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A Mathematical Model for Sorption Hysteresis I

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Sorption-desorption isotherms in a system with hysteresis form a set of curves $M(A,D)$ (M = sorbed amount, A = highest pressure on adsorption, D = final pressure on desorption). Such data can, without any detailed extra assumptions, be transformed to a map of a load function $s(a,d)$ so that $M(A,D)$ is the integral $\int s\ da dd$ over the area bounded by $a = d$, $a = A$ and $d = D$ (Fig. 2b). The surface load may in places be zero or degenerate to curve loads. The map may thus show a non-zero surface load $s(a,d)$ in certain areas, and a curve load on the reversible line $a = d$, and on lag curves $D_L(a)$. Lag curves correspond to regions with all-or-nothing sorption such as the interior of a pore. Areas with positive and negative values for s may be the result of sorption at the meniscus of a pore (reversible if the pore is filled) and at the inner surface of a pore (reversible if the pore is empty). The position of the lag curve may indicate what sorts of pores are likely and unlikely to dominate in the sample.

The phenomenon of sorption hysteresis has been known for about a century. Classical examples are the sorption of water vapor on silica gel or active charcoal.

DEFINITION OF $M(A,D)$. PORE MODELS

Let us consider a certain amount of sorbent, in apparent equilibrium at some given temperature with a gas phase which contains a single substance (the sorbate) with a pressure P. Let M be the amount of sorbate which has been taken up by the sorbent.

We start with an empty sorbent in a vacuum ($M = 0$, $P = 0$), let P increase to the value A, and wait for equilibrium. The amount then sorbed we shall denote as $M(A,A)$. Then we lower P to the value D and again wait for equilibrium at which M has a new value $M(A,D)$. (A stands for *ad*sorption, D for *de*sorption).

Let us assume that in some region there is a hysteresis loop, which means that $M(A,D) > M(D,D)$. Thus, $M(A,D)$ is a function of both A and D. So, we will have one adsorption curve, $M(P,P)$ when P goes from 0 to A, and a family of desorption curves, $M(A,P)$ when P decreases from different

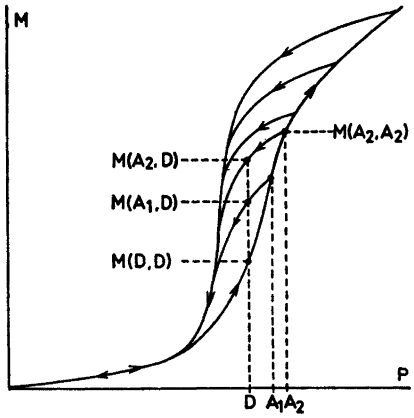

Fig. 1. Adsorption isotherm with hysteresis loop (schematic): sorbed amount M *versus* sorbate pressure P. To right, ascending (adsorption) curve $M(A,A)$. Several descending branches (scanning curves) are shown, starting from various pressures A: $M(A_1,D)$, $M(A_2,D)$ *etc.*

values of A to 0. (Fig. 1). We shall assume — as is often found in practice — that these curves are perfectly reproducible, even if the system is cycled many times. We are thus not interested in irreproducible hysteresis phenomena which may be due, *e.g.*, to impurities or deformation of the sorbent.

It is often convenient to express P, A, and D as fractions of the saturation pressure, P_0, of the liquid sorbate; this will be done in the experimental part.[7] The following treatment is, however, independent of the units used for the pressures P, A, D, or for M.

Most of the measurements that have been recorded in literature on sorption in the hysteresis region have either concerned adsorption curves $M(A,A)$, starting from an empty sorbent, or the desorption from an almost filled sorbent, $M(A,D)$ ($A \approx 1$). Only few workers (notably Katz[1] and Everett *et al.*[2-4]) have also been interested in "scanning curves" $M(A,D)$, starting from various A values, or in measurements with a still more complicated history.

Several authors have made attempts to interpret sorption hysteresis by some physical model. Generally it has been assumed that capillary condensation is important in this region. A pore of a certain shape: an open cylinder, a "bottle", or the space between packed plates or spheres, will be filled by capillary condensation only when P has reached a certain value, say A; on decreasing P, the pore may be emptied only at a lower pressure D. If A and D are expressed as fractions of P_0 (and hence are < 1), then we have the simple relationship $D = A^k$, where k (> 1) is the ratio between the efficient radius of curvature on filling and emptying the pore. For a cylindrical pore open in both ends, $k = 2$ so that $D = A^2$; for wide "bottles", k may be larger, *etc.* For a review, see the articles of de Boer and Everett[5] and the following discussion; here, for instance, the effect of various pore shapes and of interconnection of pores is discussed.

TRANSFORM FUNCTIONS IN SOME OTHER FIELDS

We have tried a somewhat more general approach, namely to make accurate measurements of a series of scanning curves, $M(A,D)$ in the hysteresis region,

and to calculate from these primary data a mathematical transform (the $s(a,d)$ map) which is easier to understand and interpret than the original data.

Analogies to this procedure may be found in other branches of physics and chemistry.

In crystal structure analysis, the primary intensity data $I(h,k,l)$ may be transformed to the Patterson function $P(u,v,w)$ without adding any extra assumption. The Patterson function is a sum of contributions, each of which has a maximum at the position corresponding to an interatomic vector. By means of this transform one can immediately screen out all those otherwise conceivable structures that will require interatomic distances which are not found among the Patterson maxima. After a more accurate analysis of the transform, and of the primary data, usually only one possible structure remains for which one may then refine the atomic positions.

Another example is taken from equilibrium analysis. Data $Z(\log a,B)$ obtained directly from EMF measurements, may be transformed to a plot $(\bar{p}, \bar{q})$ which gives the average composition of the complexes A_pB_q in each solution studied.[6] Again, the transform is calculated directly from the experimental data, without any additional assumption (except that the data contain no systematic error) and we can use the transform to screen the conceivable mechanisms; usually one gets a good clue as to which complexes predominate. The final step may be a generalized least-square refinement of the primary data.

DEFINITION OF $s(a,d)$. SURFACE LOAD AND CURVE LOAD

Our aim has been to transform the sorption data $M(A,D)$ to a map $s(a,d)$ which can more easily be used for further analysis and discussion of the data. The construction of the $s(a,d)$ map involves no extra assumptions except the very general ones inherent in its definition, and the usual working hypothesis that there are no systematic errors in the data.

The coordinates of the map we shall denote by lower case letters, a and d, as distinguished from A and D which are the two limiting pressures in a certain experiment. The map has a physical meaning only for $d \leq a$. To each point of the map we ascribe a *surface load function* $s(a,d)$ so that $s(a,d)\mathrm{d}a\mathrm{d}d$ is the amount of sorbate which is held in such sites that it is sorbed when P increases from a to $a + \mathrm{d}a$ and desorbed when P decreases from $d + \mathrm{d}d$ to d. For certain irreversible types of sorption one may think of a and d as sharp limits for the adsorption and desorption of a certain sorbed molecule in a specific site. For reversibly sorbed molecules, s must be interpreted statistically (see "application to a physical model" below).

The total amount sorbed, M, is the integral over the surface covered. Fig. 2a shows over what area to take the integral $\int s\mathrm{d}a\mathrm{d}d$ in order to obtain $M(A,A)$, and Fig. 2b shows the area corresponding to $M(A,D)$. In the case indicated by Fig. 2c, the pressure has been varied as follows: $\rightarrow A_1 \rightarrow D_1 \rightarrow A_2 \rightarrow D_2$. If our picture is correct, the sorbed amount will be given by the integral of s over the area marked out, thus $M = M(A_1,D_1) + M(A_2,D_2) - M(A_2,D_1)$.

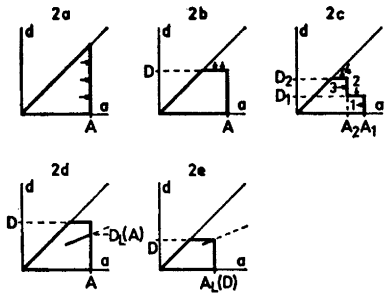

Fig. 2. Map $s(a,d)$, schematical. Thick frames surround areas over which to integrate $\int s da dd$ on (a) sorption to A, (b) sorption to A and desorption to D, (c) sequence $\rightarrow A_1 \rightarrow D_1 \rightarrow A_2 \rightarrow D_2$, (d-e) map with a lag curve $D_L(a)$: (d) for $D > D_L(A)$, (e) for $D < D_L(A)$.

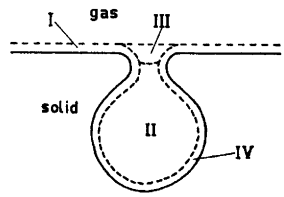

Fig. 3. Schematic picture of sorbent, with four different types of site: I: Open surface, II: interior of pore, III: top layer of meniscus when pore is filled, IV: inner surface of pore.

For a real sorbent, there may be large areas with $s = 0$. On the other hand, there may be sharp ridges in the $s(a,d)$ map, which are so steep that they cannot be distinguished experimentally from mathemathical curves with a certain *curve load*, say $l_A(a)\mathrm{d}a$, per element. In the following we shall treat such curve loads separate from the rest of the $s(a,d)$ function.

A special case is the line $d = a$, which corresponds to completely reversible sorption; the load on an element of this line will be denoted by $r(d)\mathrm{d}d$.

So let us assume that in our map we have

1) the "reversible" curve load, $\int r(d)\mathrm{d}d$, on the line $d = a$.
2) a surface load $\int s(a,d)\mathrm{d}a\mathrm{d}d$ which may be zero in certain regions
3) the "lag curve" load $\int l_A(a)\mathrm{d}a$, on the curve

$$d = D_L(a) \text{ or } a = A_L(d) \tag{1}$$

The corresponding parts of M will be denoted by M_R, M_S and M_L:

$$M = M_R + M_S + M_L \tag{2}$$

1) For the *reversible* part it follows from our definitions

$$M_R(D) = \int_0^D r(d)\mathrm{d}d \tag{3}$$

M_R depends only on the present pressure D and is independent of the history of the system, especially of A.

2) The *surface load* gives a contribution, on the adsorption branch $D = A$:

$$M_S(A,A) = \int_0^A \mathrm{d}a \int_0^a s(a,d)\mathrm{d}d \tag{4}$$

On desorption to D the remaining contribution is (compare Fig. 2b)

$$M_S(A,D) = M_S(D,D) + \int_D^A \mathrm{d}a \int_0^D s(a,d)\mathrm{d}d =$$
$$M_S(A,A) - \int_D^A da \int_D^a s(a,d)\mathrm{d}d \tag{5}$$

3) The contribution from a *lag curve load* (Fig. 2d-e) finally, is on the adsorption curve:

$$M_L(A,A) = \int_0^A l_A(a)\mathrm{d}a = L_A(A) \tag{6}$$

On desorption the contribution from the lag curve load will be the same, as long as $D > D_L(A)$, the highest value for D on the loaded curve, or, using the inverse function, (1), $A_L(D) > A$ (Fig. 2d).

When D becomes less than $D_L(A)$, part of the curve load will be desorbed, and what remains is (Fig. 2e):

$$M_L(A,D) = \int_0^{A_L(D)} l_A(a)\mathrm{d}a = \int_0^D l_D(d)\mathrm{d}d = L_D(D) \tag{7}$$

Hence, M_L is under these conditions a function of D alone; we have introduced the function l_D defined by

$$l_D(d)\mathrm{d}d = l_A(A_L(d))\,\mathrm{d}A_L(d) \tag{7a}$$

To sum up we have

$$M_L(A,D) = L_A(A) \text{ if } D > D_L(A) \tag{8a}$$

$$M_L(A,D) = L_D(D) \text{ if } D < D_L(A) \tag{8b}$$

We may now calculate the partial derivatives of M with respect to A and D. From eqns. (2—7) we find

$$\text{if } D > D_L(A)\text{: } \frac{\partial M}{\partial A} = \int_0^D s(A,d)\mathrm{d}d + l_A(A); \frac{\partial M}{\partial D} = r(D) + \int_D^A s(a,D)\mathrm{d}a \tag{9a}$$

$$\text{if } D < D_L(A)\text{: } \frac{\partial M}{\partial A} = \int_0^D s(A,d)\mathrm{d}d; \frac{\partial M}{\partial D} = r(D) + \int_D^A s(a,D)\mathrm{d}a + l_D(D) \tag{9b}$$

For the second-order derivative we find in both cases

$$\frac{\partial^2 M}{\partial A \partial D} = s(A,D) \tag{10}$$

APPLICATION TO A PHYSICAL MODEL

Any $s(a,d)$ transform might be explained as the result of all-or-nothing sorption: each site of the sorbent acts in such a way that it is filled exactly when P reaches a on adsorption, and is emptied exactly at $P = d$ on desorption; a site which corresponds to a point on the reversible line is filled at a and emptied at the same pressure, $d = a$.

It seems more realistic, however, to assume that the sorption in many sites is statistical and that at each sorbate pressure P one may ascribe to each site a certain number $x(P)$, $0 < x < 1$, which for a site of molecular

dimensions is the probability for its being filled, and for an assembly of such sites the average coverage. Different sites may have different values for x, and x may also depend on the history.

In Fig. 4 we shall now consider four conceivable types of sites, I—IV, which might all be imagined to occur for instance in a physical situation such as that in Fig. 3; "bottle" pores surrounded by open areas. The treatment, is, however, in no way restricted to this picture.

In Fig. 4 we have represented each type of site from left to right by a map, $x(P,c)$, a map $s(a,d)$, and by a diagram $M(P)$. Each element dc represents the sorption capacity of a certain site (type of sites) and $x(P,c)$dc represents the amount actually sorbed by this site at the pressure P. With other words, x is the coverage, the fraction of the sorption capacity of the site that is really being used. C_0 is the total sorption capacity of all the sites considered. The coordinates of the map are c and P, and we must imagine x as the third coordinate, perpendicular to the plane of the paper; x is not drawn in the figures but is indicated by a symbol. If there is only one symbol in the field, x is independent of the history: "0" or "1" indicates that $x = 0$ or $x = 1$, constantly, whereas the letter "x" indicates a variable $x(P,c)$ between 0 and 1. Two symbols with arrows, ↑ and ↓, indicate that in this field of the map the coverage x is different on adsorption and desorption.

Type I

Fig. 4 I represents a case of completely reversible sorption, such as might be expected for sites on or close to an open surface (I in Fig. 3) on which both sorption and desorption proceed rapidly. For each pressure P, $x(P,c)$ depends only on P and not on the earlier history. Hence we would have integrating along a horizontal line $P = D$ (see also Fig. 5 I(M)),

$$M(A,D) = \int_0^{C_0} x(D,c)\mathrm{d}c \tag{11}$$

which in this case is a function of D only, and independent of A. Differentiation and comparison with (9—10) gives

$$\frac{\partial M}{\partial A} = 0, \text{ hence } s = 0, l_A = 0 \tag{11a}$$

$$\frac{\partial M}{\partial D} = \int_0^{C_0} \frac{\partial x(D,c)}{\partial D}\,\mathrm{d}c = r(D) \tag{11b}$$

This type of site would give, in the $s(a,d)$ transform, (Fig. 4 I:2) a reversible curve load on the line $d = a$, and no surface load or lag curve. The diagram $M(P)$ gives a single curve, the same for sorption and desorption (Fig. 4 I:3).

Type II

Fig. 4 II represents sites with all-or-nothing irreversible sorption, which might correspond, for instance, to sites in the interior of a pore (II in Fig. 3); these sites are filled ($x = 1$) if the pore is filled, otherwise empty ($x = 0$).

A certain site dc remains empty ($x = 0$) until P reaches a characteristic value $A_{\mathrm{I}}(c)$, at which it is filled ($x = 1$). If P is again decreased, the site remains filled until P reaches the value $D_{\mathrm{I}}(c)$ ($< A_{\mathrm{I}}(c)$) at which it is emptied again. We arrange the elements in such an order that $A_{\mathrm{I}}(c)$ increases monotonously and assume (Fig. 4 II:1) that there is a single curve $D_{\mathrm{I}}(c)$ which also rises monotonously. One could imagine a system where this is not so. However, it will be possible to describe any system as the sum of a limited number of systems, each of which gives a single curve $D_{\mathrm{I}}(c)$ which either increases or decreases monotonously. We see no reason to discuss the treatment of such complicated systems until a practical case is met with.

We shall thus consider a system with a single rising curve $D_{\mathrm{I}}(c)$, such as that in Fig. 4 II:1 and 5 II (M), and introduce the notation:

$$c = C_A(a) \text{ if } a = A_{\mathrm{I}}(c) \tag{12a}$$

$$c = C_D(d) \text{ if } d = D_{\mathrm{I}}(c) \tag{12b}$$

$$a = A_{\mathrm{I}}(d) \text{ and } d = D_{\mathrm{I}}(a) \text{ if } a = A_{\mathrm{I}}(c) \text{ and } d = D_{\mathrm{I}}(c) \tag{13}$$

$$A_{\mathrm{I}}(0) = A_0;\ D_{\mathrm{I}}(0) = D_0 \tag{14}$$

All sites are empty ($M = 0$) if $P < D_0$. If P is raised from a low value to A, all sites are filled up to $c = C_A(A)$ so that $M = C_A(A)$. If P is then decreased, M remains unchanged until $P = D$ reaches the value $D_{\mathrm{I}}(A)$; for lower D values only sites with $c \leq C_{\mathrm{D}}(D)$ are filled so that $M = C_{\mathrm{D}}(D)$. (Fig. 5 II(M)). Hence

$$\begin{aligned} M(A,D) &= C_A(A) \text{ for } D > D_{\mathrm{I}}(A) \text{ (Fig. 5 IIa)} \\ M(A,D) &= C_D(D) \text{ for } D < D_{\mathrm{I}}(A) \text{ (Fig. 5 IIb)} \end{aligned} \tag{15}$$

Differentiation and comparison with (9) gives

$$\text{for } D > D_{\mathrm{I}}(A)\text{: } \frac{\partial M}{\partial A} = \frac{\mathrm{d}C_{\mathrm{A}}(A)}{\mathrm{d}A} = l_{\mathrm{A}}(A);\ \frac{\partial M}{\partial D} = 0 \tag{16a}$$

$$\text{for } D < D_{\mathrm{I}}(A)\text{: } \frac{\partial M}{\partial A} = 0;\ \frac{\partial M}{\partial D} = \frac{\mathrm{d}C_D(D)}{\mathrm{d}D} = l_{\mathrm{D}}(D) \tag{16b}$$

The $s(a,d)$ map (Fig. 4 II:2) will then contain a lag curve, $d = D_{\mathrm{I}}(a)$ with the load $l_A(A)$. In the $M(P)$ diagram, shown in Fig. 4 II:3, the scanning curves are horizontal lines between each A value and the corresponding $D = D_{\mathrm{I}}(A)$.

In the limiting case (not shown here) where the curves $A_{\mathrm{I}}(c)$ and $D_{\mathrm{I}}(c)$ coincide, the lag curve would coincide with the reversible curve $a = d$ and we would have a completely reversible sorption, not to be distinguished from type I by sorption measurements, although there would be only sites with all-or-nothing sorption.

Type III

Fig. 4 III shows another conceivable type of irreversible sorption, which may correspond to sites in the top layer of the meniscus at the entrance of a pore (III in Fig. 3). If the pore is filled, there is a certain probability $x(P,c)$ that an element dc will be filled by reversible sorption; otherwise the site is

"swimming" in the gas phase, and $x = 0$. As for the sites of type II, and type IV in the following, we describe the conditions for filling and emptying the pore by means of two monotonously increasing curves $A_L(c)$ and $D_L(c)$; in a real case, the total capacities C_0 involved for sorption of type II, III, and IV are surely not the same, and so the diagram $x(P,c)$ may have quite different dimensions for sites of type II, III, and IV. However, one might reasonably expect that the lag curve $D_L(a)$ will be the same for sites of types II, III, and IV if they are connected with the same system of pores.

The integration path, to find M, is indicated in Fig. 5 III(M):

$$M(A,A) = \int_0^{C_A(A)} x(A,c)\mathrm{d}c \tag{17a}$$

$$\text{if } D > D_L(A)\text{: } M(A,D) = \int_0^{C_A(A)} x(D,c)\mathrm{d}c \tag{17b, Fig 5IIIa}$$

$$\text{if } D < D_L(A)\text{: } M(A,D) = \int_0^{C_D(D)} x(D,c)\mathrm{d}c \tag{17c, Fig 5IIIb}$$

(if $D < D_0$, $C_D(D) = 0$, $M(A,D) = 0$)

Differentiation gives

$$\text{if } D > D_L(A)\text{: } \frac{\partial M}{\partial A} = x(D,C_A(A))\frac{\mathrm{d}C_A(A)}{\mathrm{d}A};\ \frac{\partial M}{\partial D} = \int_0^{C_A(A)} \frac{\partial x(D,c)}{\partial D}\mathrm{d}c;$$

$$\frac{\partial^2 M}{\partial A \partial D} = \frac{\partial x(D,C_A(A))}{\partial D} \cdot \frac{\mathrm{d}C_A(A)}{\mathrm{d}A} = s(A,D) \tag{18a}$$

$$\text{if } D < D_L(A)\text{: } \frac{\partial M}{\partial A} = 0;\ \frac{\partial M}{\partial D} = x(D,C_D(D))\frac{\mathrm{d}C_D(D)}{\mathrm{d}D} + \int_0^{C_D(D)} \frac{\partial x(D,c)}{\partial D}\mathrm{d}c;$$

$$\frac{\partial^2 M}{\partial A \partial D} = 0 \tag{18b}$$

Type IV

The behavior of a fourth type of site is indicated by Fig. 4 IV. It might apply to sites at the inner walls of a pore (IV in Fig. 3). If the pore is empty, these sites give reversible sorption, with a partial coverage $x(P,c)$. If the pore is filled, these sites are filled too ($x = 1$). We find as before (see also the integration path in Fig. 5 IV(M))

$$M(A,A) = C_A(A) + \int_{C_A(A)}^{C_0} x(A,c)\mathrm{d}c \tag{19a}$$

$$\text{if } D > D_L(A)\text{: } M(A,D) = C_A(A) + \int_{C_A(A)}^{C_0} x(D,c)\mathrm{d}c \tag{19b, Fig 5IVa}$$

$$\text{if } D < D_L(A)\text{: } M(A,D) = C_D(D) + \int_{C_D(D)}^{C_0} x(D,c)\mathrm{d}c \tag{19c, Fig 5IVb}$$

(if $D < D_0$, $C_D(D) = 0$).

Differentiating we find

$$\text{if } D > D_{\mathrm{L}}(A)\text{:}\ \frac{\partial M}{\partial A} = \frac{\mathrm{d}C_A(A)}{\mathrm{d}A}\,(1-x(D,C_A(A));$$

$$\frac{\partial M}{\partial D} = \int_{C_A(A)}^{C_0} \frac{\partial x(D,c)}{\partial D}\,\mathrm{d}c;\ \frac{\partial^2 M}{\partial A \partial D} = -\frac{\mathrm{d}C_A(A)}{\mathrm{d}A}\,\frac{\partial x(D,C_A(A))}{\partial D} = s(A)D < 0 \quad (20\mathrm{a})$$

$$\text{if } D < D_{\mathrm{L}}(A)\text{:}\ \frac{\partial M}{\partial A} = 0;\ \frac{\partial M}{\partial D} = \frac{\mathrm{d}C_D(D)}{\mathrm{d}D}\,(1-x(D,C_D(D)));\ \frac{\partial^2 M}{\partial A \partial D} = 0 \quad (20\mathrm{b})$$

CONTRIBUTIONS TO M_{R}, M_{S}, AND M_{L}

Figs. 4 and 5 also indicate what contributions each of these types of sites gives to the map $s(a,d)$, to the $M(P)$ diagram, and to the fractions M_{R}, M_{S}, and M_{L} of the total sorbed amount M.

As already mentioned, sites of type I give only a reversible curve load and hence contribute only to M_{R}, whereas type II gives only a loaded lag curve, and hence a term in M_{L}. To understand how type III and type IV act, it is instructive to consider the integral $\int x\,\mathrm{d}c$.

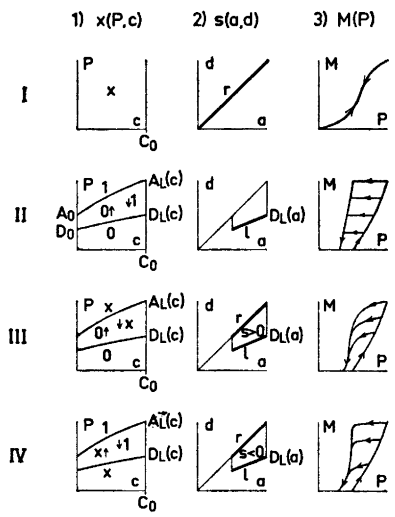

Fig. 4. Four different types of sites, which may be connected with I–IV in Fig. 3 but may also arise in other ways. For each type of site the following diagrams are given: (1) pressure P *versus* capacity c. The symbol 0, x or 1 refers to the coverage on the sites (see text). (2) Map $s(a,d)$, (3) isotherms $M(P)$ for adsorption and desorption.

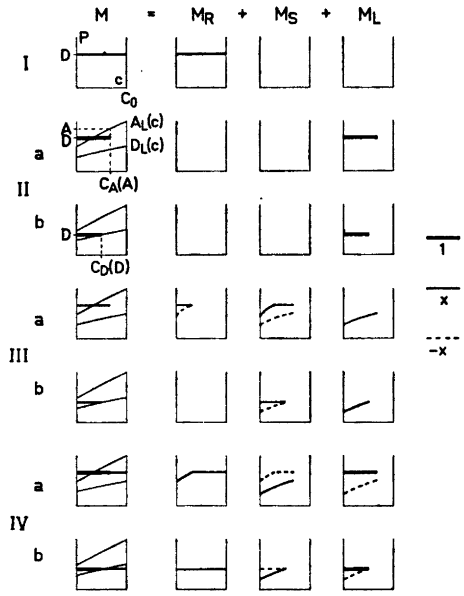

Fig. 5. Contributions from M_{R}, M_{S}, and M_{L} terms to total amounts of M for the types of sites I–IV in Fig. 4. Curves or lines indicate the paths along which one should integrate $\int x\mathrm{d}c$ in order to get the contributions in question. The thickness of the lines denote the value to be used for x under the $\int$ sign (1, $+x$, or $-x$).

Let us for instance calculate M_S for type III, if $D > D_L(A)$ and $D > A_0$ (Fig. 2 d, Fig. 5 IIIa). We apply (5) in the regions with non-zero s, and then introduce the expression (18a) for s, and the definition (12a). This gives us

$$M_S(A,D) = \int_{A_0}^{D} \mathrm{d}a \int_{D_L(a)}^{a} s\mathrm{d}d + \int_{D}^{A} \mathrm{d}a \int_{D_L(a)}^{D} s\mathrm{d}d = \int_{a=A_0}^{a=D} (x(a,C_A(a)) - x(D_L(a),C_A(a)))\,\mathrm{d}C_A(a) + \int_{a=D}^{a=A} (x(D,C_A(a)) - x(D_L(a),C_A(a)))\mathrm{d}C_A(a) = \tag{21}$$
$$= \int_0^{C_A(D)} x(A_L(c),c)\mathrm{d}c + \int_{C_A(D)}^{C_A(A)} x(D,c)\mathrm{d}c - \int_0^{C_A(A)} x(D_L(c),c)\mathrm{d}c = M_S^+ - M_S^-$$

Hence, we may write M_S as the difference between two integrals $\int x\,\mathrm{d}c$ along the paths marked out in Fig. 5 IIIa (M_S). We may proceed in the same way for decreasing values of D (Fig. 5 IIIb (M_S)) and find the same picture: M_S is composed of two curve integrals, M_S^+ and M_S^-. To the right, the integrals are limited by $C_A(A)$ or, if this is lower, by $C_D(D)$.

We shall remember that the total amount sorbed, $M(A,D)$ is the integral $\int x\,\mathrm{d}c$ along the line $P = D$, up to the right-hand limit.

The integration path for M_S^+ has to the right a horizontal part coinciding with the integration path for M, and to the left follows whatever is left of the C_A line for $P < D$. The negative term M_S^- contains the integral along what remains of the C_D curve, up to $C_A(A)$ or $C_D(D)$.

The difference, $M - M_S$ can be written as follows

$$M - M_S = M_R^+ - M_R^- + M_L \tag{22}$$

The M_R terms are connected with the C_A curve. As seen from Fig. 5 IIIa (M_R) they depend on D only, so that this contribution is reversible. The term M_L, finally, fulfills the conditions (8): for $D > D_L(A)$ it depends only on A, for $D < D_L(A)$ it depends only on D. Hence we have split up M into the terms M_R, M_S, and M_L; full-drawn or broken lines in Fig. 5 indicate if the corresponding integral $\int x\,\mathrm{d}c$, with increasing c, will be counted with a positive or negative sign in the sum for M.

One may deduce how the corresponding terms for case IV would behave, (Fig. 5 IV) for instance by considering type IV as the sum of sorption of type I with the coverage x and sorption of type III with coverage $(1-x)$. Fig. 5 IV again gives the contributions of the various terms to M for two different stages of desorption. We hope it is self-explanatory.

Hence, if we have a porous sorbent we may expect contributions to M_R from sites of types I, III, and IV; to M_S from sites of types III and IV; and to M_L from sites of types II, III, and IV. We may also expect the contributions to M_L to be concentrated to the same lag curve (or curves), and the contributions to s to be situated in the area between the corresponding lag curve and the "reversible line" $a = d$, with vertical limits at the extreme A values on the lag curves.

TREATMENT OF EXPERIMENTAL DATA

From experimental data it is usually easy to derive the approximate position of the lag curve. If the data are accurate enough, one may also estimate s in certain regions, using (10).

For sorbents of the general type indicated in Fig. 3 — or in general for sorbents containing sites of types I—IV, regardless of their physical nature — one may expect that the $s(a,d)$ map will contain one or more lag curves, and that s will have non-zero (positive or negative) values in the region which is bounded by the lag curve, the reversible line, and the vertical line with $a = A_0$, the lowest value on the lag curve. The upper limiting value for a on the lag curve is unity, which corresponds to the saturation pressure.

In the refinement of the map, it is hence a useful working hypothesis that s has non-zero values only in the range indicated. One may then (as will be seen in a following paper) divide M into terms M_R, M_S, and M_L. It is not possible to distinguish directly the contributions M_R, M_S, and M_L from various types of sites. However, it can be said that if M_S (and hence s) are positive in a region, this indicates that sites of type III predominate, whereas a negative s would indicate the influence of sites of type IV.

Approximation $s(a)$. In the few systems which we have hitherto studied,[7] this picture has been born out by the experiments. Within the limit of accuracy, s could be treated as a function of a alone, independent of d. This need not necessarily be so, as seen from eqn. (18 a), but it is surely a convenient approximation in the calculations, until the accuracy of measurements can be increased considerably.

The map would thus look as indicated in Fig. 4 III:2 and IV:2. In the calculation, it then proves convenient to introduce equal positive and negative loads $s(a)$ in the areas "M_{SL}" and "M_{SR}" indicated in Fig. 6a. We then have

$$M_S = M_{ST} - M_{SR} - M_{SL} \tag{23}$$

M_{SR} is the integral over the triangle above the reversible line, M_{SL} over the area below the lag curve and above $D = D_0$, and M_{ST} is the integral over the whole rectangle in Fig. 6a:

$$M_{ST} = (D - D_0) \int_{A_0}^{A} s(a)\mathrm{d}a; \tag{23a}$$

$$M_{SR} = \int_{A_0}^{D} (D-a)s(a)\mathrm{d}a \text{ if } D > A_0, \text{ else } M_{SR} = 0 \tag{23b}$$

$$M_{SL} = \int_{A_0}^{A} (D_L(a) - D_0)s(a)\mathrm{d}a \text{ if } D > D_L(A), \text{ else} \tag{23c}$$

$$M_{SL} = \int_{A_0}^{A_L(D)} (D_L(a) - D_0)s(a)\mathrm{d}a$$

As is seen, M_{SR} is a function of D only, and M_{SL} fulfils the conditions (8). They may hence, if one finds this more convenient, be treated as parts of

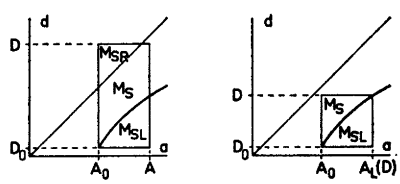

Fig. 6. Map $s(a,d)$ for a system with one lag curve, and with $s(a)$ independent of d above the curve. For convenience in calculations, one sets $M_S = M_{ST} - M_{SR} - M_{SL}$ where all the quantities are integrals of $\int s(a)\mathrm{d}a\mathrm{d}d$: M_{ST} over the whole rectangle indicated, and the others over the areas marked with these symbols.

M_R and M_L. We have thus, for convenience in calculations, added a fictitious surface load to the areas denoted by M_{SR} and M_{SL} and compensated it by equal negative terms in M_R and M_L. Figs. 6a and 6b show two successive states of desorption; the figure has here been drawn so that $A_0 > D_L(A)$, but this is surely no necessary requirement.

Recording of data. Exactly how the data should be recorded partly depends on the accuracy of the measurements. With measurements of a very high accuracy it might be possible to make a real contour map $s(a,d)$. Present accuracy only seems to allow us to divide the map into a number of regions, to each of which is assigned a constant value for s.

The contributions $M_R(D)$ and $M_L(A)$ can be recorded either as such, or by their derivatives $r(D)$ and $l_A(A)$.

The position of the lag curve has a special interest since it will be possible to say with a glance whether it is compatible with one "pore model" or another.

Of course, there is a chance that with the increasing accuracy it will be shown that our fundamental assumptions are not quite correct. This, however, need not concern us as yet.

Comparison with the treatment of Everett et al. A few years ago, D. H. Everett *et al.*[2-4] made a general mathematical approach to hysteresis phenomena including, for instance, magnetic and electric hysteresis. The most detailed mathematical analysis is made in the third paper by Everett.[4] He assumed the system to be built up of a number of domains, each of which can be in one of two states, I and II. The system is controlled by an external variable x (such as magnetic field strength or sorbate pressure) and for each domain there are two characteristic values $x(\mathrm{I} \rightarrow \mathrm{II})$ and $x(\mathrm{II} \rightarrow \mathrm{I})$ at which the transitions take place. The fact that the two values differ is the cause of the hysteresis. The distributions of these values among the domains are regulated by partition functions.

The function j used by Everett would in the case of sorption, be 1 for a filled site and 0 for an empty site. He denotes the adsorption curve by $p(x)$ (in our notation $M(A,A)$) and introduces a function g so defined that, if we replace Everett's x_u and x_l by A and D, we have the correspondence $g(D,A) = M(A,D) - M(D,D)$. He describes the properties of the system by giving a diagram of $\mathrm{d}p/\mathrm{d}x$ and $\partial g(x \text{ fixed}, x)/\partial x$ as functions of x; in our notation $\mathrm{d}M(A,A)/\mathrm{d}A$ and $\partial M(A,D)/\partial A$ as functions of A.

The "domain complexion", used by Everett, is a history of the system, corresponding, *e.g.*, to our Fig. 2c. Everett gives this in the form of a matrix. Those who are interested may easily derive other connections between our approach and Everett's.

Although the general philosophy of the approaches of Everett and ourselves are similar, we have a feeling that ours is somewhat handier, at least for the sorption case. Perhaps it is also somewhat more general. There should, by the way, be no difficulty extending our approach to other types of hysteresis.

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REFERENCES

1. Katz, S. *J. Phys. Chem.* **53** (1949) 1166.
2. Everett, D. H. and Whitton, W. I. *Trans. Faraday Soc.* **48** (1952) 749.
3. Everett, D. H. and Smith, F. W. *Trans. Faraday Soc.* **50** (1954) 187.
4. Everett, D. H. *Trans. Faraday Soc.* **50** (1954) 1077.
5. *The structure and properties of porous materials* (Eds. D. H. Everett and F. S. Stone), articles by J. H. de Boer, p. 68, D. H. Everett, p. 95, and following discussion. Butterworths, London 1958.
6. Sillén, L. G. *Acta Chem. Scand.* **15** (1962) 159. Applications, see, *e.g.*, Ingri, N. *Acta Chem. Scand.* **16** (1962) 439; Dunsmore, H. S., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **17** (1963) 2644.
7. Ekedahl, E. *Arkiv Kemi. To be published* (= Part II).

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