obtained from (44) and (46), i.e.

$$v = v_o \sum_{i=0}^{\infty} is_i = v_o \sum_{i=1}^{\infty} is_i = v_o cx^* s_o + v_o bcs_o \sum_{i=2}^{\infty} ix^{*i} \qquad (53)$$

Using, further, the equation (49), one obtains the expression for the total volume v, as

$$v = v_o cs_o x^* \left(\frac{(1 - x^*)^2 + bx^* (2 - x^*)}{(1 - x^*)^2} \right) \qquad (54)$$

The ratio v_1/v is given from (52) and (54), i.e.

$$\frac{v_1}{v} = \frac{(1 - x^*) + x^* (b - 1) (1 - x^*)}{(1 - x^*)^2 + bx^* (2 - x^*)} \qquad (55)$$

where it can be noted that for $b = 1$ the ratio v_1/v, in (39), is recovered, valid for the one-layer method.

When making special assumptions concerning the condensation heat of second-layer molecules, the volume content of this layer also becomes important. This is because this information is needed when it comes to making comparisons with calorimetric measurements. The volume of the second layer is obtained as

$$v_2 = v_o \sum_{i=2}^{\infty} s_i = v_o bcs_o \sum_{i=2}^{\infty} x^i = v_o bcs_o \frac{x^{*2}}{(1 - x^*)} \qquad (56)$$

where (44), (46) and (50) are used. Forming the ratio v_2/v by the use of (54), the result is

$$\frac{v_2}{v} = \frac{x^* (1 - x^*)}{(1 - x^*)^2 + bx^* (2 - x^*)} \qquad (57)$$

Hence, the expression for v_1 is obtained by combining (51) and (55), to yield

$$v_1 = \frac{v_m cx^* (1 + (b - 1) (2x^* - x^{*2})) ((1 - x^*) + x^* (b - 1) (1 - x^*))}{(1 - x^*) (1 + (c - 1) x^* + (b - 1) x^{*2} c) ((1 - x^*)^2 + bx^* (2 - x^*))} \qquad (58)$$

and v_2 is obtained by combining (51) and (57) to give the result

$$v_2 = \frac{v_m cx^{*2} (1 + (b - 1) (2x^* - x^{*2})) (1 - x^*)}{(1 - x^*) (1 + (c - 1) x^* + (b - 1) x^{*2} c) ((1 - x^*)^2 + bx^* (2 - x^*))} \qquad (59)$$

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The important knowledge about how the different layers are distributed in terms of volumes, given from the BET-theory, becomes crucial since the calorimetric measurements to be evaluated or any other sorption technique cannot distinguish from which layer the heat responses originated.

In the BET-theory it is often assumed that the ratio $(a_1 b_2)/(b_1 a_2)$, where a_1, b_1, a_2 and b_2 are material constants, should be approximately equal to unity, i.e. $(a_1 b_2)/(b_1 a_2) \approx 1$, when adopting the one-layer approach. By making this assumption the condensation heat involved in placing molecules on the material surface E_1 can be calculated from the material constants c and R by using the definition of c, i.e. $c = \frac{a_1 b_2}{b_1 a_2} e^{(E_1 - E_L)/(R\theta)}$, once the temperature θ is controlled and when the normal condensation heat of the vapor E_L at the adopted test temperature is known. That is, when assuming $(a_1 b_2)/(b_1 a_2) \approx 1$, the condensation heat E_1 can be calculated as: $E_1 = R\theta \ln c + E_L$.

The same type of conclusions can be made within the two-layer concept when assuming the two material constant ratios $(a_1 b_3)/(b_1 a_3)$ and $(a_2 b_3)/(b_2 a_3)$ to be equal to unity, the expressions for E_1 and E_2, in this case, become: $E_1 = R\theta \ln c + E_L$ and $E_2 = R\theta \ln b + E_L$, e.g. compare with equations (45) and (47). It is, again, noticed that when setting $b = 1$, the two-layer method reduces to the one-layer method since $E_2 = E_L$, in this case.

4 Experimental procedure

Two types of experiments are used to measure the adsorption isotherms for porous glass and micro-crystalline cellulose at room temperature. The first is the use of a sorption balance instrument which enables the user to measure both the absorption/desorption isotherms and the kinetics before reaching equilibrium. The second method of measuring is the use of a newly developed sorption micro-calorimeter from which both the absorption isotherm and the heat of adsorption can be evaluated, e.g. see [4] and [5].

The calorimeter consists of two chambers connected with a thin tube. Both chambers are equipped with heat flow sensors. In one of the chambers, a liquid is inserted at the beginning of the experiment, which is referred to as the vaporization chamber. A dry sample, divided into small parts, is placed in the other chamber. During the experiments the thermal power is measured in the two chambers. In order to evaluate the experiments, certain

assumptions must be made. It is assumed that the vapor pressure in the vaporization chamber always is at saturation. Further, the flow from the vaporization chamber to the sample chambers is assumed to be constant along the thin tube connecting the chambers at every time level. This flow, denoted F, is assumed given from a Fick's first law type of equation, i.e.

$$F = K \left(p_{vap}^s - p_{sorp} \right) \tag{60}$$

where p_{vap}^s is the constant saturation pressure in the vaporization chamber, at a given temperature, and p_{sorp} is the unknown partial vapor pressure in the sample chamber. The property K is a constant assumed given as

$$K = D_p \frac{\pi r_t^2 \varkappa}{l_t} \tag{61}$$

where r_t and l_t are the diameter and length of the tube connecting the chambers, respectively, D_p is the diffusion constant in air with vapor pressure as potential, and $\varkappa$ is a correction coefficient which can be obtained by calibration.

The thermal power $P_{vap}(t)$ and $P_{sorp}(t)$ are the measured properties in this method. From the known value of the vaporization heat $\Delta_{vap}h$ for the liquid and the measured value P_{vap} the flow F can be estimated as

$$F = \frac{P_{vap}}{\Delta_{vap}h} \tag{62}$$

Having assumed that the vapor pressure in the vaporization chamber always is at saturation, the relative humidity in the sample chamber, at every time level, can be calculated as

$$\phi_{sorp} = \frac{p_{sorp}}{p_{vap}^s} = 1 - \frac{F}{K p_{vap}^s} = 1 - \frac{P_{vap}}{K \Delta_{vap} h p_{vap}^s} \tag{63}$$

where (60), (61) and (62) are used.

The moisture content u, i.e. the mass adsorbate per mass (dry) adsorbent, in the sample is obtained by integrating the predicted flow $F(t)$ entering the sample chamber during the experiment, as

$$u(t) = u(0) + \frac{1}{m_o} \int_0^t F(t)\, dt = u(0) + \frac{1}{m_o \Delta_{vap} h} \int_0^t P_{vap}(t)\, dt \tag{64}$$

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That is, it is assumed that vapor reaching the sample chamber immediately will be adsorbed onto the sample surfaces and that the portion of molecules in the air in the sample chamber is very small compared to the molecules adsorbed onto sample.

A plot of ϕ_{sorp}, obtained from equation (63), against u, obtained from equation (64), constitutes the adsorption isotherm. Further, at each value of ϕ_{sorp}, obtained from the experiments and the assumptions explained above, the thermal power of P_{sorp} is also measured. That is, the global response of the heat of adsorption can be evaluated as a function of the relative humidity.

The heat of condensation of molecules located in first and second layers cannot be measured explicitly. The calorimetric measurements will only give the differential heat (i.e. the difference in thermal power registered in the two chambers) as a function of the predicted relative humidity ϕ_{sorp} in the sample chamber. Therefore, one must use expressions describing the growth of the first and second layers (or more layers having a condensation heat different from the normal heat of liquification) given as a function of the relative humidity. Such a relation can be derived using the basic assumptions within the BET-theory, e.g. see equations (58) and (59).

In other words, the expected development of the differential heat, as registered by the calorimeter, can be modeled by using a proper BET-equation which is used in order to evaluate the total volume of adsorbate and the volume of molecules located in the first and second layers. Since the development of the simulated volume of molecules located in the first and second layers, described as a function of the relative humidity, is proportional to global heat of differential condensation, the measured and predicted values can be matched by testing different values of E_1 and E_2. This means, further, that the ratio $(a_1 b_2) / (b_1 a_2)$, in the one-layer method and the ratios $(a_1 b_3) / (b_1 a_3)$ and $(a_2 b_3) / (b_2 a_3)$, in the two-layer method, are calculated from the results given from the measured data together with the use of the development of different layers given from the BET-equation.

In order to control the reliability of the obtained isotherm for the porous glass from the calorimetric approach, another type of experiment was performed using a sorption balance (DVS-1000). This method of measuring sorption consists of letting a dry and saturated flow of vapor mixed into desired proportions pass the sample, placed on a symmetric balance, at a velocity of approximately 1 mm/s. The relative humidity, given by the flow regulators, is changed when the registered mass change of sample is smaller than a pre-defined value of 0.0003%/minute of dry sample weight.

A regulated flow of dry nitrogen enters the instrument housed in a climate chamber. The flow is divided into two different pipes with flow regulators attached to them. One of the two pipes enters a bottle of distilled water, making the flow saturated. The two pipes are then reunited in a single pipe with a known relative humidity given from the settings on the flow regulators. In order to check the performance of the flow regulators humidity probes are situated just below the sample and reference holders in the symmetrically arranged balance.

The performance of the instrument is constantly controlled by running tests on saturated salt solutions with known saturation pressures. When such a calibration is performed the relative humidity in sample chamber is changed very slowly by a pre-defined setting, controlled by a computer. When a mass ·change very close to zero is obtained the saturation point of the tested salt is located. The reading of the relative humidity given from the flow regulators and humidity probes is compared with the saturation point of the salt in use. From this method the accuracy of the relative humidities, given from the flow regulators, was concluded to be in the range of $\pm 0.5\%$.

A porous Vycor glass sample of approximately 100 mg was used in the test. Before the sample was inserted into the instrument the balance was calibrated for the reference and sample holders used. The holders were washed with ethanol and dried at zero relative humidity before the experiment started. The finely divided porous glass sample was dried in the instrument before the test was started giving the sorption isotherm. The sample was regarded as dry when a very small weight change was obtained; this drying period typically takes about 10 hours. During measurements a step in relative humidity was taken when the registered mass change of sample was less than the pre-defined target. Typically steps about 8% in relative humidity were used up to approximately 60% relative humidity. The sample was then dried to check that the original measured weight was the same as the one measured after sorption, which was always the case, within very good accuracy.

The temperature in the instrument was controlled by the computer, attached to the instrument, using heating and cooling systems in the climate chamber. The measured temperature near the sample and reference holders differed approximately ± 0.1 degree Celsius from the desired target temperature set at 25°C.

The porous glass samples, type Vycor® from Corning, being tested in the sorption micro-calorimeter were either washed with an acid, to avoid

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effects caused by organic vapors in air reacting with material, or unprepared with regard to organic vapors. The porous glass sample being tested in the sorption balance was unprepared with regard to organic vapors. The difference in terms of sorption isotherm obtained for washed and unprepared porous glass was, however, observed to be quite small. Furthermore, the porous glass isotherm obtained from the calorimetric method was somewhat lower than the one obtained with the sorption balance. This is the expected behavior since the 'true' equilibrium path, i.e. the points on the absorption isotherm, cannot be exactly followed during sorption in the chamber of the calorimeter. When it comes to evaluating the properties E_1 and E_2 from experiments, only the absorption isotherm and the global heat as registered by the calorimeter are used. Hence, the results obtained from the sorption balance, in which only an unprepared porous glass sample was examined, are used only to check the relevance of the absorption isotherm evaluated from the calorimetric measurements and are therefore not involved in the determination of the condensation heats E_1 and E_2.

The micro-crystalline cellulose was only tested with the sorption micro-calorimeter.

5   Restrictions in BET-theory on the rate constants at equilibrium

The approach for evaluating the material constants c and b is to find the best match to the experimentally obtained data in terms of the adsorption isotherm. Further, different values of E_1 and E_2 are tested to give the best fit to the data obtained from the calorimetric measurements. This leads to a case where the material constant ratios $a_1 b_3 / (b_1 a_3)$ and $a_2 b_3 / (b_2 a_3)$ must take given values which in most cases was observed to be significantly different from unity. Here it will be shown that the values of a_1/b_1, a_2/b_2 and a_3/b_3 can be given as a function of the temperature θ, the condensation energies E_1, E_2 and E_L, and the saturated mass density of vapor ρ_{vs} in air at the studied temperature.

It is very important to note that the pressure p must develop in the correct manner. That is, the pressure involved in the basic assumption leading to the BET-equation must be compatible with a state function describing the pressure.

The state function describing the pressure p, identified as the partial pressure of the vapor above the surface of the material, can, for example, be a function of the temperature θ and the mass density of vapor ρ_v, as

$$p = \frac{R}{M_v}\theta\rho_v \tag{65}$$

where M_v is the mole weight and R is the gas constant. Further, the mass density of vapor is related to the saturation mass density ρ_{vs} through the relative humidity x, as

$$\rho_v = x\rho_{vs} \tag{66}$$

The ratio between the 'free' surface area s_o and the area occupied by one layer s_1 can be expressed as a function of the relative humidity, i.e.

$$\frac{s_o}{s_1} = \frac{s_o}{cxs_o} = \frac{1}{cx} \tag{67}$$

where (46) is used with $x \equiv x^*$ (i.e. setting r equal to unity for simplicity).

The ratio between the area occupied by one layer s_1 and by two layers s_2, is

$$\frac{s_1}{s_2} = \frac{cxs_o}{bxs_1} = \frac{cxs_o}{bcx^2s_o} = \frac{1}{bx} \tag{68}$$

where $x \equiv x^*$ and where (44) is used. According to (44) one can, further, express the relation between s_2 and s_3, as

$$\frac{s_2}{s_3} = \frac{1}{x} \tag{69}$$

From (30), (65), (66) and (67), the ratio a_1/b_1 can be written as

$$\frac{a_1}{b_1} = \frac{ce^{-E_1/(R\theta)}}{\frac{R}{M_v}\theta\rho_{vs}} \tag{70}$$

where $r = 1$, again, is used. It is noted that the value a_2/b_2 can be determined in the same manner, as

$$\frac{a_2}{b_2} = \frac{be^{-E_2/(R\theta)}}{\frac{R}{M_v}\theta\rho_{vs}} \tag{71}$$

and a_3/b_3 becomes

$$\frac{a_3}{b_3} = \frac{e^{-E_L/(R\theta)}}{\frac{R}{M_v}\theta\rho_{vs}} \tag{72}$$

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It can be assumed that $a_1 b_3/(b_1 a_3) \approx 1$ and $a_2 b_3/(b_2 a_3) \approx 1$; this will, however, imply that the material constants c and b must be related to E_1, E_2 and E_L as given from (70), (71) and (72). The performed experiments did not confirm such a relation. This subject will be discussed later.

It is observed that (70), (71) and (72), gives

$$\frac{a_1}{b_1}\Big/\frac{a_3}{b_3} = ce^{(E_L - E_1)/(R\theta)} \tag{73}$$

and

$$\frac{a_2}{b_2}\Big/\frac{a_3}{b_3} = be^{(E_L - E_2)/(R\theta)} \tag{74}$$

That is, the definition of c and b is recovered.

It is concluded that the value of a_1/b_1, a_2/b_2 and a_3/b_3 must be compatible with the measured values of E_1, E_2, and E_L and the values of c and b (giving the best fit to the measured adsorption isotherm), other wise the state function describing the pressure and the basic assumption (41) will not be consistent. Further it is noted that no restrictions are placed on the ratios $a_1 b_3/(a_3 b_1)$ and $a_2 b_3/(a_3 b_2)$.

A more general discussion of different types of equilibrium conditions will be performed in the next section where thermodynamical arguments originating from the combination of constitutive assumptions and the second axiom of thermodynamics will be studied.

6 Thermodynamic considerations concerning adsorption

In this section an expression for the pressure in the adsorbed water will be derived by using some simplifying assumptions. The Helmholz free energy for the vapor and for the adsorbate will be assumed to depend on temperature and its mass densities only. Different equilibrium results are discussed and several thermodynamic restrictions are pointed out. The basic assumption concerning the two considered constituents is that the stress can be given as $\mathbf{T}_a = -p_a \mathbf{I}$, where $\mathbf{T}_a$ is the stress tensor and p_a is the pressure for an arbitrary constituent denoted a. That is, the adsorbed molecules and the vapor are assumed not to be able to sustain shear stress. Further, the 'global' velocities $\mathbf{x}'_a$ for the two constituents are assumed to be zero, which can be interpreted as an explicitly assumed equilibrium condition.

The mass balance and energy balance equations together with the entropy inequality will be used. These equations is presented in the form as described in [6].

Consider the second axiom of thermodynamics, as expressed in terms of the Helmholz free energy ψ_a and the entropy η_a, written in local form, as

$$
\begin{aligned}
0 \;\leq\; & -\sum_{a=1}^{\Re} \rho_a \psi'_a - \sum_{a=1}^{\Re} \rho_a \eta_a \dot{\theta} + \sum_{a=1}^{\Re} \mathrm{tr}\, \mathbf{T}_a^{\mathrm{T}} \mathbf{L}_a \\
& - \sum_{a=1}^{\Re} \left(\mathbf{q}_a + \rho_a \theta \eta_a \mathbf{u}_a \right) \cdot \mathrm{grad}\,(\theta)\,/\theta \\
& - \sum_{a=1}^{\Re} \mathbf{u}_a \cdot \hat{\mathbf{p}}_a - \sum_{a=1}^{\Re} \hat{c}_a \left(\psi_a + \tfrac{1}{2} u_a^2 \right)
\end{aligned}
\tag{75}
$$

where ρ_a is the mass density concentration of a constituent denoted a, ψ'_a is the material time derivative of the Helmholtz free energy following the motion of the a:th constituent, $\dot{\theta}$ is the rate of change of temperature of the mixture of all considered $\Re$ constituents with respect to the motion of the whole mixture, $\mathbf{T}_a$ is the stress tensor, $\mathbf{L}_a$ is the velocity gradient, $\mathbf{q}_a$ is the heat flux vector, $\mathbf{u}_a$ is the diffusion velocity related to the velocity of the mixture, $\hat{\mathbf{p}}_a$ is the momentum supply to the a:th constituent from all other constituents present in the mixture, $\hat{c}_a$ is the mass supply to the a:th constituent from all other constituents and u_a^2 denotes the scalar product $\mathbf{u}_a \cdot \mathbf{u}_a$.

A case where the Helmholtz free energy depends only on the temperature and the mass density will be studied, i.e.

$$
\psi_a = \psi_a \left(\theta, \rho_a \right)
\tag{76}
$$

This type of constitutive assumption is referred to as a simple fluid. The partial hydrostatic pressures p_a can be defined with the help of the Helmholtz free energy ψ_a described through (76). In order to define the pressure p_a, consider the derivative of (76), i.e.

$$
\rho_a \psi'_a = \rho_a \frac{\partial \psi_a}{\partial \theta} \theta' + \rho_a \frac{\partial \psi_a}{\partial \rho_a} \rho'_a
\tag{77}
$$

It should further be noted that $\mathrm{div}\, \mathbf{x}'_a = \mathrm{tr}\,(\mathrm{grad}\, \mathbf{x}'_a) = \mathrm{tr}\, \mathbf{L}_a$, where $\mathbf{x}'_a$ denotes the velocity of the a:th constituent, which allows the mass balance equation

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expressed with the material derivative of the mass density, i.e. $\rho'_a + \rho_a \text{divx}'_a = \hat{c}_a$, to be written

$$\rho'_a = -\rho_a \operatorname{tr} \mathbf{L}_a + \hat{c}_a \tag{78}$$

If (77) and (78) are combined

$$\rho_a \psi'_a = \rho_a \frac{\partial \psi_a}{\partial \theta} \theta' - \rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \operatorname{tr} \mathbf{L}_a + \rho_a \frac{\partial \psi_a}{\partial \rho_a} \hat{c}_a \tag{79}$$

is yielded.

Only the terms in the second axiom of thermodynamics (75) containing the term $\mathbf{L}_a$ will be considered at this stage. It is concluded that the first term and the third term in (75) together with (79) result in a validation of the following restriction:

$$\sum_{a=1}^{\Re} \operatorname{tr} \left(\rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \mathbf{I} + \mathbf{T}_a^{\mathrm{T}} \right) \mathbf{L}_a \geq 0 \tag{80}$$

Since $\mathbf{L}_a$ is arbitrary, it follows that the parenthesis in equation (80) must be equal to zero in order to satisfy the part of the inequality containing the velocity gradient term. This makes it possible to define the thermodynamic law for the stress tensor as

$$\mathbf{T}_a = -\rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \mathbf{I} \tag{81}$$

where the stress tensor is described with the hydrostatic pressure only, i.e.

$$\mathbf{T}_a = -p_a \mathbf{I} \tag{82}$$

Following the thermodynamic law (81) as well as (82), the expression for the hydrostatic pressure can be written as

$$p_a = \rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \tag{83}$$

The following discussion will concern two constituents denoted v and am, denoting the vapor phase and the material with adsorbed molecules on it, respectively. For simplicity, the following restrictions will be assumed:

$$\begin{aligned} \mathbf{x}'_v \left(\mathbf{x}, t \right) &= \mathbf{0} \\ \mathbf{x}'_{am} \left(\mathbf{x}, t \right) &= \mathbf{0} \end{aligned} \; ; \tag{84}$$

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This means that the velocity of the mixture $\dot{\mathbf{x}}$ and the diffusion velocities $\mathbf{u}_a$ are also restricted to be zero. That is, a problem with heat conduction and mass exchanges between constituents will be studied, in which the constituents have zero velocities and where the pressures for the constituents are defined by $p_v = \rho_v^2 \partial \psi_v / \partial \rho_v$ and $p_{am} = \rho_{am}^2 \partial \psi_{am} / \partial \rho_{am}$, i.e. by the equation (83).

The fifteen unknown properties in this problem involving the heat conducting and reacting constituents v and am are:

$$
\begin{array}{cccccc}
\rho_v\left(\mathbf{x}, t\right) & & \hat{c}_v\left(\mathbf{x}, t\right) & \eta_v\left(\mathbf{x}, t\right) & \psi_v\left(\mathbf{x}, t\right) & \mathbf{q}_v\left(\mathbf{x}, t\right) \\
\rho_{am}\left(\mathbf{x}, t\right) & ; \ \theta\left(\mathbf{x}, t\right) ; & \hat{c}_{am}\left(\mathbf{x}, t\right) ; & \eta_{am}\left(\mathbf{x}, t\right) ; & \psi_{am}\left(\mathbf{x}, t\right) ; & \mathbf{q}_{am}\left(\mathbf{x}, t\right) ;
\end{array}
\tag{85}
$$

where the independent variables are the mass densities ρ_v and ρ_{am} and the temperature θ. The rest of the properties listed in (85) are the constitutive variables. It should be noted that the heat fluxes $\mathbf{q}_v$ and $\mathbf{q}_{am}$ involve three unknown properties each.

Following the assumptions in (84), the inequality (75) is simplified to

$$
-\sum_{a=1}^{2} \rho_a \dot{\psi}_a - \rho \eta \dot{\theta} - \sum_{a=1}^{2} \mathbf{q}_a \cdot \operatorname{grad}(\theta) / \theta - \sum_{a=1}^{2} \hat{c}_a \psi_a \geq 0
\tag{86}
$$

where $\psi_a' = \dot{\psi}_a$ due to the restriction of zero velocities for the two considered constituents, in this case.

It is assumed that the Helmholtz free energy ψ for the constituents v and am is given as functions of the temperature θ and the mass densities ρ_v and ρ_{am}, e.g. see (76), as

$$
\begin{aligned}
\psi_v &= \psi_v\left(\theta, \rho_v\right) \\
\psi_{am} &= \psi_{am}\left(\theta, \rho_{am}\right)
\end{aligned}
\tag{87}
$$

The entropies η for the constituents v and am are assumed to depend on the same quantities, i.e.

$$
\begin{aligned}
\eta_v &= \eta_v\left(\theta, \rho_v\right) \\
\eta_{am} &= \eta_{am}\left(\theta, \rho_{am}\right)
\end{aligned}
\tag{88}
$$

The chemical reaction rate $\hat{c}_v$ is constituted as a function of the temperature θ and the mass density of the constituents.

$$
\begin{aligned}
\hat{c}_v &= f_v\left(\theta, \rho_v, \rho_v\right) \\
\hat{c}_{am} &= f_{am}\left(\theta, \rho_{am}, \rho_{am}\right)
\end{aligned}
\tag{89}
$$

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Finally, the heat fluxes is constituted as

$$\mathbf{q}_v = \mathbf{f}_v \left(\mathrm{grad}\, \theta \right)$$
$$\mathbf{q}_{am} = \mathbf{f}_{am} \left(\mathrm{grad}\, \theta \right) \tag{90}$$

where $\mathbf{f}_v$ and $\mathbf{f}_{am}$ are tensor functions relating the gradient on temperature to the heat flux vector.

The differentiation of ψ_v and ψ_{am}, given from (87), yields

$$\dot{\psi}_v = \frac{\partial \psi_v}{\partial \theta} \dot{\theta} + \frac{\partial \psi_v}{\partial \rho_v} \dot{\rho}_v \tag{91}$$

$$\dot{\psi}_{am} = \frac{\partial \psi_{am}}{\partial \theta} \dot{\theta} + \frac{\partial \psi_{am}}{\partial \rho_{am}} \dot{\rho}_{am} \tag{92}$$

The total entropy density η and the mass density ρ of the whole mixture is related to the individual entropies and mass densities through the definition

$$\rho \eta = \sum_{a=1}^{\Re} \rho_a \eta_a \tag{93}$$

If (91), (92), and (93) are introduced into the simplified inequality (86), the result is

$$-\sum_{a=1}^{2} \rho_a \left(\frac{\partial \psi_a}{\partial \theta} \dot{\theta} + \frac{\partial \psi_a}{\partial \rho_a} \dot{\rho}_a \right) - \sum_{a=1}^{2} \rho_a \eta_a \dot{\theta} - \sum_{a=1}^{2} \mathbf{q}_a \cdot \mathrm{grad}\,(\theta)\,/\theta - \sum_{a=1}^{2} \hat{c}_a \psi_a \geq 0 \tag{94}$$

The mass balance for constituents v and am is broken down to

$$\dot{\rho}_v = \hat{c}_v \tag{95}$$
$$\dot{\rho}_{am} = \hat{c}_{am} \tag{96}$$

since the spatial derivative $\partial \rho_a / \partial t$ is identical with the material derivative, i.e. $\partial \rho_a / \partial t = \dot{\rho}_a$ when $\mathbf{x}'_a$ and $\dot{\mathbf{x}}$ are equal to zero, and also due to the possibility to write the mass balance, using the spatial derivative, in a form given as: $\partial \rho_a / \partial t + \mathrm{div} \mathbf{x}'_a = \hat{c}_a$.

The constraint on the mass balance equation is

$$\sum_{a=1}^{2} \hat{c}_a = 0 \tag{97}$$

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In other words, no net production of mass can occur solely due to mass exchange among constituents. If the mass balance equations (95), (96), and the constraint (97) are introduced into (94),

$$-\sum_{a=1}^{2} \rho_a \left(\frac{\partial \psi_a}{\partial \theta} + \eta_a \right) \dot{\theta} - \sum_{a=1}^{2} \left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a \right) \dot{\rho}_a - \sum_{a=1}^{2} \mathbf{q}_a \cdot \mathrm{grad}\,(\theta)\,/\theta \geq 0$$

(98)

is yielded. Since $\dot{\theta}$ is an arbitrary quantity, it seems natural to define the thermodynamic 'laws'

$$\frac{\partial \psi_v}{\partial \theta} = -\eta_v;$$

(99)

$$\frac{\partial \psi_{am}}{\partial \theta} = -\eta_{am};$$

(100)

which assure that the first terms in (98) fulfill the reduced inequality.

A so-called dissipation inequality is introduced for the second term in (97) by replacing $\dot{\rho}_v$ with $\hat{c}_v$ and also $\dot{\rho}_{am}$ with $\hat{c}_{am}$. In other words, the equations (95) and (96) are inserted into the second term in (98). This yields the dissipation inequality

$$\varphi_{chem.} = -\sum_{a=1}^{2} \left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a \right) \hat{c}_a \geq 0$$

(101)

This inequality is valid only when the velocity of both constituents is zero, i.e. when the relation $\dot{\rho}_a = \hat{c}_a$ holds for the constituents v and am. The property $\varphi_{chem.}$ can be referred to as the chemical dissipation.

It can be established that the dissipation inequality (101) is positive by making a proper constitutive assumption for the rate of the chemical reaction $\hat{c}_a$, rather than introducing thermodynamic definitions or laws.

To obtain a constitutive relation, which describes the reaction kinetics, (97) must be considered, which yields

$$\hat{c}_v = -\hat{c}_{am}$$

(102)

The chemical dissipation $\varphi_{chem.}$ for the constituents v and am then becomes

$$\varphi_{chem.} = -\sum_{a=1}^{2} \left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a \right) \hat{c}_a = - \left(\rho_v \frac{\partial \psi_v}{\partial \rho_v} + \psi_v - \rho_{am} \frac{\partial \psi_{am}}{\partial \rho_{am}} - \psi_{am} \right) \hat{c}_v$$

(103)

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This makes the constitutive relation describing the chemical reaction rate $\hat{c}_a$ restricted. The following natural choice appears attractive:

$$\hat{c}_v = \dot{\rho}_v = -G\left(\rho_v \frac{\partial \psi_v}{\partial \rho_v} + \psi_v - \rho_{am}\frac{\partial \psi_{am}}{\partial \rho_{am}} - \psi_{am}\right) \tag{104}$$

where G is a positive scalar quantity denoting a material property, which describes the reaction kinetics. From (104) and (101) it is concluded that the chemical dissipation is always positive, in this case, since $\varphi_{chem.}$ is a quadratic assumption. It is noted that the chemical reaction rate $\hat{c}_v$ is a function of the mass densities ρ_v and ρ_{am} and the temperature θ, compare (89). This is due to the fact that ψ_v and ψ_{am} depend on the same quantities, compare (87).

It is noted that the term in parentheses in (104) has a special meaning. This can be seen by considering the definition of the chemical potential tensor $\mathbf{K}_a$, i.e.

$$\mathbf{K}_a = \psi_a \mathbf{I} - \mathbf{T}_a^{\mathrm{T}}/\rho_a \tag{105}$$

Using the assumption (82) the chemical potential tensor takes the form $\mathbf{K}_a = \mu_a \mathbf{I}$, where μ_a is the chemical potential for a simple fluid. The chemical potential can, therefore, in this case, be written as

$$\mu_a = \psi_a + p_a/\rho_a \tag{106}$$

where (82) is used. Further, by using the thermodynamic 'law' for the pressure p_a, i.e. equation (83), the expression (106) can be written

$$\mu_a = \psi_a + \rho_a \frac{\partial \psi_a}{\partial \rho_a} \tag{107}$$

That is, the classical result that $\mu_v = \mu_{am}$ is obtained when the equilibrium condition, defined by $\dot{\rho}_v = \dot{\rho}_{am} = 0$, holds. This can be seen by inserting (107) into (104), hence

$$\dot{\rho}_v = -G\left(\mu_v - \mu_{am}\right) \tag{108}$$

It should be carefully noted that this result is in no way general, since it depends on the structure of the constitutive assumptions for the Helmholtz free energy and the entropy for the constituents.

The so-called thermal dissipation is the last term in the reduced inequality (98), i.e.

$$\varphi_{therm.} = -\frac{\sum_{a=1}^{2} \mathbf{q}_a}{\theta}.\mathrm{grad}\,\theta \geq 0 \tag{109}$$

If an isotropic heat flux is assumed, the thermal dissipation can be assured to be a non-negative quantity by introducing the constitutive relations

$$\mathbf{q}_1 = -\tilde{\lambda}_1 \operatorname{grad} \theta \tag{110}$$

$$\mathbf{q}_2 = -\tilde{\lambda}_2 \operatorname{grad} \theta \tag{111}$$

which means that the dissipation is quadratic in $\operatorname{grad} \theta$. Both material constants $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$ are restricted to be positive scalar numbers. When studying anisotropic heat flux problems, i.e. using an assumption of the type $\mathbf{q}_a = -\mathbf{C}_{(\lambda)a} \operatorname{grad} \theta$, the thermal dissipation inequality, i.e. $\varphi_{therm.} \geq 0$, imposes the restriction that the conductivity tensor $\mathbf{C}_{(\lambda)a}$ must be positive definite.

From the introduced thermodynamic laws (99) and (100), the expression for the rate of change of the entropies $\dot{\eta}_a$ for the constituents v and am takes the form

$$\dot{\eta}_v = -\frac{\partial^2 \psi_v}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_v}{\partial \theta \partial \rho_v} \dot{\rho}_v \tag{112}$$

$$\dot{\eta}_{am} = -\frac{\partial^2 \psi_{am}}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_{am}}{\partial \theta \partial \rho_{am}} \dot{\rho}_{am} \tag{113}$$

where it is assumed that η_v and η_{am} depend on the same quantities as ψ_v and ψ_{am} do, compare (88).

The energy balance equation written in terms of the Helmholtz free energy ψ_a and the entropy η for the whole mixture, can be written as

$$\rho \theta \dot{\eta} + \operatorname{div} \mathbf{h} + \sum_{a=1}^{\Re} \mathbf{u}_a \cdot \hat{\mathbf{p}}_a + \sum_{a=1}^{\Re} \hat{c}_a \tfrac{1}{2} u_a^2 - \rho r \tag{114}$$

$$= -\sum_{a=1}^{\Re} (\rho_a \psi_a' + \hat{c}_a \psi_a) - \rho \eta \dot{\theta} + \operatorname{tr} \sum_{a=1}^{\Re} \mathbf{T}_a^{\mathrm{T}} \mathbf{L}_a$$

With the constraints in (84), the simplified version of the energy equation (114) is

$$\rho \theta \dot{\eta} + \operatorname{div} \sum_{a=1}^{2} \mathbf{q}_a + \sum_{a=1}^{2} \rho_a \dot{\psi}_a + \sum_{a=1}^{2} \hat{c}_a \psi_a + \rho \eta \dot{\theta} = 0 \tag{115}$$

It follows from (93) that

$$\eta = \frac{1}{\rho} \sum_{a=1}^{\Re} \rho_a \eta_a \tag{116}$$

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By the differentiation of the quantity η as

$$\dot{\eta} = \frac{1}{\rho} \sum_{a=1}^{2} (\dot{\rho}_a \eta_a + \rho_a \dot{\eta}_a) \tag{117}$$

where it should be observed that $\rho = const.$ due to the simplified mass balance equations (95) and (96) and due to (97), i.e.

$$\sum_{a=1}^{2} \hat{c}_a = \dot{\rho}_{am} + \dot{\rho}_v = \dot{\rho} = 0 \tag{118}$$

where the mass balance for the mixture, i.e. $\dot{\rho} + \rho \text{div} \dot{x}$, and the assumption $\dot{x} = 0$ are also used.

If the assumed expressions are introduced for $\dot{\eta}_a$ and $\dot{\psi}_a$, the energy equation (114) can be written, in terms of the Helmholtz free energy and the heat flux vector, as

$$\begin{aligned}
0 &= \theta \sum_{a=1}^{2} \left(\dot{\rho}_a \left(-\frac{\partial \psi_a}{\partial \theta} \right) + \rho_a \left(-\frac{\partial^2 \psi_a}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_a}{\partial \theta \partial \rho_a} \dot{\rho}_a \right) \right) \\
&\quad + \text{div} \sum_{a=1}^{2} \mathbf{q}_a + \sum_{a=1}^{2} \rho_a \left(\frac{\partial \psi_a}{\partial \theta} \dot{\theta} + \frac{\partial \psi_a}{\partial \rho_a} \dot{\rho}_a \right) \\
&\quad + \sum_{a=1}^{2} \hat{c}_a \psi_a + \sum_{a=1}^{2} \rho_a \left(-\frac{\partial \psi_a}{\partial \theta} \right) \dot{\theta}
\end{aligned} \tag{119}$$

where (117), (112), and (113) together with the thermodynamic laws (99) and (100) are used. If this expression is rearranged and $\hat{c}_v$ and $\hat{c}_{am}$ are replaced by $\dot{\rho}_v$ and $\dot{\rho}_{am}$, through the use of the mass balance equations, i.e. (95) and (96), the result is

$$\begin{aligned}
0 &= \theta \sum_{a=1}^{2} \left(\dot{\rho}_a \left(-\frac{\partial \psi_a}{\partial \theta} \right) + \rho_a \left(-\frac{\partial^2 \psi_a}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_a}{\partial \theta \partial \rho_a} \dot{\rho}_a \right) \right) \\
&\quad + \text{div} \sum_{a=1}^{2} \mathbf{q}_a + \sum_{a=1}^{2} \rho_a \frac{\partial \psi_a}{\partial \rho_a} \dot{\rho}_a + \sum_{a=1}^{2} \dot{\rho}_a \psi_a
\end{aligned} \tag{120}$$

This expression can be referred to as a generalization of the standard heat conduction equation.

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The Helmholtz free energy ψ_v is specified in a more detailed manner by introducing direct constitutive relations containing the material constants C_v, R/M_v, and L_v as

$$\psi_v\left(\theta, \rho_v\right) = C_v\theta\left(1 - \ln\theta\right) - \frac{R}{M_v}\theta\left(1 - \ln\rho_v\right) + L_v \qquad (121)$$

where C_v is the heat capacity for the vapor in air, R/M_v represents a factor describing the dependency of the Helmholtz free energy on the composition and temperature. The pressure p_v should in this case, according to the thermodynamic law (83), be given as $p_v = \rho_v^2\partial\psi_v/\partial\rho_v$. From (121) it is then concluded that the state function for the vapor pressure is $p_v = \frac{R}{M_v}\theta\rho_v$ which is the perfect gas law.

At equilibrium, it is now concluded that $\mu_v = \mu_{am}$ and $\dot{\rho}_v = \dot{\rho}_{am} = 0$ holds. Furthermore, it will be explicitly assumed that a measured adsorption isotherm is in equilibrium condition, hence $\mu_v = \mu_{am}$ must hold at every point on the adsorption isotherm. That is, the state function relating ρ_v and ρ_{am}, e.g. given from the 'best' fit of the BET-equation to the experimental data, must also be added to the list of conditions valid at equilibrium.

As it is assumed that the vapor is a perfect gas, according to (121), the chemical potential for the vapor is, at equilibrium, obtained as

$$\mu_v = \psi_v + \rho_v\frac{\partial\psi_v}{\partial\rho_v} = C_v\theta\left(1 - \ln\theta\right) + \frac{R}{M_v}\theta\ln\rho_v + L_v = \mu_{am}\left(\theta, \rho_{am}\right) \qquad (122)$$

It is realized that the function describing the chemical potential for the adsorbed gas is known since the chemical potential is given from the assumption of the Helmholtz free energy. However, it is very difficult to find an explicit physically meaningful expression for μ_{am} in terms of the temperature θ and the mass density of adsorbed gas, ρ_{am}, which satisfies $\mu_v = \mu_{am}$.

Integration of the derived relation $\mu_v = \mu_{am}$ yields, simply

$$\dot{\mu}_v = \dot{\mu}_{am} \qquad (123)$$

Assuming that adsorption can occur without significantly affecting the temperature, i.e. $\dot{\theta} = 0$, the thermodynamic relations (91) and (92) are simplified as

$$\dot{\psi}_v = \frac{\partial\psi_v}{\partial\rho_v}\dot{\rho}_v \qquad (124)$$

$$\dot{\psi}_{am} = \frac{\partial\psi_{am}}{\partial\rho_{am}}\dot{\rho}_{am} \qquad (125)$$

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For $\dot{\theta} = 0$ the relations (112) and (113) for the rate of change of the entropy become

$$\dot{\eta}_v = -\frac{\partial^2 \psi_v}{\partial \theta \partial \rho_v} \dot{\rho}_v \qquad (126)$$

$$\dot{\eta}_{am} = -\frac{\partial^2 \psi_{am}}{\partial \theta \partial \rho_{am}} \dot{\rho}_{am} \qquad (127)$$

The rate of change of the chemical potential $\mu_a \left(\theta, \rho_a \right)$ is, in the general case, obtained as

$$\dot{\mu}_a = \frac{\partial \mu_a}{\partial \theta} \dot{\theta} + \frac{\partial \mu_a}{\partial \rho_a} \dot{\rho}_a \qquad (128)$$

With the same assumption used above, i.e. $\dot{\theta} = 0$, one obtains

$$\dot{\mu}_v = \frac{\partial \mu_v}{\partial \rho_v} \dot{\rho}_v \qquad (129)$$

$$\dot{\mu}_{am} = \frac{\partial \mu_{am}}{\partial \rho_{am}} \dot{\rho}_{am} \qquad (130)$$

for the two considered constituents. From (123), (129) and (130) one obtains

$$\frac{\partial \mu_v}{\partial \rho_v} \dot{\rho}_v = \frac{\partial \mu_{am}}{\partial \rho_{am}} \dot{\rho}_{am} \qquad (131)$$

The property $\dot{\rho}_v$ is in the general case allowed to be arbitrary, which means that the thermodynamic relation between the chemical potentials for the two considered constituents can be written

$$\frac{\partial \mu_v}{\partial \rho_v} = -\frac{\partial \mu_{am}}{\partial \rho_{am}} \qquad (132)$$

where (118) is used, i.e. $\dot{\rho}_v = -\dot{\rho}_{am}$.

The term $\partial \mu_v / \partial \rho_v$ is expressed with the explicit expression given from the constitutive relation for the Helmholtz free energy, i.e. equation (122), as

$$\begin{aligned}
\frac{\partial \mu_v}{\partial \rho_v} &= \frac{\partial}{\partial \rho_v} \left(\psi_v + \rho_v \frac{\partial \psi_v}{\partial \rho_v} \right) \\
&= \frac{\partial}{\partial \rho_v} \left(C_v \theta \left(1 - \ln \theta \right) + \frac{R}{M_v} \theta \ln \rho_v + L_v \right) \qquad (133) \\
&= \frac{R\theta}{M_v \rho_v}
\end{aligned}$$

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Using (132) and (133) gives

$$-\frac{\partial \mu_{am}}{\partial \rho_{am}} = \frac{\partial \mu_v}{\partial \rho_v} = \frac{R\theta}{M_v \rho_v} \qquad (134)$$

According to (106) the derivative of the chemical potential with respect to the mass density can be expressed as

$$\frac{\partial \mu_v}{\partial \rho_v} = \frac{\partial \psi_v}{\partial \rho_v} + \frac{\partial \left(p_v/\rho_v\right)}{\partial \rho_v} \qquad (135)$$

for the vapor and

$$\frac{\partial \mu_{am}}{\partial \rho_{am}} = \frac{\partial \psi_{am}}{\partial \rho_{am}} + \frac{\partial \left(p_{am}/\rho_{am}\right)}{\partial \rho_{am}} \qquad (136)$$

for the adsorbed gas. By multiplying (136) by ρ_{am}^2 to obtain

$$\rho_{am}^2 \frac{\partial \mu_{am}}{\partial \rho_{am}} = \rho_{am}^2 \frac{\partial \psi_{am}}{\partial \rho_{am}} + \rho_{am}^2 \frac{\partial \left(p_{am}/\rho_{am}\right)}{\partial \rho_{am}} \qquad (137)$$

it is realized that the first term on the right-hand side of (137) represents the thermodynamic definition of the pressure in the adsorbed gas, i.e. see equation (83), therefore

$$\rho_{am}^2 \frac{\partial \mu_{am}}{\partial \rho_{am}} = p_{am} + \rho_{am}^2 \frac{\partial \left(p_{am}/\rho_{am}\right)}{\partial \rho_{am}} \qquad (138)$$

is obtained. Taking the partial derivatives of the second term on the right-hand side of (138), the expression for the derivative $\partial \mu_{am}/\partial \rho_{am}$ is obtained, as

$$\frac{\partial \mu_{am}}{\partial \rho_{am}} = \frac{p_{am}}{\rho_{am}^2} + p_{am} \frac{\partial \left(1/\rho_{am}\right)}{\partial \rho_{am}} + \frac{1}{\rho_{am}} \frac{\partial p_{am}}{\partial \rho_{am}} \qquad (139)$$

Noting, further, that the two first terms on the right-hand side of this expression cancel each other out. This means that the chemical potential μ_{am} and the pressure p_{am} are related, as

$$\rho_{am} \frac{\partial \mu_{am}}{\partial \rho_{am}} = \frac{\partial p_{am}}{\partial \rho_{am}} \qquad (140)$$

Using (134) and (140) it is concluded that

$$\rho_{am} \frac{\partial \mu_{am}}{\partial \rho_{am}} = -\frac{\rho_{am} R\theta}{M_v \rho_v} = \frac{\partial p_{am}}{\partial \rho_{am}} \qquad (141)$$

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That is, the pressure in the adsorbed gas p_{am} (which is in contact with an ideal gas) can be expressed as

$$\frac{\partial p_{am}}{\partial \rho_{am}} = -\frac{\rho_{am} R \theta}{M_v \rho_v} \tag{142}$$

This relation is noticed to be somewhat similar to another equation leading to the so-called Kelvin equation. It is realized that the so-called capillary pressure p_{cap}, e.g. see [7], is obtained by integrating the left-hand side of (142), as

$$p_{cap} = -\int_{\check{\rho}_v}^{\check{\rho}_{vs}} \frac{\check{\rho}_{am} R \theta}{M_v \check{\rho}_v} d\check{\rho}_v = \frac{\check{\rho}_{am} R \theta}{M_v} \ln\left(\frac{\check{\rho}_v}{\check{\rho}_{vs}}\right) \tag{143}$$

where $\check{\rho}_{am}$ is assumed to be constant. The notations $\check{\rho}_v$ and $\check{\rho}_{am}$ are used to stress that these properties are not mass concentrations in a representative volume where both constituents are present, but mass concentrations in material points where only one constituent is present at micro-scale. This means that $\check{\rho}_{am}$ is the density of the adsorbed gas, e.g. for adsorbed water vapor $\check{\rho}_{am} \approx 1000$ kg/m^3. That is, a very important difference in the definition of the state variables used in receiving an expression for the capillary pressure p_{cap} are used, compared with the ones used in receiving the relation (142). The pressure p_{cap} should, therefore, not be confused with the measure p_{am}, which has a different meaning.

It is noticed that the term ρ_v can be eliminated in expression (142) by using a relation of the format $\rho_{am} = f(\rho_v)$, which is the sorption isotherm as described by experiments or from the BET-equation. The derivative $\partial p_{am}/\partial \rho_{am}$ is therefore, as expected, concluded to be given from the shape of the sorption isotherm, when assuming that the Helmholtz free energies are expressed as functions of temperature and its corresponding mass concentrations, i.e. $\psi_v = \psi_v(\theta, \rho_v)$ and $\psi_{am} = \psi_{am}(\theta, \rho_{am})$.

From the defined thermodynamic relations in this section, it is concluded that it is difficult to find an explicit expression for the chemical potential for the adsorbed gas, describing adsorption in a stringent manner, even though very simple assumptions are introduced for the Helmholtz free energies for the two considered constituents. The reason is that the energy equation should result in a realistic prediction of the temperature, when at the same time requiring the derived thermodynamic relations to be satisfied.
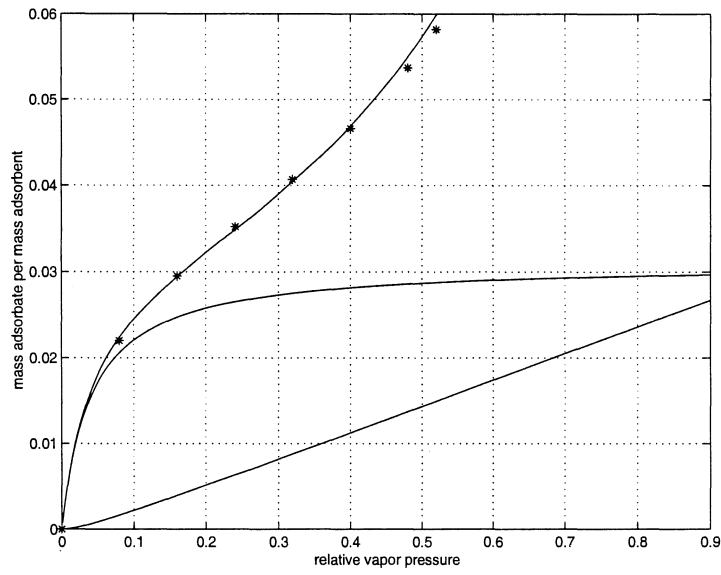
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Figure 1: *Absorption of water vapor on unprepared porous glass at 25 degree Celsius, measured with the sorption balance. Lower curve, calculated mass adsorbate per mass adsorbent located in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the one-layer BET-equation. The stars represent measured values.*
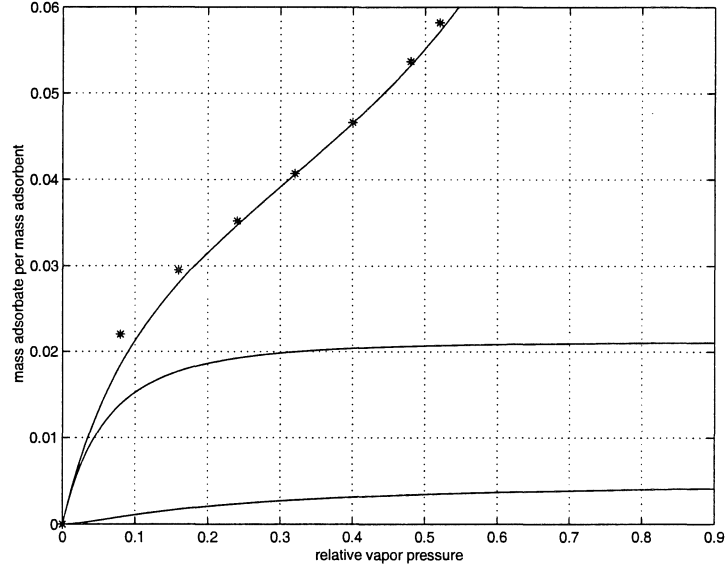
37

Figure 2: *Absorption of water vapor on unprepared porous glass at 25 degree Celsius, measured with the sorption balance. Lower curve, calculated mass adsorbate per mass adsorbent located 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.*

7 Results

Results of absorption isotherms for washed and unprepared porous Vycor glass and micro-crystalline cellulose, measured at room temperature, are presented. Further, the measured global heat of adsorption is presented for the same two materials, [8]. The material constants c and v_m, giving the 'best' fit to measured data, are used when adopting the one-layer method, where the term 'one layer' refers to the first layer of adsorbed water molecules having a heat of sorption different from the normal condensation heat. In the so-called two-layer method, in which the two first layers have a special condensation heat, the fitting parameters c, b and v_m are used.

The condensation heat involved when the first and second layers form are analyzed in two ways. The first is the calculated heat obtained by using the

Table 1: Results for unprepared porous glass at 25 degree Celsius. Material constants and evaluation of specific surface area obtained from the one- and two-layer BET-equation. The absorption isotherm was measured with the sorption balance instrument.

	One-layer BET	Two-layer BET
c (-)	25.71	16.7
b (-)	(1)	5.00
v_m (-)	0.0298	0.0211
S (m^2/g)	105.45	74.87
$E_1^{BET} - L$ (J/kmol)	$7.95 \cdot 10^6$	$6.83 \cdot 10^6$
$E_2^{BET} - L$ (J/kmol)	(0)	$3.44 \cdot 10^6$

proposed expression within the BET-theory. The second approach is to use a value of the condensation heat for the first or for the first and second layer giving the best match to the experimentally obtained condensation heats. As will be seen, the calculated and matched values of the condensation heats differ significantly. It should be carefully observed that the method of fitting the condensation heat involved in creating adsorbed layers at material surfaces needs information given from the BET-theory. That is, the fraction of total adsorbed water located in the first and second layers must be predicted. The expressions describing these relations were derived directly from the basic assumptions within the BET-theory in section 3.

The material parameter v_m, obtained from tests on porous glass and micro-crystalline cellulose, becomes significantly smaller when fitting the BET-equation valid for two layers than when one layer has a condensation heat different from normal condensation, e.g. compare Figures 1 and 3 with Figures 2 and 4. This will mean that different specific surface areas will be obtained since v_m represents the volume adsorbate required to form a complete mono-layer.

When using the one-layer method very little influence of third layer molecules was observed, which can be seen by summing the first and second layer contributions and comparing this sum with the total adsorbed volume. For example, the development of a third layer becomes significant at approximately 35% relative humidity when using the one-layer method, compared to when using the two-layer method in which the development of the third-layer molecules becomes significant at approximately 10%, e.g. compare
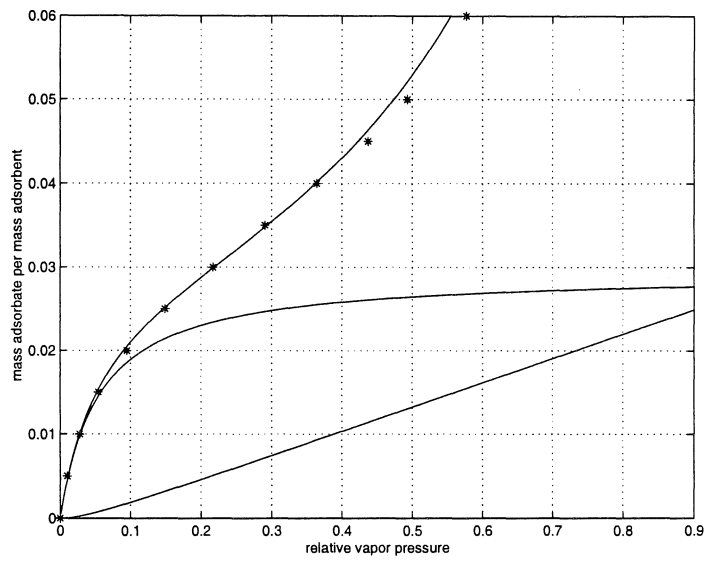
Figure 3: *Absorption of water vapor on washed porous glass at 25 degree Celsius, measured with the calorimetric method. Lower curve, calculated mass adsorbate per mass adsorbent located in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the one-layer BET-equation. The stars represent measured values.*
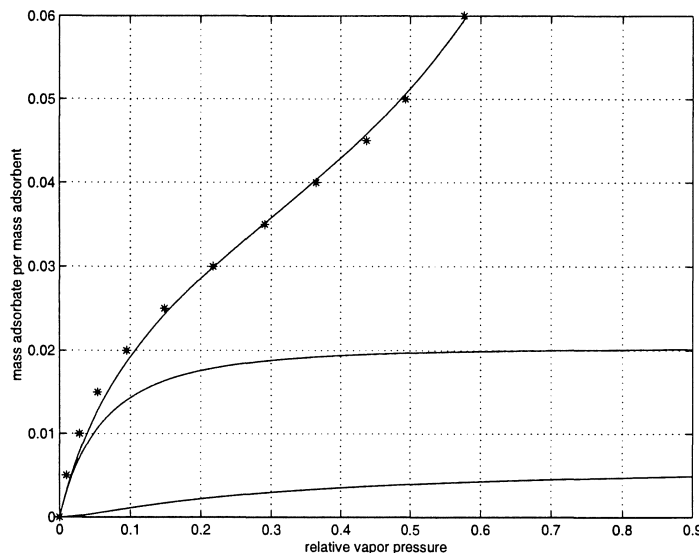
Figure 4: *Absorption of water vapor on washed porous glass at 25 degree Celsius, measured with the calorimetric method. Lower curve, calculated mass adsorbate per mass adsorbent located in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the two-layer BET-equation. The stars represent measured values.*

Figures 1 and 2. This is due to the distributions of areas occupied by different layers derived in section 3, i.e. in the one-layer approach the areas are distributed as $s_{i-1}/s_i = 1/x$, except for the first layers which is distributed as: $s_o/s_1 = 1/(cx)$. In the two-layer approach the areas are distributed as $s_{i-1}/s_i = 1/x$, except for the two first layers which is distributed as: $s_o/s_1 = 1/(cx)$ and $s_1/s_2 = 1/(bx)$, where x is the relative humidity and c and b are material constants.

A general situation observed was that a better fit was obtained at low relative vapor pressures when using the one-layer method compared with the two-layer method. On the other hand, a better match was obtained at medium relative vapor pressure when using the two-layer method than with the one-layer method.

When using the two-layer method, the growth of the molecules located in

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first layer reaches values close to zero earlier than when using the two-layer method, e.g. see Figures 1 and 2. This conclusion will only be correct if one obtains a satisfying match between measured sorption data and values given from the one- and two-layer BET-equations. This stabilized volume of molecules, present in the first layer, corresponds to the v_m value, which for porous glass is also presented in Table 1. Because different v_m values are obtained depending on whether the first- or the second-layer method is used, the evaluation of specific surface area will also be affected. It is explicitly assumed that the specific surface S is proportionally related to v_m as: $S = kv_m$, 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 Å^2 on the material surface.

The difference between calculated specific surface areas using the one- or two-layer method was significant for all three tests performed, see Tables 1-3. For unprepared porous glass the one-layer method gave 40% higher specific surface areas compared to the two-layer method, when using the sorption balance measurements. The same number for the calorimetric measurements on washed porous glass was 38%. The difference between the results in terms of specific surface areas on unprepared porous glass obtained from the sorption balance and calorimetric measurements differed by 9% using the one-layer method and by 10% using the two-layer method, see Tables 1 and 4.

The test on micro-crystalline cellulose gave a specific surface area 65% higher when using the one-layer method than the two-layer approach. It should be noted that the two-layer approach gave a significantly better match to the experimentally obtained data, in terms of sorption, i.e. compare Figures 7 and 8. A higher specific surface area was obtained on micro-crystalline cellulose than on porous glass.

The results of the measured sorption on porous glass and micro-crystalline cellulose, using the sorption micro-calorimeter, are used together with the global measured heat of sorption. That is, the development of the mass of molecules per mass adsorbent located in first layer or in the first and second layers as shown in, for example, Figures 3 and 4, is used when modeling the global response in terms of the condensation heat of sorption. This will result in a measure of the sorption heat when creating first and second layers. The values of the condensation heats of the first and second layers used are the ones giving the best fit to the measured global adsorption heats.

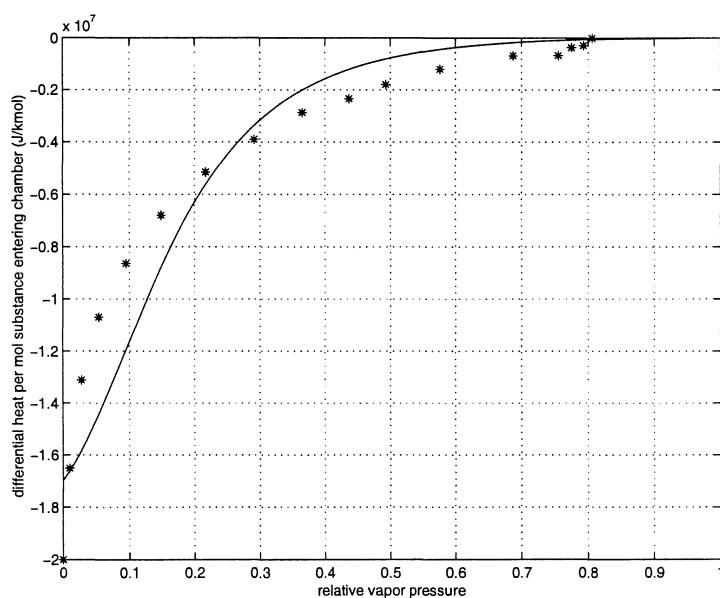For porous glass the measured differential heats, at different relative hu-

Figure 5: *Comparison of the measured differential heat of adsorption on porous glass with predicted values from the one-layer BET-equation. The stars represent the global differential heats, measured by the calorimeter, at different relative vapor pressures.*
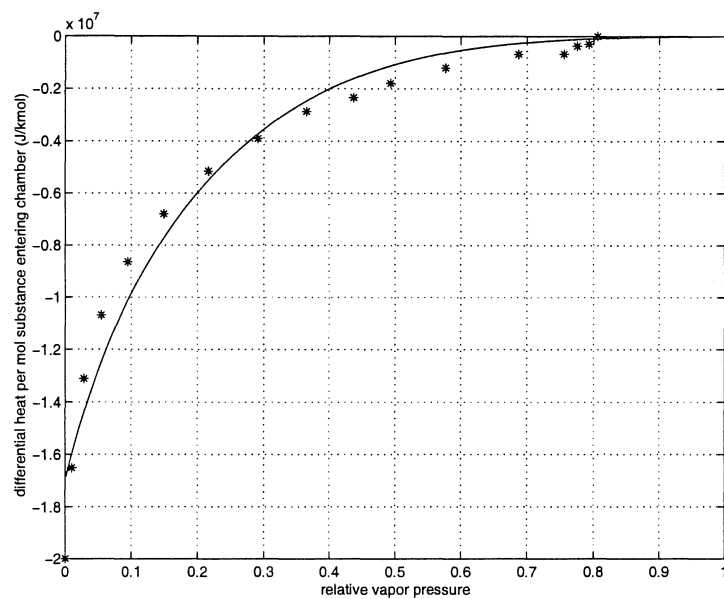
Figure 6: *Comparison of the measured differential heat of adsorption on porous glass with predicted values from the two-layer BET-equation. The stars represent the global differential heats, measured by the calorimeter, at different relative vapor pressures.*

Table 2: Results for washed porous glass at 25 degree Celsius. Material constants and evaluation of specific surface area obtained from the one- and two-layer BET-equation. The measured data analyzed are using the calorimetric approach.

	One-layer BET	Two-layer BET
c (-)	19.22	17.00
b (-)	(1)	4.00
v_m (-)	0.0278	0.0202
S (m^2/g)	98.64	71.68
$E_1 - L$ (J/kmol)	$17.00 \cdot 10^6$	$17.00 \cdot 10^6$
$E_2 - L$ (J/kmol)	(-)	$17.00 \cdot 10^6$
$(a_1 b_2) / (b_1 a_2)$ (-)	0.020	(-)
$(a_1 b_3) / (b_1 a_3)$ (-)	(-)	0.018
$(a_2 b_3) / (b_2 a_3)$ (-)	(-)	0.004
$E_1^{BET} - L$ (J/kmol)	$7.29 \cdot 10^6$	$7.02 \cdot 10^6$
$E_2^{BET} - L$ (J/kmol)	(0)	$3.43 \cdot 10^6$

midities, are shown by the dots in Figures 5 and 6. The solid lines in these figures represent calculated values obtained from the distribution of layers among the total volume and by assigning a value of the condensation heat involved in placing molecules in first layer, Figure 5, or in the first and second layers, Figure 6. As seen from, for example, Figure 3 all molecules entering the sample chamber in the calorimeter will contribute to a heat response at relative humidities between about 0 and 3%, which is because all these molecules will be located in the first layer, as predicted by the BET-equation. Therefore, the initially obtained value of condensation heat in the calorimeter, presented as Joule per mole substance, is used as the test value of differential condensation heat. The development of the differential heat is then only determined by the distribution of adsorbed first and second layers among the total volume of adsorbate as described by equations (58) and (59). The simulated results of the development of the differential heat as a function of relative humidity are presented in Figure 5, one-layer method, and in Figure 6, two-layer method. It is seen that an overall better fit was obtained when assuming that the adsorbed molecules present in the two first layer gives a condensation heat significantly different from normal condensation heat.

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For the porous glass, the simulated development of the differential heat is quite satisfying, i.e. see Figure 6. It is noted, however, that the measured heat of condensation differs significantly from the one proposed in the BET-theory in which the material constant ratios $a_1 b_3 / (b_1 a_3)$ and $a_2 b_3 / (b_2 a_3)$ are set to unity. The differences are shown in Tables 1-3, where $E_1 - L$ and $E_2 - L$ are the measured differential heats, for the first and second layer, respectively, and where $E_1^{BET} - L$ and $E_2^{BET} - L$ are the differential heats as calculated from setting $a_1 b_3 / (b_1 a_3) = 1$ and $a_2 b_3 / (b_2 a_3) = 1$ in the BET-theory.

Due to the large difference in the predicted values $E_1^{BET} - L$ and $E_2^{BET} - L$ compared to the measured values $E_1 - L$ and $E_2 - L$, it is noted that the method of evaluating properties describing sorption, as discussed in section 3, instead can be used to identify the ratios $a_1 b_3 / (b_1 a_3)$ and $a_2 b_3 / (b_2 a_3)$ which are in no way restricted to be equal to unity. The obtained values of these ratios for porous glass are shown in Table 2 and the same values for micro-crystalline cellulose are presented in Table 3.

The relevance of the BET-theory, when regarding the possibilities to match the adsorption isotherm and, at the same time, requiring a satisfying agreement of the development of the differential heats with the relative humidity, could not be confirmed for the tested micro-crystalline cellulose. That is, even though a good fit of the measured sorption isotherm was obtained using the BET-equation, this did not by any means make it possible for the development of the differential heat to be followed correctly. This is, most probably, due to that other effects than those included in the BET-theory are active.

8 Conclusions

The material constants a_1, b_1, a_2, b_2, a_3 and b_3 are involved in describing the equilibrium conditions between pressure in the vapor phase, temperature and amount of water adsorbed in different layers, see section 3. One of the main results from the investigation is that the assumption of letting these material constants a_1, b_1, a_2, b_2, a_3 and b_3 be related as $a_1 b_3 / (b_1 a_3) \approx 1$ and $a_2 b_3 / (b_2 a_3) \approx 1$, leading to a theoretical expression for the heat involved to place vapor molecules in the first and second layers, respectively, cannot be verified by the experiments performed using the theory described in this report. The result show that the ratios $a_1 b_3 / (b_1 a_3)$ and $a_2 b_3 / (b_2 a_3)$ between the material constants can take values significantly different from
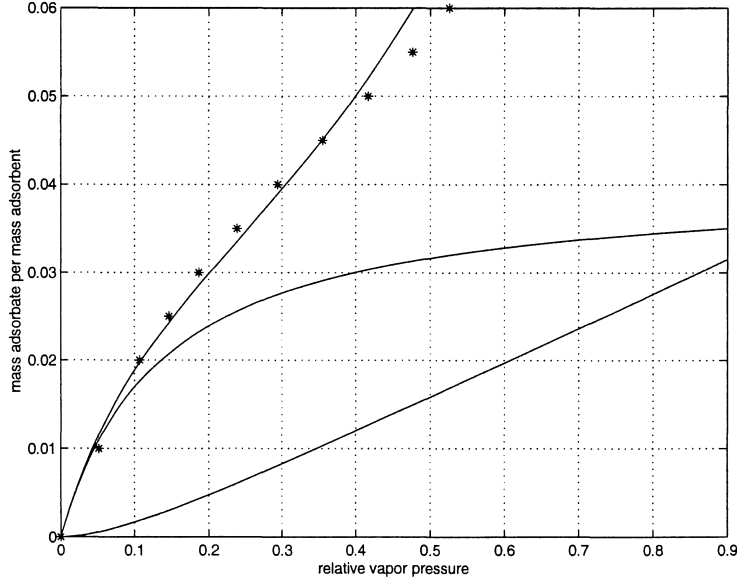
Figure 7: *Absorption of water vapor on micro-crystalline cellulose at 25 degree Celsius, measured with the calorimetric method. Lower curve, calculated mass adsorbate per mass adsorbent located in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the one-layer BET-equation. The stars represent measured values.*

unity. These proposed conditions are not in conflict with the derived expressions in sections 3, 5 and 6. By choosing values c, b, v_m, E_1 and E_2 that give the best fit to the measurements, the ratios a_1/b_1, a_2/b_2 and a_3/b_3 can be calculated, using the equations (72), (73) and (74), respectively, which assumes that the vapor phase can be described as an ideal gas. The individual values of the constants a_1, b_1, a_2, b_2, a_3 and b_3, are, however, as seen above, difficult to predict.

The simulated development of global heat of sorption, on porous glass, obtained by using the condensation heats E_1 and E_2 giving the best fit, resulted in a better match between experiments and model being obtained when using the two-layer method compared with one layer having a condensation heat different from normal heat of condensation, see Figure 5 and 6.
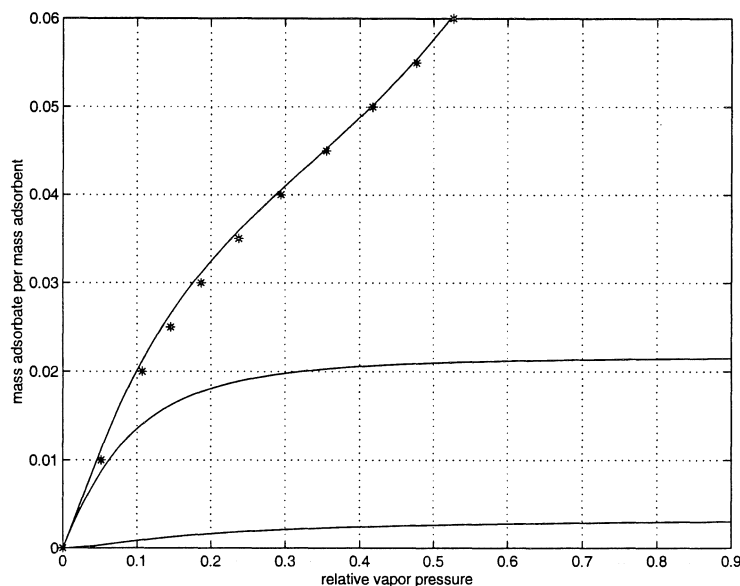
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Figure 8: *Absorption of water vapor on micro-crystalline cellulose at 25 degree Celsius, measured with the calorimetric method. Lower curve, calculated mass adsorbate per mass adsorbent located in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve 'best' fit of the two-layer BET-equation. The stars represent measured values.*

These results should also be judged according to how well the BET-equations for the one-layer and two-layer approaches, fit the experimental adsorption results. This is important since these equations predict the development of layers contributing to heats of sorption different from normal condensation.

Even though an excellent match between the BET-equation (using the two-layer method) and the measured sorption on micro-crystalline cellulose was obtained, it was by no means the result that the evaluation of differential heats of sorption could be followed by assigning different test values of heats involved in creating first and second layers. This can be due to different causes. One of them is that the BET-method does not simulate the development of different layers in a correct manner. These kind of contradictory results for the tested micro-crystalline cellulose were not markedly observed
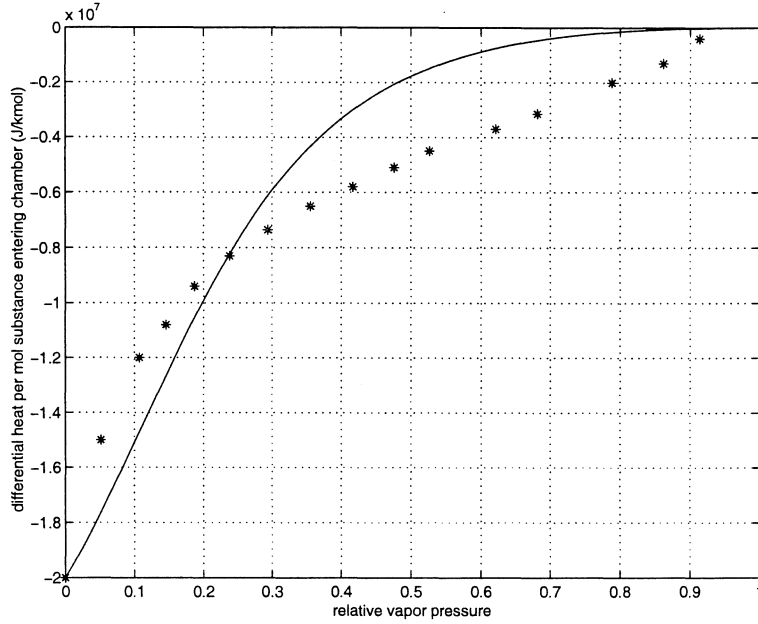
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Figure 9: *Comparison of the measured differential heat of adsorption on MCC with predicted values from the one-layer BET-equation. The stars represent the global differential heats measured by the calorimeter at different relative vapor pressures.*

when examining the measured data obtained for the porous glass, which probably is explained by the fact that this material fulfills the assumptions behind the BET-equation quite well.

The main difference between the measured global heat of condensation on porous glass and micro-crystalline cellulose was that higher values were obtained for the latter. This effect was most dominant for medium and high relative humidities.

From the thermodynamic relations and constitutive relations discussed in section 6, it was concluded that a relation between the pressure in vapor phase above the material surface and in the adsorbed layer could be obtained. No special properties were assigned to different discrete layers of adsorbed molecules in this study. The approach was to use the Helmholtz free energies ψ_v and ψ_{am} as the constitutive dependent properties for the vapor phase and adsorbed water, respectively. The Helmholtz free energies for the two consid-

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ered constituents were assumed to be given as a function of temperature and the mass density of constituent, only, which is referred to as the simple fluid assumption. The classical result $\dot{\rho}_v = -G\left(\mu_v - \mu_{am}\right)$, where G is a material constant, was derived, i.e. when defining the rate of mass density change $\dot{\rho}_v = 0$, to be an equilibrium condition, the chemical potential for vapor μ_v and adsorbed water μ_{am} must be equal. Another classical result from the thermodynamic considerations, using the simple fluid assumptions for the two constituents, was the expressions for the pressures, i.e. $p_v = \rho_v^2 \partial \psi_v / \partial \rho_v$ and $p_{am} = \rho_{am}^2 \partial \psi_{am} / \partial \rho_{am}$. When choosing an assumption for Helmholtz free energy in a way that the vapor pressure is given by the ideal gas assumption and also assuming that temperature is constant, i.e. $\dot{\theta} \approx 0$, the relation between the pressure in the adsorbed water p_{am} and mass density concentration of vapor ρ_v, mass density concentration of adsorbed water ρ_{am} and temperature θ, was forced to be related as: $\partial p_{am} / \partial \rho_{am} = -\rho_{am} R\theta / (M_v \rho_v)$. This means that a quantitative measure of the pressure in the adsorbed water p_{am} can be calculated by using the measured relation between ρ_{am} and ρ_v, i.e. the absorption isotherm, and an integrated version of the expression described above for $\partial p_{am} / \partial \rho_{am}$.

From the thermodynamic considerations in section 6 it can, further, be concluded that the equilibrium condition $\mu_v = \mu_{am}$ (and $\dot{\rho}_v = -\dot{\rho}_{am} = 0$), cannot be exactly satisfied during the sorption process, as measured by the sorption micro-calorimeter. This is due to the rate of change of the mass concentration of vapor and adsorbed water, denoted $\dot{\rho}_v$ and $\dot{\rho}_{am}$ (which is related as: $\dot{\rho}_v = -\dot{\rho}_{am}$), being the main factor contributing to a (small) registered temperature change $\dot{\theta}$ in the test chamber, resulting in a heat flow registered by the heat flow sensors. Assuming that $\dot{\theta} \approx 0$ and that the temperature remains constant in the spatial domain, i.e. $\mathrm{div}\,\mathbf{q} = \mathbf{0}$ in sample tested, it can be seen from the energy equation (120) that all terms left in this case include $\dot{\rho}_v$. Treating the measured thermal power as a boundary condition in the energy equation (120), in which only terms involving $\dot{\rho}_v$ are considered, it is concluded that ψ_v and ψ_{am} (or more correctly the difference between ψ_v and ψ_{am}) must be related in a very special way, which can be seen as a restriction imposed by thermodynamic reasons when assuming $\dot{\theta} \approx 0$ during the process of sorption. This method can be used as an instrument calculating the difference between $\psi_v\left(\theta, \rho_v\right)$ and $\psi_{am}\left(\theta, \rho_{am}\right)$. The whole concept is, however, realized to be somewhat complex since the equilibrium condition $\partial \mu_v / \partial \rho_v = -\partial \mu_{am} / \partial \rho_{am}$ also should hold, see the derivation leading to equation (132), where it is noted that the Helmholtz free energies ψ_v and
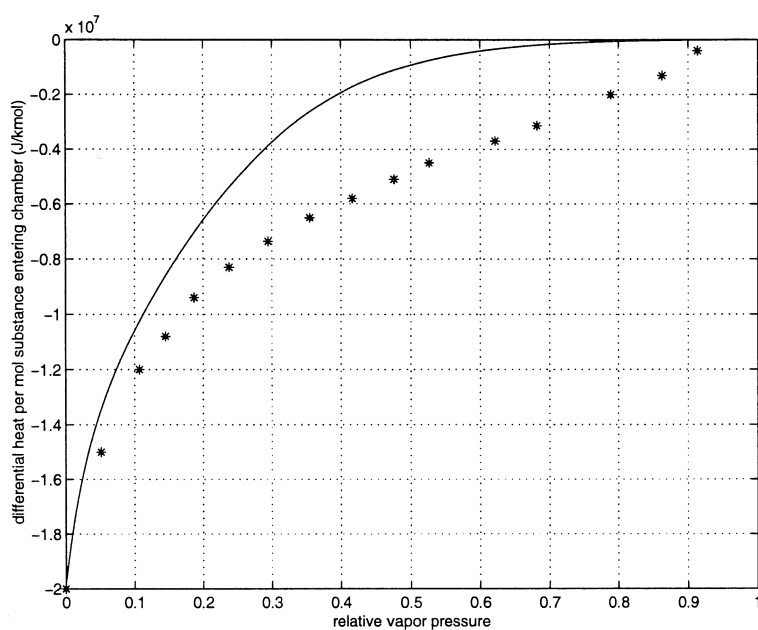
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Figure 10: *Comparison of the measured differential heat of adsorption on MCC with predicted values from the two-layer BET-equation. The stars represent the global differential heats measured by the calorimeter at different relative vapor pressures.*

Table 3: Results for micro-crystalline cellulose, MCC, at 25 degree Celsius. Material constants and evaluation of specific surface area obtained from the one- and two-layer BET-equation. The measured data analyzed are from the calorimetric approach.

	One-layer BET	Two-layer BET
c (-)	8.25	10.00
b (-)	(1)	7.00
v_m (-)	0.0355	0.0215
S (m^2/g)	125.67	76.08
$E_1 - L$ (J/kmol)	$20.00 \cdot 10^6$	$20.00 \cdot 10^6$
$E_2 - L$ (J/kmol)	(-)	$20.00 \cdot 10^6$
$(a_1 b_2) / (b_1 a_2)$ (-)	0.0026	(-)
$(a_1 b_3) / (b_1 a_3)$ (-)	(-)	0.0031
$(a_2 b_3) / (b_2 a_3)$ (-)	(-)	0.0022
$E_1^{BET} - L$ (J/kmol)	$5.23 \cdot 10^6$	$5.70 \cdot 10^6$
$E_2^{BET} - L$ (J/kmol)	(0)	$4.82 \cdot 10^6$

ψ_{am} are to be related to the chemical potentials μ_v and μ_{am} as given by the relation (107).

An interesting extension to this study is to examine the heat of condensation of different adsorbed layers at different test temperatures. By making such experiments in the calorimeter the temperature dependence of the material ratios, the ratios a_1/b_1, a_2/b_2 and a_3/b_3 can be examined. If such a dependence can be shown to be weak the relevance of the use of the Arrhenius function, included as one of the main assumptions in the BET-theory, can be motivated. Further, a more general model must be established, concerning both the physical and chemical sorption in order to study the heat effects during fixation of vapors on surfaces for material with similar behavior to micro-crystalline cellulose.
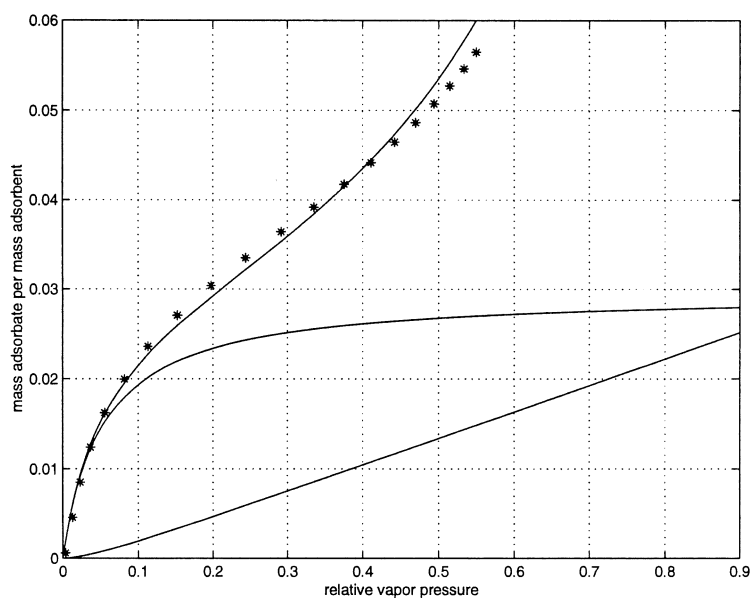
9 Acknowledgments

Figure 11: *Absorption of water vapor on porous glass at 25 degree Celsius. 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.*
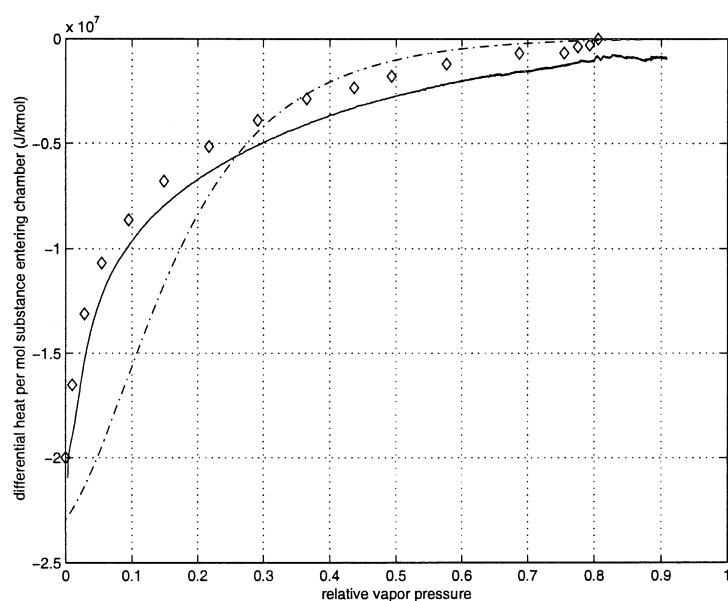
Figure 12: *Comparison of the measured differential heat of adsorption with predicted values from the one-layer BET-equation (dashed line). The measurements were performed at 25 degree Celsius. The diamonds represent a few of the points evaluated from the calorimetric measurements on washed porous glass. The solid line represents the measured differential heat on unprepared porous glass.*
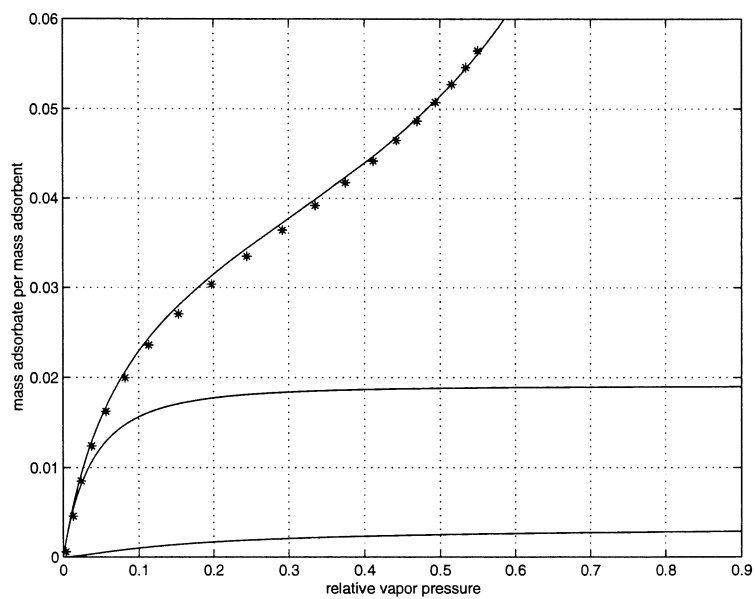
Figure 13: *Absorption of water vapor on porous glass at 25 degree Celsius. Lower curve, calculated mass adsorbate per mass adsorbent in the second layer. Middle curve, calculated mass adsorbate per mass adsorbent located in the first layer. Upper curve, 'best' fit of the two-layer BET-equation. The stars represent measured values on unprepared porous glass using the calorimetric method.*
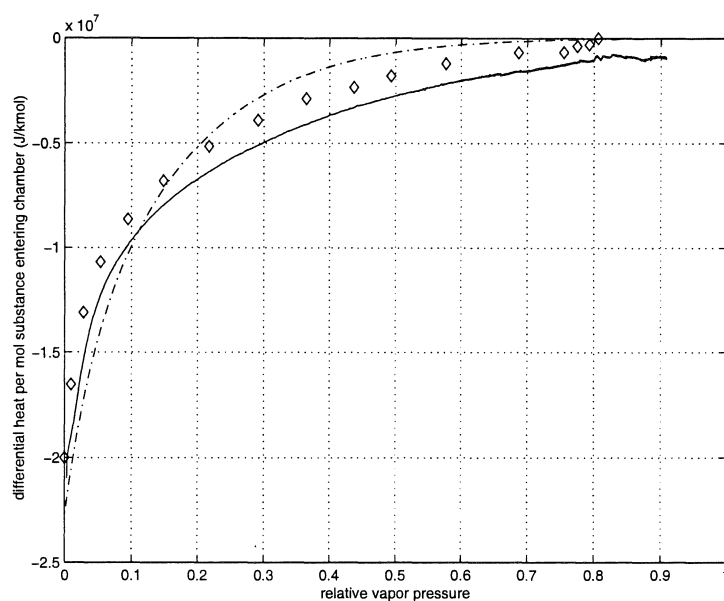
Figure 14: *Comparison of the measured differential heat of adsorption with predicted values from the two-layer BET-equation (dashed line). The measurements were performed at 25 degree Celsius. The diamonds represent a few of the points evaluated from the calorimetric measurements on washed porous glass. The solid line represents the measured differential heat on unprepared porous glass.*

Table 4: 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.

	One-layer BET	Two-layer BET
c (-)	19.77	27.00
b (-)	(1)	6.50
v_m (-)	0.0281	0.0190
S (m^2/g)	95.50	67.26
$E_1 - L$ (J/kmol)	$23.00 \cdot 10^6$	$23.00 \cdot 10^6$
$E_2 - L$ (J/kmol)	(-)	$23.00 \cdot 10^6$
$(a_1 b_2)/(b_1 a_2)$ (-)	0.00184	(-)
$(a_1 b_3)/(b_1 a_3)$ (-)	(-)	0.00252
$(a_2 b_3)/(b_2 a_3)$ (-)	(-)	0.00061
$E_1^{BET} - L$ (J/kmol)	$7.40 \cdot 10^6$	$8.17 \cdot 10^6$
$E_2^{BET} - L$ (J/kmol)	(0)	$4.64 \cdot 10^6$

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