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The Temperature Dependence of Isosteric Heat of Adsorption on the Heterogeneous Surface

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The determination of the isosteric heat of adsorption, q_{st}, from a series of adsorption isotherms can provide information on the energetics of the gas-solid interface as well as the distribution of energetic sites on the solid surface. In practice, q_{st} is often assumed to be independent of temperature within a short temperature range. This is generally verified by the linearity of the Clausius-Clapeyron plot. However, there are a few instances in which a considerable temperature coefficient of q_{st} has been observed. The present work indicates that, under certain conditions, this could be due to the surface heterogeneity, the curvature of the Clausius-Clapeyron plot occurring at the transition from one type of site to the other. The adsorption of nitrogen on highly dehydrated silica-alumina provides an example of this possibility. A model of the adsorption equation considering two types of surface sites and describing satisfactorily both the adsorption isotherms and the temperature dependence of the isosteric heat of adsorption is presented.

INTRODUCTION

The study of gas adsorption on the solid surface has the objective to understand the adsorbate-adsorbent interaction and the energetic site distribution on the solid surface. The measurement of a series of adsorption isotherms and to derive from them the heat of adsorption is one way to obtain this information. Particularly, the isosteric heat of adsorption, q_{st}, has the expression

$$q_{st} = -R\left(\frac{\partial \ln p}{\partial(1/T)}\right)_{\theta}, \qquad (1)$$

where p and T are, respectively, the equilibrium pressure and temperature of the adsorption system, θ is the surface coverage and R is the universal gas constant. That is, the isosteric heat of adsorption is determined from the slope of the Clausius-Clapeyron plot (log p vs $1/T$) at a constant surface coverage.

For practical application, it is almost always assumed that q_{st} is independent of temperature over a short temperature range so that Eq. (1) becomes

$$\ln\frac{p_2}{p_1} = -\frac{q_{st}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{(at constant } \theta\text{)} \qquad (2)$$

The assumption is reasonable and has been justified by the linearity of the Clausius-Clapeyron plot from extensive experimental results. In fact, if the data points are scattered and deviate from linearity, it is usually considered as due to the experimental error. Up to the present, there has been little experimental information available which covers a sufficiently wide temperature range to further justify the above assumption. This is often due to the limitation of ordinary experimental measurements in which the span of temperature has mostly been less than 200°C.

Strictly speaking, the isosteric heat of adsorption is dependent upon temperature as indicated in the following equation

$$\frac{dq_{st}}{dT} = -\Delta\bar{C}_p = (C_g - \bar{C}_a)_p, \qquad (3$$

where C_g is the molar heat capacity of the gaseous molecules and $\bar{C}_a$ is the partial molar heat capacity of the adsorbate. Hence, the temperature coefficient of q_{st} is not zero so long as the heat capacity of the adsorbed state is different from that of the gas phase.

As a first attempt, the heat capacity may be estimated by means of statistical mechanics. This is easy for a gaseous molecule but more difficult for the adsorbate because of the lack of information on the adsorbed state. Nevertheless, the latter can be estimated by assuming a simple classical model for the adsorbed state. We further assume that the differential molar heat capacity is approximately equal to the integral molar quantity, since the latter is referred to by the calculation of statistical mechanics (*1*).

Consider two extreme cases of the adsorbed state of a molecule: the localized model and the two-dimensional gas model. For a monatomic gas, the adsorbed state has three vibrational degrees of freedom on localized adsorption, but has only one vibrational degree of freedom and two translational degrees of freedom if it behaves like a two-dimensional gas on the surface. A diatomic gas molecule has six degrees of freedom: three translational, two rotational and one internal vibrational. At the usual temperatures of adsorption measurements, the internal vibration for most gases is not excited, so that we only have to consider five degrees of freedom. On extremely localized adsorption, the three translational and two rotational degrees of freedom would be transformed into five vibrational modes with the surface. The internal vibration will not likely be perturbed in the case of physical adsorption. At the other extreme, a two-dimensional gas model will have one vibrational, two translational and two rotational degrees of freedom. A polyatomic gas can be considered in a similar way, but will not be discussed here. The heat capacities of monatomic and diatomic molecules in the two extremes of adsorbed states and in the gas phase are listed in Table 1. The difference in heat capacities between the gas phase and the adsorbed state is then an indication of the temperature coefficient of the heat of adsorption. For localized adsorption, the change in heat for a temperature range of 100°C would be about —0.1 and —0.3 kcal/mole for monatomic and for diatomic gas molecules, respectively. In other words, the heats of adsorption determined at lower temperatures would be higher in the case of localized adsorption. The variation with temperature would hardly be noticeable if all of adsorption isotherms measured are within a narrower temperature range. In reality, the adsorbed states are intermediate between the two extreme cases. Consequently, the temperature dependence of the heat of adsorption is less likely to be observed by ordinary measurement of adsorption isotherms.

The task is easier by means of the calorimetric method. In fact, much work has

TABLE 1
HEAT CAPACITIES OF ADSORBATES (CAL/MOLE °K)

	$(C_g)_p$	C_a	$(C_g - C_a)_p$
I. Calculated from statistical mechanics			
Monatomic			
Localized (3v)	$(5/2)R^a$	$3R$	$-(1/2)R$
Mobile (2t, 1v)	$(5/2)R$	$2R$	$(1/2)R$
Diatomic			
Localized (5v)	$(7/2)R$	$5R$	$-(3/2)R$
Mobile (2t, 2r, 1v)	$(7/2)R$	$3R$	$(1/2)R$
II. Experimental data			
Ar on rutile, $\Theta = 0.13$ (Ref. 3)	5	11	−6
N_2 on rutile, $\Theta = 0.1$ (Ref. 4)	7	17	−10

[a] $R = 1.987$ cal/mole °K.

been done in the measurement of heats of adsorption and heat capacities of adsorbates (*2*). Morrison and his coworkers (*3*, *4*) have shown that the heat capacity of the adsorbate obtained from direct measurement and from the temperature coefficient of the heat of adsorption is in good agreement. The heat capacities of adsorbed argon and nitrogen on rutile in the higher temperature region of about 120°K are indicated in Table 1 for comparison with values estimated by the model. Obviously, the discrepancy is quite large and experimental values are rather high. A satisfactory interpretation of high heat capacities of adsorbates has yet to be reached.

The variation of the isosteric heat of adsorption with temperature, obtained by means of the measurement of adsorption isotherms, has been reported by Barrer and Stuart (*5*) on the adsorption of nitrogen on Li–, Na–, and K–X zeolites. The temperature coefficients over the range 173–273°K were found to be about 15, 15 and 7 cal/mole deg, respectively, for the three different cation-exchanged samples. The value for K–X, which was found to be homogeneous with respect to nitrogen adsorption, is close to that observed on rutile by means of calorimetric measurement (*4*). However, the values for Li– and Na–X are much greater. Recently, Huang and Emmett (*6*) have also indicated a non-linearity of the Clausius–Clapeyron plot for the adsorption of nitrogen at surface coverages near 0.1% on amorphous silica-alumina evacuated at 800°C. The variation of q_{st} with temperature is shown on Fig. 1 together with the work of Barrer and Stuart. The temperature coefficient of q_{st} in the case of amorphous silica-alumina was found to be about 30 cal/mole deg, a value much too large to be accounted for by the previous discussion.

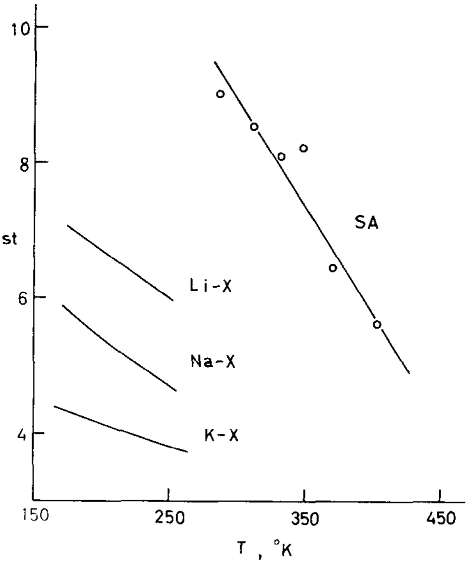

FIG. 1. Dependence of isosteric heat, q_{st}, on the temperature of adsorption. N_2 on silica-alumina (SA) ($\Theta = 0.0013$): Huang and Emmett (*6*); N_2 on Li–, Na–, and K–X ($\Theta \cong 0.1$): Barrer and Stuart (*5*).

A different approach which considers the effect of surface heterogeneity will be attempted.

Heterogeneous Surface

On a homogeneous surface, the localized monolayer adsorption can often be described by the Langmuir isotherm:

$$\Theta = \frac{v}{v_m} = \frac{bp}{1 + bp}, \tag{4}$$

where v is the amount adsorbed, v_m is the amount corresponding to monolayer adsorption, and b is a constant which can be expressed as

$$b = b_0 e^{q/RT}, \tag{5}$$

where q is the heat of adsorption and b_0 is a term related to the entropy of adsorption. At low coverages, $bp \ll 1$ so that

$$\Theta = bp. \tag{6}$$

This is known as Henry's Law.

On a heterogeneous surface where there are several types of energetic sites, the adsorption may be formulated as the sum of contributions from all types of sites

$$v = \sum \frac{v_{mi} b_i p}{1 + b_i p} \tag{7}$$

or by the integral form

$$v = \int_0^\infty \frac{v_m(b)bp}{1 + bp}\, db, \tag{8}$$

where $v_m(b)$ is the distribution function of energetic sites. Attempts to solve Eq. (8) with models of the distribution function or to obtain the distribution function from experimentally determined isotherms are abundant in the literature (*7*). However, the effort in this area is fraught with uncertainties and is often encountered with limited applicability because of the complexity of real surfaces.

To characterize a heterogeneous surface, a proper adsorption equation must contain adjustable energy and capacity factors, as pointed out by Freeman and Kolb (*8*). The energy factor is related to the isosteric heat of adsorption and the capacity factor to the surface area. Before contributions from the two factors are resolved, a direct interpretation of the experimental data could be misleading. The possibility of having a non-linear Clausius–Clapeyron plot for surfaces with more than one kind of adsorption sites has been discussed by Huang, Benson and Boudart (*9*). In particular, the adsorption in the Henry's law region on a surface with two kinds of sites was illustrated in terms of the magnitude and the difference in heats of adsorption, the temperature, and the fractional distribution of sites. At the transition from one type of site to the other, the Clausius–Clapeyron plot would exhibit a significant curvature. Fortunately, the study of nitrogen adsorption on silica–alumina provides an example of this phenomenon (*6*).

For a sample evacuated at 800°C overnight, the isosteric heat of nitrogen adsorption at room temperature was as high as 9 kcal/mole at a surface coverage of about 0.1%, but decreased to about 4 kcal/mole above 1% coverage (*6*). Even though no datum is available at higher coverages, it is believed that the heat would fall from 4 to about 2 kcal/mole near the monolayer coverage, as has been observed on many supports or oxides (*10, 11*). The change in the heat of adsorption with coverage is relatively small and gradual on the majority of sites, but more abrupt in the range between 0.1 and 1% coverages. Thus, the surface can be approximated by a model consisting of two kinds of sites: one having a larger fraction but with lower heat of adsorption and the other having a very small fraction but with considerably higher heat. It would be interesting to find out whether the curvature of the Clausius–Clapeyron plot would occur within the experimental region under these conditions. The parameters of the adsorption equation, which will be determined by fitting the experimental data, will also serve to check the validity of this model.

Adsorption Equation

According to Eq. (7), the localized adsorption on a surface with two kinds of sites can be expressed as the following:

$$v = \frac{v_{m1}b_1p}{1 + b_1p} + \frac{v_{m2}b_2p}{1 + b_2p}, \tag{9}$$

which can be simplified to

$$v = v_{m1}b_1p + \frac{v_{m2}b_2p}{1 + b_2p} \left(\frac{v}{v_{m1}} \ll 1\right), \tag{10}$$

if only a small fraction of the type 1 sites is adsorbed. Indeed, the surface coverage within the experimental region was only a few percent, and adsorption isotherms were linear with pressure at higher pressures and temperatures. Each isotherm appeared to be the superposition of a Langmuir's and a Henry's isotherm. The use of Eq. (10) has the advantage that no model of the adsorbed state has to be implied for adsorption on the majority of sites, since it approaches the Henry's law region at very low coverages. Introducing a parameter, f_1, as the fraction of type 1 sites on the surface, we have

$$\begin{aligned} v_{m1} &= f_1 v_m \\ v_{m2} &= (1 - f_1)v_m, \end{aligned} \tag{11}$$

where

$$v_m = v_{m1} + v_{m2}.$$

Through the use of Eqs. (5) and (11), Eq. (10) becomes

$$v = v_m \left\{ f_1 b_{10} e^{q_1/RT} p + (1 - f_1) \frac{b_{20} e^{q_2/RT} p}{1 + b_{20} e^{q_2/RT} p} \right\}. \tag{12}$$

Variables: v, p, T; Parameters: f_1, b_{10}, q_1, b_{20}, q_2.

The three variables are determined experimentally, the five parameters are obtained by means of data-fitting procedure. A value determined by the nitrogen BET method, which was 80.1 cc(STP)/g for the sample, was assigned to v_m, the adsorption corresponding to a monolayer coverage.

The method of least-squares requires minimization of the quantity

$$Q = \sum_i^n [(v_i)_{\mathrm{calc}} - (v_i)_{\mathrm{obs}}]^2 \qquad (13)$$

where $(v_i)_{\mathrm{calc}}$ is the value calculated from Eq. (12), and $(v_i)_{\mathrm{obs}}$ is the experimental value at pressure p and temperature T. v is expressed in units of cc(STP)/g. The problem is then to solve the five simultaneous equations

$$\frac{\partial Q}{\partial f_1} = 0,\ \frac{\partial Q}{\partial b_{10}} = 0,\ \frac{\partial Q}{\partial q_1} = 0,\ \frac{\partial Q}{\partial b_{20}} = 0,\ \frac{\partial Q}{\partial q_2} = 0 \qquad (14)$$

for the five parameters.

Since Eq. (12) is a nonlinear regression function, the method of least-squares fitting can only be accomplished by means of a first order approximation. The method has been described in detail by Hartley (*12*). The operation, which included 55 data points out of 8 adsorption isotherms ranging from −23.5–148°C (*6*), was carried out by a high-speed electronic computer (IBM 360/65).

A set of trial values for the parameters had to be properly chosen so that the iteration process would converge, and the experimental results indicated previously were used as a general guide. To avoid instability due to overcorrection, since both q_1 and q_2 are involved in the exponential form, a damping factor, K, was used such that the value for the $(n + 1)^{\mathrm{th}}$ iteration is

$$q_{n+1} = q_n + K\Delta q_n,\ 0 < K < 1, \qquad (15)$$

where Δq_n is the correction term determined in the n^{th} iteration.

RESULTS

The parameters and the corrections determined at the final stage of the iteration procedure are indicated in Table 2.

TABLE 2

PARAMETERS OF THE ADSORPTION EQUATION DETERMINED BY METHOD OF LEAST-SQUARES USING THE DATA OF HUANG AND EMMETT

Parameter	Value	Correction	Unit
f_1	0.994794	0.000003	—
$(1 - f_1)$	0.005206	—	—
b_{10}	1.94×10^{-5}	0.00×10^{-5}	atm^{-1}
q_1	3548.9	3.3	cal/mole
b_{20}	9.03×10^{-7}	-0.08×10^{-7}	atm^{-1}
q_2	9925.7	12.6	cal/mole

Standard deviation: σ = 0.0156 cc(STP)/g.

The standard deviation which is defined as

$$\sigma = \sqrt{\frac{\sum_i^n [(v_i)_{\mathrm{calc}} - (v_i)_{\mathrm{obs}}]^2}{n - 5}} \qquad (16)$$

is 0.0156 cc/g. The data-fitting is quite satisfactory in view of the fact that the experimental error of the adsorption measurement is about 0.01 cc/g at lower temperatures and lower pressures, and about 0.03 cc/g at the highest pressure and the highest temperature of the experimental region (*6*). Adsorption isotherms, both experimental and calculated, are shown in Fig. 2. The Clausius–Clapeyron plots for coverages at 0.1 and 0.2 cc/g are also shown (Fig. 3).

DISCUSSION

The parameters of Eq. (12) determined by the data-fitting procedure are in close agreement with the expected values. In particular, the surface of highly dehydrated silica–alumina consists of about 0.5% of higher energetic sites with a heat of nitrogen adsorption of 9.9 kcal/mole. The rest of the surface could be considered as lower energetic sites with an average heat value of about 3.5 kcal/mole for nitrogen adsorption. Actually, the majority of sites could

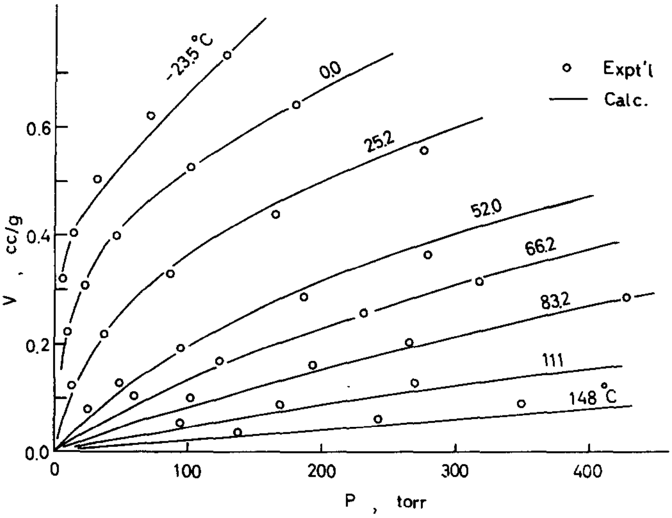

FIG. 2. Adsorption isotherms of nitrogen on silica-alumina evacuated at 800°C. (The experimental data are obtained from Huang and Emmett (*6*).)

possibly be of a Gaussian or other distribution, as indicated by the work of Ross and coworkers (*13*). The variation in energy within a Gaussian curve would be quite small, however, as compared to the difference between the two types of sites indicated above. For the purpose of the present work, the model is not too simplified.

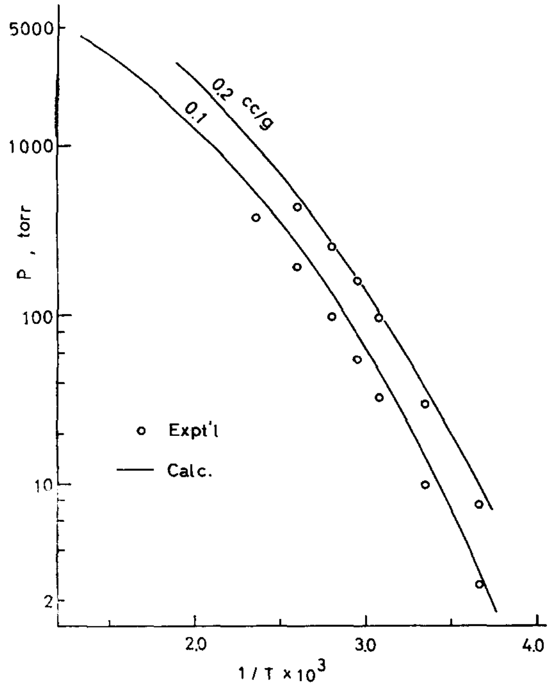

FIG. 3. Clausius-Clapeyron plot (N_2 on silica-alumina): P in Torr; T in °K.

The values of the pre-exponential factors, b_{10} and b_{20}, should also be discussed. These are related to the entropies of adsorption. According to the derivation of Fowler (*14*), the constant b in the Langmuir adsorption isotherm has the following expression

$$b = \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \frac{fa(T)}{fg(T)} e^{\epsilon/RT}, \tag{17}$$

in which h is Planck's constant, m is the mass of a gas molecule, $fa(T)$ and $fg(T)$ are the internal partition functions of a molecule in the adsorbed state and in the gas phase, respectively, and ϵ is the energy of adsorption at 0°K. From Eq. (5), we then have

$$b_0 = \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \frac{fa(T)}{fg(T)} \tag{18}$$

assuming that $\epsilon \cong q$. For the adsorption at room temperature, b_0 is estimated to be in the range of 10^{-5}–10^{-7}, depending on the adsorbed state of a molecule and the vibrational frequency of the adsorbate–adsorbent interaction (10^{12}–10^{13} sec^{-1}). Hence, the values of b_{10} and b_{20} obtained from the method of least-squares are reasonable.

Thus, the result of the data-fitting indicates that Eq. (12) describes fairly well the adsorption of nitrogen on amorphous silica–alumina which has been subjected to extensive dehydration or dehydroxylation pretreatment, at least within the rather wide experimental region. It also, as the main objective of this work, elucidates the curvature of the Clausius–Clapeyron plot observed at very low coverages. At lower temperatures, the slope approaches that corresponding to the higher energetic sites; while at higher temperatures, the lower energetic sites. The curvature occurs at the transition zone, where both terms in the adsorption equation are approximately equal in magnitude. In general, the transition would occur roughly under the condition

$$\frac{v_{m1}}{v_{m2}} \sim e^{(q_2-q_1)/RT}, \qquad (19)$$

if the difference $(q_2 - q_1)$ is not too large. By a proper choice of the temperature and pressure regions, the transition could, in principle, be located. However, to ensure the curvature of a Clausius–Clapeyron plot, a wide range of temperatures must be covered, although this is not always feasible because of the limitation of experimental investigation.

It is interesting to examine the distribution of adsorbed molecules on the two types of sites at very low coverages. Intuitively, one would expect that the higher energetic sites be fully occupied before the adsorption takes place on the lower energetic sites. But, according to Eq. (12), either term could be predominant depending on the total surface coverage, the ratio of the site fractions, the difference in heats of adsorption, and the temperature. The relative contributions to adsorption from both types of sites at a total surface coverage of about 0.13% (or 0.1 cc/g) were calculated as a function of temperature, using the parameters determined, and the results are indicated in Table 3. Apparently, the fraction covered on the higher energetic sites decreases with increasing temperature. If this is the case, it seems that any direct correlation between the adsorption data, which are often taken at a lower temperature region, and the activity of a catalyst, which is usually studied at much higher temperatures, needs to be carefully examined.

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REFERENCES

1. HILL, T. L., *in* Advances in Catalysis (W. G. Frankenburg, V. I. Komarewsky, and E. K.

TABLE 3

THE DISTRIBUTION OF NITROGEN ADSORPTION ON TWO TYPES OF SITES AS CALCULATED FROM EQUATION (12)

Temperature (°K)	Pressure (Torr)	Amount adsorbed, cc(STP)/g: V_1[a]	V_2	V	V_2/V
273.2	5.0	0.0069	0.1421	0.1490	0.95
298.4	15.0	0.0119	0.1037	0.1156	0.90
325.2	50.0	0.0242	0.0906	0.1148	0.79
356.4	140.0	0.0419	0.0703	0.1122	0.63
421.2	525.0	0.0726	0.0337	0.1063	0.32
500.0	1265.0	0.0897	0.0132	0.1029	0.13
600.0	2480.0	0.0970	0.0050	0.1020	0.05
700.0	3900.0	0.0997	0.0024	0.1021	0.02

[a] V_1, V_2 = Adsorption on types 1 and 2 sites, respectively.
$V = V_1 + V_2$.

Rideal, eds.), Vol. 4, p. 211. Academic Press, New York and London, 1952.

2. Young, D. M., and Crowell, A. D., "Physical Adsorption of Gases," Chapters 3 and 9. Butterworths, London, 1962.
3. Morrison, J. A., Los, J. M., and Drain, L. E., *Trans. Faraday Soc.* **47,** 1023 (1951).
4. Drain, L. E., and Morrison, J. A., *Trans. Faraday Soc.* **49,** 654 (1953).
5. Barrer, R. M., and Stuart, W. I., *Proc. Roy. Soc.* (London) **A249,** 464 (1959).
6. Huang, Y. Y., and Emmett, P. H., paper presented at the Second North American Meeting of the Catalysis Society, Houston, Texas, February, 1971.
7. Young, D. M., and Crowell, A. D., "Physical Adsorption of Gases," Chapter 7. Butterworths, London, 1962.
8. Freeman, M. P., and Kolb, K., *J. Phys. Chem.* **67,** 217 (1963).
9. Huang, Y. Y., Benson, J. E., and Boudart, M., *Ind. Eng. Chem., Fundamentals* **8,** 346 (1969).
10. Flood, E. A., "The Solid–Gas Interface," Vol. 1, p. 131. Marcel Dekker, New York, 1967.
11. Linsen, B. G., "Physical and Chemical Aspects of Adsorbents and Catalysts," p. 166. Academic Press, New York, 1970.
12. Hartley, H. O., *Technometrics* **3,** 269 (1961).
13. Ross, S., and Olivier, J. P., "On Physical Adsorption," Chapter VII. John Wiley & Sons, Inc., New York, 1964.
14. Fowler, R. H., *Proc. Cambridge Phil. Soc.* **31,** 260 (1935).