

## BET ADSORPTION ISOTHERM AND SURFACE HETEROGENEITY

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The BET adsorption isotherm is modified in order to take account of surface heterogeneity. The adsorption isotherm is obtained following the statistical mechanics formalism, proposed by Steele, and the effect of surface heterogeneity is limited to the first layer. A Gaussian adsorption energies distribution function is used to describe surface heterogeneity. The variations of the  $C$  parameter, multilayer formation and the inversion of adsorption isotherms are analysed.

The BET model for multilayer adsorption is a generalization of Langmuir's model. The basic assumptions are: surface homogeneity and neglect of lateral interactions, furthermore, the structure of all layers, except the first, is considered identical and pure liquid like. This model, even though strongly criticized is currently used to determine the specific surface area of solids. There are several published papers<sup>1,2</sup> presenting experimental results that demonstrate the variations of the BET  $C$  parameter. Those results enabled the determination of the maximum surface coverage degree for the first layer and the relative pressure corresponding to the statistical monolayer completion. The degree of surface homogeneity can also be inferred from  $\ln C$  vs relative pressure profiles. It is also possible to estimate the degree of surface homogeneity and the point where multilayer formation begins from the relation between the excess adsorption energy and the energy of a molecule in the first layer. In an effort to reproduce these experimental results surface heterogeneity is introduced in the BET model following the formalism stated by Steele<sup>3</sup>.

The heterogeneity introduced in this way alters the shape of the isotherms, the monolayer completion and the parameter  $C$ . Another feature of the modified model is that it can account for experimentally observed inversions of adsorption isotherms obtained at neighbouring temperatures.

## THEORETICAL

If it is assumed that there are  $\beta$  surface sites, the macrocanonical partition function can be written in the following way:

$$\Xi^{(s)} = \xi^\beta, \quad (1)$$

where

$$\xi = 1 + q_1 e^{\mu/kT} + q_1 q_2 e^{2\mu/kT} + \dots = 1 + \sum_{N>0}^{\infty} e^{N\mu/kT} \prod_{j=1}^N q_j, \quad (2)$$

where  $N$  is the number of adsorbed molecules,  $\mu$  is the chemical potential and  $q_j$  are the molecular partition functions for molecules in the  $j$ -th adsorbed layer. If all adsorbed layers, except the first, have the same structure it is possible to write:

$$q_j = q_{\text{liq}} \quad \forall j > 1. \quad (3)$$

Defining

$$C = \frac{q_1}{q_{\text{liq}}} \quad (4)$$

and, from Eqs (2), (3) and (4),

$$\xi = 1 + \sum_{N \geq 1}^{\infty} C [q_{\text{liq}} e^{\mu/kT}]^N = \frac{1 + C q_{\text{liq}} e^{\mu/kT}}{1 - q_{\text{liq}} e^{\mu/kT}}. \quad (5)$$

We define now:

$$\frac{p}{p_0} = x = e^{[(\mu - \mu^{(1)})/kT]}, \quad (6)$$

where  $p$  is the equilibrium pressure and  $p_0$  is the saturation pressure at temperature  $T$ . Using Eq. (6), (5) can be modified to (7)

$$\xi = 1 + \frac{Cx}{1 - x}, \quad (7)$$

The adsorption isotherm is obtained from Eqs (7) and (1) with the aid of the following relations:

$$N^{(s)} = kT \left( \frac{\partial \ln \Xi^{(s)}}{\partial \mu} \right)_{T,V} = \left( \frac{\partial \ln \Xi^{(s)}}{\partial \ln x} \right)_{T,V} \quad (8)$$

and

$$\Theta = \frac{N^{(s)}}{\beta}, \quad (9)$$

where  $\Theta$  is the surface coverage. The resulting adsorption isotherm is the original BET isotherm. To introduce the surface heterogeneity we assume that not all surface sites have the same adsorption potential and that this potential is distributed according to certain distribution function,  $f(M)$ . Now the expression for the macro-canonical partition function is the following:

$$\Xi^{(h)} = \prod [\xi(M)]^{\beta f(M)}, \quad (10)$$

where  $\beta f(M)$  is the number of type  $M$  sites. Following the same procedure as in the homogeneous case, the isotherm obtained is:

$$\Theta = \sum f(M) x \left( \frac{\partial \ln \xi(M)}{\partial x} \right)_T = \sum f(M) \theta(M), \quad (11)$$

where  $\Theta$  is the total surface coverage and  $\theta(M)$  is the coverage on the  $M$  type site. If we assume a continuous distribution it is possible to replace the summation by an integral, so:

$$\Theta = \int_{-\infty}^{+\infty} f(U) \theta(U) dU, \quad (12)$$

where  $U$  is the adsorption potential and:

$$\theta(U) = x \left( \frac{\partial \ln \xi(U)}{\partial x} \right)_T. \quad (13)$$

Since the parameter  $C$  reflects gas-solid interactions, it must take different values depending on which site is occupied, and a distribution of  $C$  values must be generated by surface heterogeneity. To take this into account, Eq. (7) must be modified to:

$$\xi(U) = 1 + \frac{C(U) x}{1 - x} \quad (14)$$

and

$$\theta(U) = \frac{x(C(U) - 1)}{1 + x(C(U) - 1)} + \frac{x}{1 - x}, \quad (15)$$

where  $C(U)$  is given by:

$$C(U) = e^{[(U - E_1)/RT]} \quad (16)$$

and  $E_1$  is the energy of a molecule in the first adsorbed layer. The total surface coverage can be obtained from Eqs (15), (16) replaced in Eq. (12). The integral is numerically evaluated. The  $-\infty$  and  $+\infty$  integration limits can be restricted. It is interesting to note that the first term on the right side of Eq. (15) is the Langmuir isotherm deduced for a heterogeneous surface<sup>3</sup> and the second term can be considered as a multilayer correction factor. The heterogeneity introduced in this way modifies the first adsorbed layer only, the remaining postulates of the original BET model are retained.

Several distribution functions were employed, i.e. Gauss, Weibull and a double Gaussian. Their mathematical expression are the following:

$$f(U) = a_0 \exp [-0.5 \{(U - U_0)/\gamma RT\}^2] \quad (\text{Gauss}) \quad (17)$$

$$f(U) = \left(\frac{c}{a}\right) \left[\frac{(U - a)}{b}\right]^{c-1} \exp\left[-\left\{\frac{(U - a)}{b}\right\}^c\right] \quad (\text{Weibull}) \quad (18)$$

$$f(U) = a_0(g_1 + g_2) \quad (\text{double Gaussian}), \quad (19)$$

where  $g_1$  and  $g_2$  are Gaussian functions characterized by  $a_1$ ,  $U_{01}$ ,  $\gamma_1$ ,  $a_2$ ,  $U_{02}$  and  $\gamma_2$ . The Weibull's distribution is a generalized form of the exponential distribution with three parameters instead of one, with the following restrictions:  $a \leq U$ ,  $b > 0$  and  $c > 0$ .

The distribution functions were normalized and the integrations were made by applying Simpson's rule in such a way that 99% of the total area was included within the integration interval.

If the isosteric enthalpy is computed from the BET model by differentiating the isotherm it is easily shown<sup>1</sup> that:

$$\frac{(Q_{st} - \Delta H_v)}{(E_1 - L)} = \frac{(1 - x)^2}{[1 + x^2(C - 1)]}, \quad (20)$$

where  $Q_{st}$  is the isosteric heat,  $\Delta H_v$  is the vaporization enthalpy,  $E_1$  is the energy of a molecule in the first layer and  $L$  is the energy of a molecule in the liquid state. Plots of the ratio  $(Q_{st} - \Delta H_v)/(E_1 - L)$  indicate that the excess heat of adsorption  $(Q_{st} - \Delta H_v)$  is equal to  $(E_1 - L)$  up to the point where filling in of the second layer begins. The location of this point depends on the value of the parameter  $C$  since it is a measure of the adsorbent-adsorbate interaction energy. As could be expected, our model predicts that the relation given by Eq. (20) can be altered by the selection of adsorption energy distribution function.

## RESULTS AND DISCUSSION

The adsorption isotherms at 77.5 K calculated with three distribution functions are shown in Fig. 1. In all cases the adsorption potentials were limited to the range 0

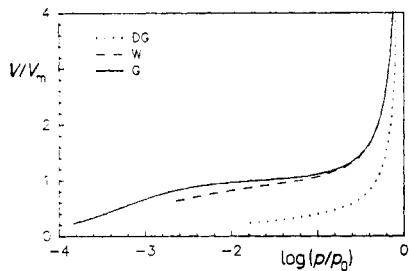


FIG. 1

Adsorption isotherms at 77.5 K with different distribution functions. The parameters employed for each function are the following: Gauss:  $U = 10.45 \text{ kJ/mol}$ ,  $\gamma = 0.1$  and  $\Delta H_v = 5.56 \text{ kJ/mol}$ ; Weibull:  $a = 0.01$ ,  $b = 2.5$  and  $c = 10$ ; double Gaussian:  $a_1 = 2$ ,  $U_{01} = 4.18 \text{ kJ/mol}$ ,  $\gamma_1 = 1$ ,  $a_2 = 4$ ,  $U_{02} = 6.27 \text{ kJ/mol}$  and  $\gamma_2 = 1$ .

to 20.9 kJ/mole and the specific surface area was kept constant for all isotherms. As would be expected the main differences between those isotherms appear in the monolayer region. The following discussion shall be restricted to the case of the Gaussian distribution function (Eq. (17)). This function was selected because its parameters are easily related to surface homogeneity ( $\gamma$ ) and vertical interactions ( $U_0$ ). In what follows we shall discuss the influence each variable (temperature, heterogeneity, adsorption potential and lateral interactions) has on the adsorption isotherm.

In Fig. 2 the adsorption isotherms calculated for different temperatures are shown. It can be seen that monolayer completion is achieved at higher relative pressures as temperature increases.

The parameter  $\gamma$  measures the heterogeneity because it is related to the width of the distribution function. In Fig. 3 the effect of  $\gamma$  on the adsorption isotherm is shown. In the multilayer region all isotherms are coincident because all layers, except the first, are considered identical.

The other parameter of the distribution function,  $U_0$ , defines the depth of the most probable surface potential well. This parameter is directly related to the strength of gas-solid interactions. In Fig. 4 the isotherms calculated for several values of  $U_0$  and  $\gamma = 0.1$  are displayed. The shape of the isotherm, for a given surface, is quite dependent on  $U_0$ , particularly in the low pressure region. This dependency is actually determined by the parameter  $C$ , since it depends on the implicit relation that exists between  $U_0$  and the energy of the adsorbate in the first layer (see Eq. (16)). The isotherms shown in Fig. 4 were calculated for different  $U_0$  and the same  $\gamma$ . They are in agreement with the fact that low  $C$  values (low  $U_0$ ) correspond to weak gas-solid interactions and in consequence the multilayer formation starts at higher relative pressures.

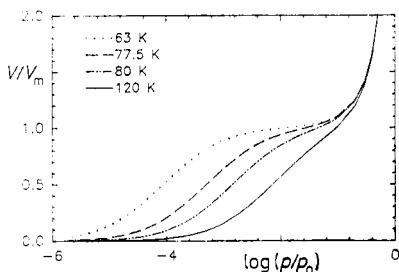


FIG. 2

Calculated adsorption isotherms with a gaussian distribution function where  $U_0 = 10.45$  kJ/mol and  $\gamma = 1$

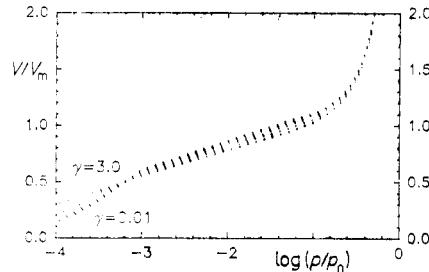


FIG. 3

Effect of surface heterogeneity on adsorption isotherms with  $U_0 = 10.46$  kJ/mol and  $T = 80.2$  K.  $\gamma = 0.01, 0.05, 0.1, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5$  and  $3.0$

Another experimental fact reproduced by our model is the adsorption isotherm crossing or inversion that has been discussed by different authors<sup>4</sup>. This anomalous behavior appears when two or more adsorption isotherms, obtained in a narrow range of temperature, are plotted using relative pressure as  $x$ -axis. Several crossing points have been detected for experimental isotherms generally obtained over very homogeneous surfaces. There are at least two cases<sup>5</sup> where this isotherm crossing coexists with a two-dimensional phase transition at relative pressures of 0.09 for graphite and 0.05 for boron nitride, but the relationship between them remains unexplained.

The adsorption isotherms calculated at different temperatures are plotted in Fig. 5. These isotherms are inverted from low relative pressures up to 0.9. Our analysis shows that the inversion depends on the values given to  $U_0$  and  $\Delta H_v$ . It could be

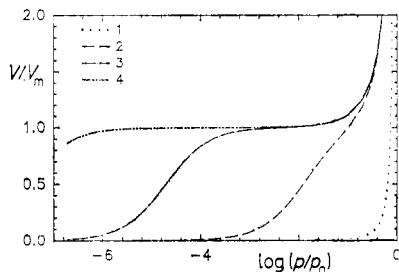


FIG. 4  
Adsorption isotherms calculated for different  $U_0$  values; 4: 16.73 kJ/mol; 3: 12.55 kJ/mol; 2: 8.37 kJ/mol and 1: 4.18 kJ/mol

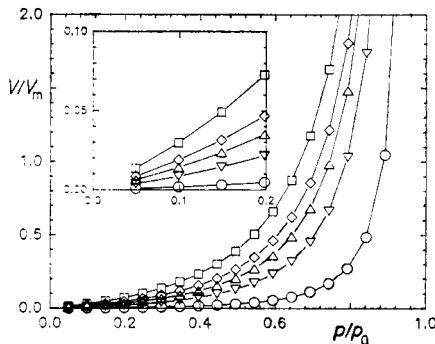


FIG. 5  
Crossing of adsorption isotherms calculated for different temperatures;  $\circ$  63,  $\nabla$  77,  $\Delta$  80,  $\diamond$  90 and  $\square$  120 K

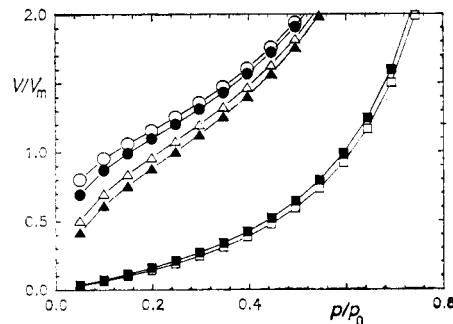


FIG. 6  
Calculated adsorption isotherms over the same surface for  $N_2$  ( $\circ$ ),  $Ar$  ( $\Delta$ ) and  $Kr$  ( $\square$ ) at  $T = 77.5$  (open symbols) and 90 K (filled symbols)

assumed that  $U_0$  is a measure of vertical interactions and  $\Delta H_v$  is a quantity proportional to the lateral ones. The last assumption is valid for the upper adsorbed layers where the adsorbate structure is probably liquid-like. In the case of the first layer a different physical meaning should be assigned to  $\Delta H_v$ , i.e. as lateral interaction energy parameter. When lateral interactions are greater than the vertical ones,

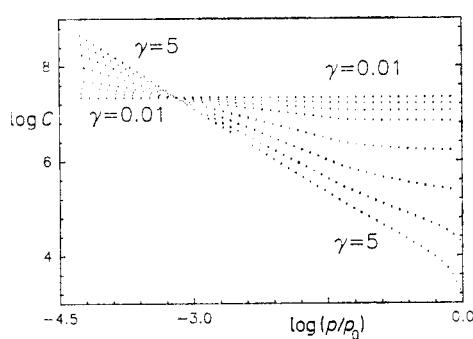


FIG. 7

BET  $C$  parameter calculated as in ref.<sup>1</sup>,  $U_0 = 10.46$  kJ/mol,  $T = 80.2$  K and  $\gamma = 0.01, 0.05, 0.1, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5$  and  $3.0$

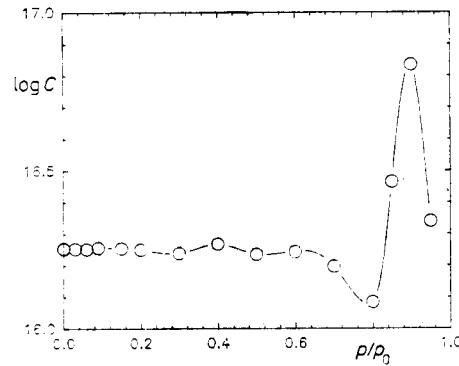


FIG. 8

Profile of  $C$  parameter, high pressure region, calculated for  $T = 80.2$  K,  $\gamma = 1$  and  $U_0 = 16.73$  kJ/mol

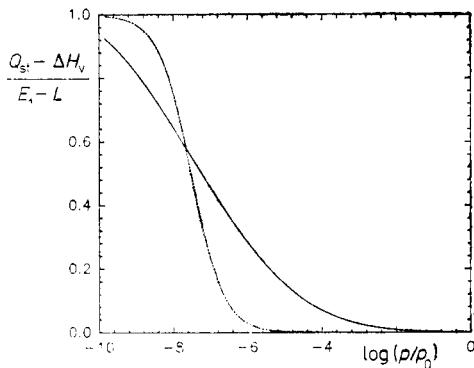


FIG. 9

Equation (20) calculated for  $T = 77.5$  K,  $U_0 = 16.73$  kJ/mol and  $\gamma = 0.1$  and  $5.0$

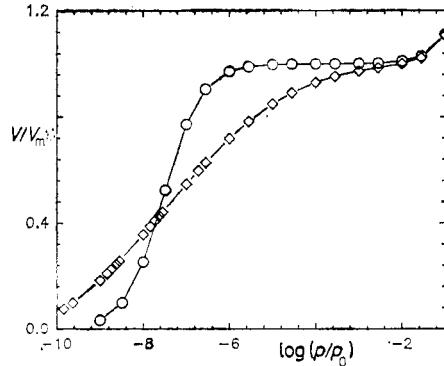


FIG. 10

Adsorption isotherms calculated for  $T = 77.5$  K,  $U_0 = 16.73$  kJ/mol and  $\gamma = 0.1$  (◊) and  $5.0$  (○)

$U_0 < \Delta H_v$ , the isotherms are inverted. The adsorption isotherms at 77.5 K and 90 K for N<sub>2</sub>, Ar and Kr over the same surface are shown in Fig. 6; it can be seen that only Kr isotherms are inverted ( $U_0 < \Delta H_v$ ).

Previous studies dealing with isotherm crossing<sup>5</sup> suggested that this anomalous behavior was only possible for very homogeneous surfaces and it was proposed as a surface homogeneity criterion. In order to test this hypothesis several isotherms were calculated using  $U_0 < \Delta H_v$  and  $\gamma$  running from 0.01 (very homogeneous surface) to 5. Our results show that the inversion persists for all  $\gamma$  values. We also calculated the isotherms with  $U_0 > \Delta H_v$  (no inversion condition) for the same  $\gamma$  range. As expected, the isotherms did not show the inversion. It can be concluded that, according to our model, the inversion phenomenon does not depend on surface heterogeneity but on the ratio between lateral and vertical interactions.

At the beginning of this paper we noted that the adsorption energy distribution must generate a distribution of  $C$  values. Following the method described elsewhere<sup>1</sup> we calculated for each point of the isotherm the corresponding values of  $C$ . In Figs 7 and 8,  $\ln C$  versus relative pressures is plotted to show how these curves are altered by the surface heterogeneity. For homogeneous surfaces the  $C$  parameter remains constant for all pressures. This is due to the fact that our model agrees with the original BET model for low values of  $\gamma$ . When the heterogeneity increases ( $\gamma > 0.1$ ),  $C$  values are increasingly altered. The  $C$  parameter is a measure, as in the original model, of vertical interactions so low values of  $U_0$  produce low values of  $C$ .

The relative pressure at which multilayer adsorption begins must depend on the surface degree of heterogeneity. This point is easily detected by plotting the relation given by Eq. (20) as a function of the relative pressure. An example of this is presented in Fig. 9 where several values of  $\gamma$  were employed. For  $\gamma = 5$ , the most heterogeneous surface, it can be observed that multilayer formation begins at lower relative pressures than in the other cases. The corresponding isotherms are plotted in Fig. 10. It must be pointed out that isotherms of type II (BDDT classification) are obtained for quite heterogeneous surfaces.

## CONCLUSIONS

The proposed model introduces surface heterogeneity in the BET model. Even though heterogeneity considerations in our model produces only first layer modifications, these are sufficient to explain several experimental facts like the non constancy of the parameter  $C$  and the inversion of the adsorption isotherms determined at neighbouring temperatures. The model predicts that the isotherm inversion occurs when lateral interactions are greater than the vertical ones. It is also shown that the inversion is independent of surface heterogeneity.

## SYMBOLS

$a_0$	normalizer factor
$a, b, c$	Weibull's function parameters
$C$	BET equation parameter
$E_1$	energy of a molecule in the first adsorbed layer
$f(M)$	distribution function of surface sites
$\Delta H_v$	adsorbate vaporization enthalpy
$k$	Boltzmann constant
$L$	adsorbate liquefaction heat
$M$	generic surface site
$N$	number of adsorbed molecules
$p$	adsorbate equilibrium pressure
$p_0$	adsorbate saturation pressure
$q_j$	partition function for a molecule in the $j$ -th adsorbed layer
$q_{\text{liq}}$	partition function for a molecule in the liquid phase
$Q_{\text{st}}$	isosteric heat of adsorption
$T$	absolute temperature
$U$	adsorption potential
$U_0$	most probable adsorption potential for the Gauss distribution
$V$	system volume
$x$	adsorbate relative equilibrium pressure
$\beta$	number of surface sites
$\gamma$	heterogeneity parameter for the Gauss distribution function
$\theta(M)$	surface coverage on the $M$ type site
$\Theta$	surface coverage degree
$\mu$	chemical potential for adsorbed molecules
$\mu^{(1)}$	chemical potential for molecules in the liquid phase
$\xi$	grand partition function for molecules in one stack
$\Xi$	macrocanonical partition function

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