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Multilayer Adsorption on Heterogeneous Surfaces

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Although adsorption forces are usually short range in character, multilayer adsorption also concerns the energetic heterogeneity of the adsorbing surface. In this paper we assume that each energetically homogeneous patch forming the heterogeneous surface follows the Brunauer, Emmett, and Teller (BET) adsorption isotherm, while in the submonolayer range the whole surface follows the Dubinin and Radushkevich (DR) isotherm. By so assuming we are able to obtain the multilayer adsorption isotherm for the whole heterogeneous surface, and to compare BET and DR surface areas.

1. INTRODUCTION

When the temperature of a solid surface is lower than the critical temperature of the adsorbate, multilayer adsorption usually occurs. In this paper we shall consider the effects of the energetic heterogeneity of the adsorbing surface on the multilayer adsorption isotherm. The hypotheses of this work are essentially the following: (a) the adsorbing surface is energetically heterogeneous and is formed by a set of noninteracting, homotattic (i.e., energetically homogeneous) patches; (b) each homogeneous patch follows the Brunauer, Emmett, and Teller (BET) adsorption isotherm; and (c) at very low coverages, in the submonolayer range, the whole surface follows the Dubinin and Radushkevich (DR) adsorption isotherm.

In general, in order to find the multilayer overall adsorption isotherm we can operate as follows: (a) deriving the submonolayer local isotherm from the multilayer local isotherm (if the multilayer local isotherm is the BET isotherm, then the submonolayer local isotherm is the Langmuir isotherm);

(b) solving the integral equation (1) which gives the energy distribution function in the homotattic patch approximation; and (c) computing, by means of Eq. (12), the multilayer overall adsorption isotherm, since at this point we know the multilayer local isotherm (BET) and the energy distribution function.

2. HOMOTATTIC PATCH AND CONDENSATION APPROXIMATIONS

The *continuum* limit of the homotattic patch approximation[1] states that the overall isotherm $\vartheta(p)$ (i.e., the law that relates the average coverage ϑ of the whole surface to the pressure p) is connected to the local isotherm $\Theta(p, q)$ (i.e., the isotherm holding on the patch with binding energy q with adsorbate) through the equation*

$$\vartheta(p) = \int_0^{+\infty} \Theta(p, q)\varphi(q)\, dq \tag{1}$$

where $\varphi(q)\, dq$ is the fraction of surface with binding energy between q and $q + dq$. By definition, the energy distribution function $\varphi(q)$ is

$$\int_0^{+\infty} \varphi(q) dq = 1 \tag{2}$$

The problem in which we are firstly interested is the following: find the energy distribution function $\varphi(q)$ satisfying Eq. (1) when the local isotherm $\Theta(p, q)$ and the overall isotherm $\vartheta(p)$ are known functions. In particular, we shall focus our attention on the Langmuir isotherm for $\Theta(p, q)$ and on the DR isotherm for $\vartheta(p)$.

The Langmuir isotherm was firstly obtained[3] imposing the kinetic equilibrium between adsorption and desorption rates, supposing adsorption and desorption first order in kinetics. The statistical mechanical derivation of this isotherm can be obtained[4] assuming a perfect gas and an adsorbed phase formed by localized, noninteracting adatoms, bounded to their equivalent, distinguishable sites. The Langmuir isotherm has been chosen as the local isotherm for the following reasons: it is the submonolayer limit of the BET isotherm, and, in some cases, a well-defined activation energy for surface migration has been observed, such energy being much greater than the kinetic energy for two translational degrees of freedom along the surface at the usual adsorption temperatures (70–100 K). The experimental molar activation energy for surface diffusion of some noble gases on tungsten are

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*Sparnaay[2] considered the limit of Eq. (1) for scarcely heterogeneous surfaces and showed that, for a particular choice of the distribution function, the overall isotherm is similar to the DR isotherm.

the following[5]: Ar, 0.6 kcal/mole; Kr, >1.1 kcal/mole; Xe, 3.8 kcal/mole. At liquid-nitrogen temperature (77.3 K) the molar energy for two translational degrees of freedom RT is about 0.15 kcal/mole, so that the adsorbate can be thought as localized, and the Langmuir isotherm gives a picture better than that of the Hill and De Boer isotherm.[6]*

Furthermore, the previous results can be applied to practically all other bcc metals—such as, zirconium and molybdenum, for which DR plots have been obtained (see Table I)—using the numerical computations of Neustadter and Bacigalupi.[8] All these considerations suggest the choice of the Langmuir isotherm as the local isotherm:

$$\Theta(p, q) = p/[p + p_L \exp(-q/k_B T)] \tag{3}$$

where p_L is a characteristic pressure, k_B is the Boltzmann constant, and T is the absolute temperature.

In this case, Eq. (1) can be solved, using the Sips' method,[9] only if the overall isotherm satisfies some regularity requisites; since the DR isotherm does not have these properties[10] we shall use an approximate method. The simplest is the condensation approximation,[11] which consists of replacing the true kernel (3) by a "condensation isotherm," i.e., a step function which suddenly rises from 0 to 1 as soon as p exceeds a "condensation pressure," generally depending on the binding energy q.

If we define $Q(p)$ as the least energy for which, at pressure p, the condensation isotherm has unit coverage, Eq. (1) becomes

$$\int_{Q(p)}^{+\infty} \varphi_c(q)\, dq = \vartheta(p) \tag{4}$$

where $\varphi_c(q)$ is the approximate energy distribution function.

The value of the condensation pressure is conveniently chosen to minimize the distance between the Langmuir isotherm and the condensation isotherm[12] (see Appendix A). This determines $Q(p)$:

$$Q(p) = k_B T \ln(p_L/p) \tag{5}$$

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*Mahajan and Walker[7] showed that adsorption of xenon on heterogeneous carbon (obtained after partial oxidation of highly graphitized carbon blacks in a stream of dry air at 500°C) practically follows a Hill and De Boer isotherm whose critical temperature for two-dimensional condensation depends on the heterogeneity of the surface. That is, Mahajan and Walker showed that a heterogeneous surface whose homotattic patches follow the Hill and De Boer isotherm does not follow the DR isotherm.

TABLE I

Systems Following the DR Isotherm[a]

Gas	Surface	Authors	Reference
He	Pyrex glass	Hobson	16
Ar	Pyrex glass	Hobson and Armstrong	18
		Haul and Gottwald	21
		Ricca, Medana, and Bellardo	22
		Schram	24
	Pyrex and other glasses	Kindl, Negri, and Cerofolini	28
	zirconium	Hansen	17
	nickel	Schram	24
	silver	Hobson	26
Kr	Pyrex glass	Endow and Pasternak	20
		Haul and Gottwald	21
		Ricca, Medana, and Bellardo	22
	Pyrex and other glasses	Kindl, Negri and Cerofolini	28
	zirconium	Hansen	17
	molybdenum	Endow and Pasternak	20
		Ricca and Bellardo	23
	tungsten	Ricca and Bellardo	23
	silver	Hobson	26
	304 stainless steel	Troy and Wightman	29
Xe	Pyrex glass	Endow and Pasternak	20
		Haul and Gottwald	21
		Ricca, Medana, and Bellardo	22
	zirconium	Hansen	17
	molybdenum	Endow and Pasternak	20
		Ricca and Bellardo	23
	tungsten	Ricca and Bellardo	23
	silver	Hobson	26
N_2	Pyrex glass	Hobson and Armstrong	18
		Tuzi and Saito	25
	304 stainless steel	Troy and Wightman	27
CH_4	Pyrex glass	Ricca and Medana	19

[a] The adsorption temperatures usually range from 4.2 (He adsorption on Pyrex glass[16]) to 110 K (Ar adsorption on nickel[24]). Only those adsorbate–nonporous surface systems for which a DR plot has been explicitly obtained are reported in the table; probably the number of systems following the DR isotherm is much larger.

Expressing, by means of Eq. (5), p as a function of Q, and differentiating both members of Eq. (4) with respect to Q, we obtain

$$\varphi_c(Q) = -(d/dQ)\tilde{\vartheta}(Q) \qquad (6)$$

where $\tilde{\vartheta}(Q) = \vartheta[p(Q)]$.

The errors introduced with the condensation approximation have been considered in detail by Harris,[11] who showed that the approximate solution (6) becomes more effective as the absolute temperature tends to zero.

3. THE DR ISOTHERM AND THE MEANING OF ITS PARAMETERS

The DR isotherm, firstly proposed[13] and widely verified[14] for porous adsorbents, has been found to hold for many heterogeneous, nonporous surfaces in the submonolayer range (see Table I). According to the analysis of Marsh and Rand,[15] the DR isotherm is not related to the (presumed) fact that a log–log^2 plot linearizes almost all adsorption isotherms. This suggests that the DR behavior is due to a particular (equilibrium?) structure of the adsorbing surface.

We shall write the DR isotherm in the form

$$\vartheta(p) = \begin{cases} \exp\{-B[k_B T \ln(p/p_m)]^2\} & p \le p_m \\ 1 & p > p_m \end{cases} \tag{7}$$

where the parameters B and p_m are two characteristic constants whose microscopic meaning will be seen later. Following the suggestions of Hobson and Armstrong,[18] p_m is usually assumed to be the vapor pressure p_s of the adsorbate in the liquid phase,[16–21,23,27–29] although in some cases[22,28] the choice of p_m as the vapor pressure of the adsorbate in the solid phase has been found to be more convenient. Writing, by means of Eq. (5), the DR isotherm (7) in the form

$$\vartheta(Q) = \begin{cases} \exp[-B(Q - Q_m)^2] & Q \ge Q_m \\ 1 & Q < Q_m \end{cases} \tag{8}$$

where

$$Q_m = k_B T \ln(p_L/p_m) \tag{9}$$

assuming that the DR behavior is due to a Langmuir adsorption on each homogeneous patch forming the heterogeneous surface, and inserting Eq. (8) into Eq. (6), we obtain

$$\varphi_c(Q) = \begin{cases} 2B(Q - Q_m)\exp[-B(Q - Q_m)^2] & Q \ge Q_m \\ 0 & Q < Q_m \end{cases} \tag{10}$$

From this result we see that Q_m represents the least binding energy of the surface (see Fig. 1).

If we consider p_m as a parameter not known *a priori* (as it is usually considered), but whose value is determined by a best fit of experimental data plotted according to Eq. (7), the number of systems following the DR isotherm increases (surely it does not decrease); furthermore, from the knowledge of p_m [and Q_m, because of Eq. (9)] we have information concerning the structure of the surface, and the choice of p_m as a free parameter can justify the previously quoted, sometimes large discrepancies in the choice

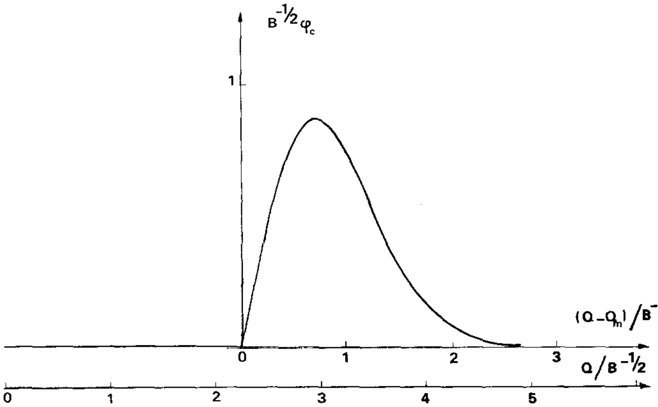

Fig. 1. The energy distribution function $\varphi_c(Q)$ [Eq. (10)] plotted vs. $Q - Q_m$. The figure clearly shows that Q_m represents the least adsorption energy of the surface.

of this quantity. Since Q_m represents the least adsorption energy, it is a characteristic of the surface–adsorbent pair and must be temperature independent; we can then determine both p_L and Q_m by carrying out DR measurements at various temperatures, and by making an Arrhenius plot of the equation

$$p_m = p_L \exp(-Q_m/k_B T)$$

i.e., plotting $\ln p_m$ (determined with best fits) vs. $1/k_B T$: the slope of the straight line gives $-Q_m$, while the intercept at $1/k_B T = 0$ gives $\ln p_L$.

The value of the parameter B gives information concerning the nature of the energy distribution function. More precisely,[12] $B^{-1/2}$ is approximately the spread of the distribution and is related to the average binding energy $\bar{q}$ by

$$\bar{q} = \int_0^{+\infty} q\varphi_c(q)\,dq = Q_m + \sqrt{\pi/4}B^{-1/2} \tag{11}$$

4. MULTILAYER ADSORPTION ON HETEROGENEOUS SURFACES

We consider here only surfaces whose temperatures are lower than the critical temperature of the gas; in this case multilayer adsorption usually occurs and the pressure can range only from 0 to p_s, at which the gas liquifies independently of the existence of the adsorbing surface. If the homotattic patch approximation holds in the multilayer range also, we can write

$$\vartheta_M(p) = \int_0^{+\infty} \Theta_M(p, q)\varphi(q)\, dq \tag{12}$$

where $\vartheta_M(p)$ is the multilayer overall isotherm, and $\Theta_M(p, q)$ is the multilayer local isotherm. If $\Theta_M(p, q)$ is theoretically known (e.g., the BET isotherm) we are able to find its submonolayer limit $\Theta(p, q)$ (e.g., the Langmuir isotherm); if, furthermore, the submonolayer overall isotherm $\vartheta(p)$ is experimentally known (e.g., the DR isotherm) we can solve Eq. (1) and obtain the energy distribution function $\varphi(q)$. This function, inserted into Eq. (12), reduces the problem of finding $\vartheta_M(p)$ simply to an integration.

Although quite general, the described method has the defect that eventual errors introduced in the computation of $\varphi(q)$ (when using approximate methods such as the condensation one) transfer into the computation of $\vartheta_M(p)$. There exist at least two simple cases for which the step requiring the solution of the integral equation (1) can be bypassed. The first is when the multilayer local isotherm has the form

$$\Theta_M(p, q) = f(p)\Theta(p, q) \tag{13}$$

where $f(p)$ is a function such that $p \to 0 \Rightarrow f(p) = O(1)$, and $p \to p_s \Rightarrow f(p) \to +\infty$; Eqs. (1) and (12) give

$$\vartheta_M(p) = f(p) \int_0^{+\infty} \Theta(p, q)\varphi(q)\, dq = f(p)\vartheta(p) \tag{14}$$

The second case is when

$$\Theta_M(p, q) = g(p) + \Theta(p, q)$$

where $g(p)$ is a function such that $p \to 0 \Rightarrow g(p) \to 0$, and $p \to p_s \Rightarrow g(p) \to +\infty$; Eqs. (1), (2), and (12) give

$$\vartheta_M(p) = g(p) \int_0^{+\infty} \varphi(q)\, dq + \int_0^{+\infty} \Theta(p, q)\varphi(q)\, dq = g(p) + \vartheta(p)$$

Now we can apply the previous considerations to the BET isotherm*:

$$\tilde{\Theta}_M(x, c) = cx/[(1 - x)(1 + cx - x)]$$

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*The BET isotherm, first obtained with kinetic arguments,[30] can be obtained, using statistical mechanics,[31] assuming that adsorption takes place on equivalent, distinguishable sites on each of which an indefinite number of molecules can be adsorbed in a vertical pile. The hypotheses of the equivalence of the second, third, fourth, ... layers and of the absence of lateral interactions lead to the BET equation. If only a definite number of layers can be adsorbed on account of the geometric (porous or zeolite type) structure of the adsorbing surface, then the local isotherm cannot be the considered BET; the isotherm in this case can be a BET of the fourth or fifth type when there is capillary condensation, or an isotherm of the type reported by Daunt and Rosen[32] when there is adsorption on zeolite.

where

$$x = p/p_s$$
$$c = (p_l/p_L)\exp[(q - q_s)/k_BT] \tag{15}$$

q_s is the sublimation heat of the adsorbate in the liquid phase, and p_l is the preexponential factor of the vapor pressure:

$$p_s = p_l \exp(-q_s/k_BT) \tag{16}$$

In fact, if the parameter c is much greater than 1, the BET equation can be written in the form[31]

$$\Theta_M(p, q) = [1/(1 - p/p_s)]\{p/[p + p_L \exp(-q/k_BT)]\} \tag{17}$$

so that Eq. (17) falls exactly into the case described by Eq. (13). Then Eq. (14) gives the solution we looked for:

$$\vartheta_M(p) = \frac{1}{1 - p/p_s}\begin{cases}\exp\{-B[k_BT\ln(p/p_m)]^2\} & p \le \min\{p_m, p_s\}\\ 1 & p > \min\{p_m, p_s\}\end{cases} \tag{18}$$

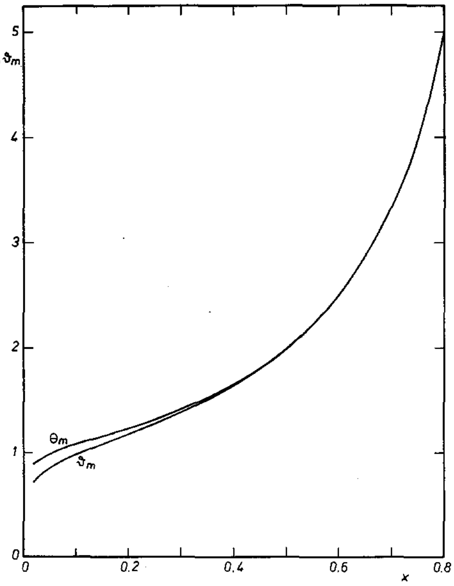

Fig. 2. The multilayer modified DR isotherm ($B^{-1/2}$ = 1 kcal/mole, $RT = 0.15$ kcal/mole, $p_m = p_s$) compared with the BET isotherm of a homogeneous surface having an adsorption energy equal to the average binding energy of the heterogeneous surface ($c = 368$). The plots show that the isotherms are practically coincident for x greater than 0.01.

From Eq. (18) we immediately see that

$$p \to 0 = \vartheta_M(p) \sim \vartheta(p)$$

as consistency reasons invoke [see hypothesis (c) in Section 1].

Although formally solved, the problem of finding the multilayer overall isotherm requires a further physical analysis: in fact, if the homotattic patch approximation is not too far from reality in the submonolayer range, it might be false in the multilayer range. However, if we admit the validity of the BET isotherm on each homotattic patch, then we are sure that lateral interactions are not important; and if lateral interactions can be neglected on each zone, *a fortiori* they can be disregarded between adjacent patches. This allows us to write Eq. (12). Equation (18) clearly shows that the heterogeneity modifies the adsorption isotherm in the whole range; however, as soon as $p/p_s \to 1$ the function (18) becomes asymptotic to $1/(1 - p/p_s)$; i.e., behaves *grosso modo* as the BET isotherm. We obtain in this way the intuitive result that the heterogeneous character of a solid surface is important at low coverages and is gradually lost when more layers are adsorbed. Figure 2 confirms this.

5. COMPARISON BETWEEN BET AND DR SURFACE AREAS

Historically, the DR isotherm was proposed by Dubinin and Radushkevich[13] in the form

$$\ln N = C - B[k_B T \ln (p/p_s)]^2 \tag{19}$$

where N is the number of adsorbed molecules, and C is a constant characteristic of the surface. Only later Kaganer,[33] comparing BET and DR measurements, proposed to identify (in some cases) C with $\ln N_s^{\mathrm{BET}}$, where N_s^{BET} is the BET number of sites of the surface. Successively, the value $N_s^{\mathrm{DR}} = \exp C$ has been defined, also for nonporous solids, the DR number of sites of the adsorbing surface, if the adsorption follows Eq. (19). In this section we try to theoretically compare BET and DR surface areas in order to justify the (in some cases) substantial identity of N_s^{BET} and N_s^{DR}.

In reality, if the surface is energetically heterogeneous, the multilayer overall isotherm cannot be a BET isotherm; a BET plot can be obtained only if few points are determined in the submonolayer range (see Figs. 2 and 3). If a BET plot can be done, the value of c is obtained by choosing it in a way to satisfy the least-square condition

$$\int_0^1 [\tilde{\vartheta}_M(x) - \tilde{\Theta}_M(x, c)]^2 \, dx = \min$$

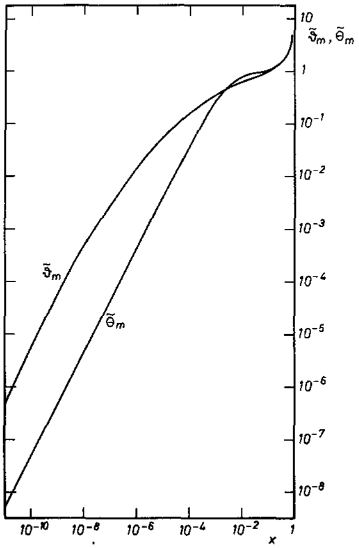

Fig. 3. Although practically coincident in the multilayer range, the BET and modified DR isotherms greatly differ in the submonolayer range. The parameters are the same as in Fig. 2. The transition from the DR to the Henry isotherm has not been shown; it should occur[12] at $x = 2.2 \times 10^{-10}$.

It is easily seen that this is a complicated implicit equation which can be numerically solved; this equation gives c as a function of $1/B(k_B T)^2$ only, i.e., of $B^{-1/2}/k_B T$, and not of B and T separately.

However, in analogy to Eq. (15) and supported by Fig. 2, we can suppose that the value of the constant c is given by

$$c = (p_l/p_L) \exp [(\bar{q} - q_s)/k_B T] \qquad (20)$$

where $\bar{q}$ is the average binding energy of the whole surface. If the condensation approximation holds true, the value of $\bar{q}$ is given by Eq. (11), so that Eq. (20) becomes

$$c = (p_l/p_L) \exp [(Q_m + \sqrt{\pi/4}B^{-1/2} - q_s)/k_B T] \qquad (21)$$

In this work we shall limit our attention to the case $p_m = p_s$. If we insert into Eq. (9) the value of p_s as given by Eq. (16) we obtain

$$Q_m = k_B T \ln (p_L/p_s) = k_B T \ln (p_L/p_l) + q_s$$

and this value, placed into Eq. (21), gives

$$c = \exp (\sqrt{\pi/4}B^{-1/2}/k_B T) \qquad (22)$$

This result satisfies the requirement that c is a function of $B^{-1/2}/k_B T$ only, and for typical* values of $B^{-1/2}$ (4.34 eV/molecule, whose corresponding

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*Some molar values of $B^{-1/2}$ for noble gases on Pyrex glass surfaces are the following: He, 0.158 kcal/mole (from Hobson[16]); Ar, 1.165 kcal/mole; Kr, 1.379 kcal/mole; Xe, 1.543 kcal/mole (from Ricca, Medana, and Bellardo[22]).

molar value is 1 kcal/mole) and T (from 75 to 100 K) we obtain from Eq. (22) that c lies between 370 and 84, in perfect accord with the requirement $c \gg 1$.

We now determine for what value of x the BET isotherm ($c \gg 1$),

$$\tilde{\Theta}_M(x, c) = cx/[(1 - x)(1 + cx)]$$

has unit coverage (BET area of the surface). This value $\bar{x}$ of x is given by the positive root of the following equation:

$$cx^2 + x - 1 = 0$$

i.e.,

$$\bar{x} = (-1 + \sqrt{1 + 4c})/2c \sim c^{-1/2}$$

when $c \to +\infty$ (and then $c \gg c^{1/2} \gg 1$). The last value, inserted into Eq. (18) ($p_m = p_s$), gives

$$\begin{aligned}
\vartheta_M(\bar{x}) &= [1/(1 - \bar{x})] \exp[-B(k_BT)^2 \ln^2 \bar{x}] \\
&= [1/(1 - c^{-1/2})] \exp[-B(k_BT)^2 \ln^2(c^{-1/2})] \\
&\sim \exp\{-B(k_BT)^2 \ln^2 [\exp(-\sqrt{\pi/4}B^{-1/2}/2k_BT)]\} \\
&= \exp\{-B(k_BT)^2[\pi/16B(k_BT)^2]\} \\
&= \exp(-\pi/16) \simeq 0.82 \qquad (23)
\end{aligned}$$

The result (23) shows that the BET area ($\Theta_M = 1$) corresponds to a coverage only slightly different from the DR coverage ($\vartheta_M = 0.82$).

6. CONCLUSIONS

The results obtained in this work are the following.

(1) A model for the DR isotherm, based on the concept of surface heterogeneity, has been developed, and the meaning of empirical parameters contained in that equation clarified.

(2) The effects of surface heterogeneity on the multilayer coverage have been evaluated, and a simple overall isotherm—reducing to the DR isotherm in the submonolayer range and similar to the BET in the multilayer range—proposed.

(3) This isotherm allows the comparison of BET and DR areas, which (in the case $p_m = p_s$) are practically coincident, justifying the empirical observation of Kaganer.

APPENDIX A

The Choice of the Condensation Pressure

The condensation pressure is the following function:

$$\Theta_c(p,q) = \begin{cases} 0 & p \le p_c \\ 1 & p > p_c \end{cases}$$

where p_c is the condensation pressure depending, in a general way, on q.

The strategy of choosing the condensation pressure may be the following: (a) we define a distance between $\Theta(p,q)$ and $\Theta_c(p,q)$, a distance which generally depends on q and parametrically on p_c; (b) we choose p_c in such a way that this distance is a minimum; and (c) the function $p_c(q)$ so obtained must not depend too strongly on the choice of the distance.

The simplest definition of distance is the Lagrangian:

$$d[\Theta,\Theta_c] = \sup_{p\in(0,+\infty)} |\Theta(p,q) - \Theta_c(p,q)| \qquad \text{(A1)}$$

If $\Theta(p,q)$ is an arbitrary continuous local isotherm, then the condition on the distance (A1) to be a minimum becomes

$$\Theta(p_c,q) = \tfrac{1}{2} \qquad \text{(A2)}$$

This implicit equation, when solved, gives p_c as a function of q. The same function is obtained if we choose p_c in a way such that $\Theta_c(p,q)$ gives a least-square best fit to $\Theta(p,q)$; in fact, using the $L^2(0,+\infty)$ distance, we have

$$\begin{aligned} 0 &= (\partial/\partial p_c)\int_0^{+\infty} [\Theta(p,q) - \Theta_c(p,q)]^2\,dp \\ &= (\partial/\partial p_c)\left\{\int_0^{p_c} \Theta(p,q)^2\,dp + \int_{p_c}^{+\infty} [1-\Theta(p,q)]^2\,dp\right\} \\ &= \Theta(p_c,q)^2 - [1-\Theta(p_c,q)]^2 \end{aligned}$$

from which we derive exactly the implicit equation (A2). When applied to the Langmuir isotherm, Eq. (A2) leads exactly to Eq. (5).

APPENDIX B

An Isotherm from the Henry Range to the Multilayer Range

It is claimed[34] that the DR isotherm must reduce to the Henry isotherm in the very-low-pressure limit. According to this conjecture, we self-consistently proposed[12] an overall submonolayer isotherm which, using the symbols of the present work, becomes

$$\vartheta(p) = \begin{cases} kp & p \leq p_H \\ \exp\{-B[k_B T \ln(p/p_m)]^2\} & p_H < p \leq p_m \\ 1 & p_m < p \end{cases} \tag{B1}$$

where

$$p_H = p_m \exp[-1/2B(k_B T)^2]$$
$$k = (1/p_m)\exp[1/4B(k_B T)^2]$$

Inserting Eq. (B1) into Eq. (14) we obtain

$$\vartheta_M(p) = [1/(1 - p/p_s)]\begin{cases} kp & p \leq p_H \\ \exp\{-B[k_B T \ln(p/p_m)]^2\} & p_H < p \leq \min\{p_m, p_s\} \\ 1 & \min\{p_m, p_s\} < p \leq p_s \end{cases} \tag{B2}$$

Equation (B2) seems to us to be the first theoretically derived adsorption isotherm holding from the Henry range to the BET. We wish to remark that this equation is built on a simple theoretical model, and does not consider (as Hobson[26] did for his isotherm) any empirical isotherm in any range, the exception being the DR isotherm in the DR range. It shall then be interesting to determine if the DR isotherm is related to an equilibrium distribution of faces emerging on the surface, in order to explain also the large number of systems following the Dubinin and Radushkevich isotherm.

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