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SURFACE HETEROGENEITY FROM LOW TEMPERATURE ISOTHERMS

By

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Abstract

Low temperature isotherms have been analyzed by the method of Ross and Olivier for adsorption of hydrogen and nitrogen at 78–90 K and benzene at 273–298 K on about 20 solid systems.

In most cases the experimental data fit upto a coverage of 0.7–0.8 with the theoretical isotherms drawn on the basis of Hill-de Boer model of local adsorption, but the monolayer volumes derived thus are much greater than the experimental values. There is no fitting of the experimental data with the theoretical isotherms for adsorption of benzene at 293 K on active carbons and hexagonal form of boron nitride, whereas for hydrogen adsorption on alumina-promoted iron catalyst at 77.3 and 90.1 K the fitting is excellent.

The disagreement has been explained on the basis of interactions occurring during the process of adsorption and it has been suggested that such curve-fitting may be used as a rapid method to scan the surface heterogeneity or to assess the extent of interaction between a particular adsorbate and a number of adsorbents prepared by different formulations.

Introduction

The surface of a solid is seldom homogeneous. It contains numerous topographical defects like cracks, fissures, dislocations, edges, corners, etc. and each such defect centre has an adsorption potential different from the mean adsorption potential of the solid. By nomenclature, this is termed as 'surface heterogeneity' and is represented by the distribution function of site energy over a stretch of solid surface.

Since adsorption on a homogeneous patch of surface, i , is a function of only equilibrium pressure p and adsorption potential ϵ_i of the particular surface, *i. e.*, $\theta_i = \theta(p, \epsilon_i)$, the over-all coverage at the equilibrium pressure p is given by

$$\theta(p) = \int_{-\infty}^{+\infty} \theta(p, \epsilon_i) g(\epsilon) d\epsilon \quad (1)$$

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where $g(\varepsilon)$ is the site energy distribution function characterizing surface heterogeneity.

All theoretical methods¹⁻⁸⁾ of surface heterogeneity estimation aim at the solution of Equation 1 for evaluation of $g(\varepsilon)$ from the experimental values of $\theta(p)$ obtained at low temperature, low pressure and low coverage — a condition where all interactions are considerably suppressed. The first step in the solution is an assumption regarding the model of adsorption on the small patch of homogeneous surface, i , that is, $\theta(p, \varepsilon_i)$; thereafter, the methods differ.

Sips¹⁾ assumed $\theta(p, \varepsilon_i)$ or local adsorption to be of Freundlich-type and solved Equation 1 analytically with the help of Stieltjes transformation. Similar solutions have been obtained by Misra,²⁾ Toth³⁾ and Jaroniec⁴⁾ for other models of local adsorption. Equation 1 was also solved by Harris⁵⁾ and Hsu *et al.*⁶⁾ using a novel method of “condensation approximation” along with Sommerfeld integrals.

At the same time a numerical method was developed by Ross and Olivier⁷⁾ which was refined further by Adamson *et al.*⁸⁾ with the introduction of an iterative procedure. The basic assumptions of the numerical method^{7,8)} are :

(i) the distribution of site energy is Gaussian around a mean adsorption potential, ε_0 , that is,

$$g(\varepsilon) = \frac{1}{n} e^{-\gamma(\varepsilon_1 - \varepsilon_0)^2} \quad (2)$$

where n = total number of sites in the solid and γ is surface heterogeneity parameter which is a positive integer ; (As γ increases, surface heterogeneity decreases.)

(ii) the local adsorption, $\theta(p, \varepsilon_i)$, is either mono-layer without any interactions (Langmuir or Hill-de Boer Model), or localized monolayer with lateral interaction (Fowler-Guggenheim model).

From these assumptions a four-parameter equation⁷⁾ was formulated to compute the right hand side of Equation 1 for different values of the parameters and to match with experimental $\theta(p)$.

Needless to say, in comparison with the analytical techniques of Sips and other workers,¹⁻⁶⁾ the method of Ross and Olivier⁷⁾ provides an easier means for estimation of surface heterogeneity, because a simple matching of the experimental isotherm with the theoretical isotherms would yield the heterogeneity parameter γ and the mean adsorption potential of the solid.

Though there are a number of very sophisticated methods like studies on temperature programmed desorption from the surface or the various

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spectroscopic analyses of the surface to indicate the nature and extent of heterogeneity of the surface, there is still need of a routine method which would predict at least qualitatively the surface heterogeneity of a number of catalyst samples prepared by different formulations. There is no reason why the method of Ross and Olivier⁷ would not be able to serve the purpose, particularly when a set of theoretical isotherms is available and the adsorption data are taken at sufficiently low temperature and pressure so as to minimize any interaction during the process of adsorption.

But so far its application has been restricted to relatively ideal systems such as adsorption of Kr, Ar or N₂ on BN, graphite, diamond, rutile, etc.,⁷ Kr on anatase,^{9,10} Ar on carbon black,¹¹ Ar and Kr on NaCl,¹² etc. The only application of the method to a 'real' catalyst system is the analysis of Ar adsorption data at 77.5 K on silica-alumina catalyst,¹¹ but the computational technique has been the iterative procedure of Adamson *et al.*⁸

This limited application is understandable because the basic assumptions of the theory, as mentioned above, conform with a rather ideal situation. But most of the 'real' adsorbent systems are porous and microporous bodies experiencing multilayer adsorption even at a low over-all coverage. Moreover, the components of such 'real' systems usually have polarizabilities and magnetic susceptibilities in sufficient magnitudes so that the forces of van der Waals interaction are not insignificant.

So it would be interesting to find out the nature and extent of deviations when Ross-Oliver theory is applied to 'real' gas - solid systems. The deviations may be in the form of the difference in the calculated monolayer volume from the value derived experimentally and/or in the form of poor-fitting or complete non-fitting of the experimental adsorption data with the theoretical isotherms constructed as per the conditions of the experiment.

Systems of study

The isotherm data, chosen for the purpose, are :

- (i) the results of N₂ adsorption at 80.1 K on silica gel, chromia gel, copper and three different types of ammonia synthesis catalysts, namely, unpromoted iron, iron promoted with 1.5% Al₂O₃, and iron promoted with 1.3% Al₂O₃ and 1.59% K₂O, as reported by Brunauer *et al.*¹³ (to validate the contentions of BET theory);
- (ii) H₂ adsorption data on Al₂O₃ promoted iron at 77.3 and 90.1 K, as reported by Emmett and Harkness;¹⁴
- (iii) Kaganer's data¹⁵ (which have been found to obey the Dubinin-Radush-

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- kevich (DR) equation) for N_2 adsorption at 77.1 K on microporous adsorbents like silica gel S-200, silica gel S-204 (also at 90.1 K), silica aerogel, coconut charcoal, charcoal SKT, active carbon and chabazite ;
- (iv) benzene adsorption data¹⁶⁾ at 293 K on progressively activated carbons from sucrose and polyvinylidene chloride ;
- (v) benzene adsorption data of Pierotti and Smallwood¹⁷⁾ on hexagonal BN and graphite at 273 & 298 K.

Computation Procedure

The theoretical isotherms were constructed following the procedure of Ross and Olivier,⁷⁾ as exemplified by Jaycock *et al.*^{9,10)}

The solid was assumed to consist of 50 homotactic patches with a total span of 5 kcal/mol for adsorption potential, so that this for each homogeneous patch varied by 0.1 kcal/mol. The local adsorption, *i. e.*, $\theta(p, \epsilon_1)$, was assumed to follow the Hill-de Boer isotherm and its solution for estimation of local coverage, θ_1 , was done graphically. In the region of two-dimensional critical state, the local surface coverage values were taken according to the principle described by Jaycock *et al.*⁹⁾

The calculations were done partly in a computer of ICL-1900 A Series with a program developed by Mr. S. Ahmed. The rest was done manually in a high-speed desk electronic calculator.

For estimation of the mean adsorption potential of the solid, the relationship developed by Ross and Olivier⁷⁾ between the Hill-de Boer adsorption constant and the thermodynamic properties of the adsorbed state was used with insertion of parameters characteristic of the specific adsorbates.

Results

Figs. 1-4 show the fitting of the experimental adsorption data with the theoretical isotherms. The experimental data are represented by points and the theoretical isotherms, by solid lines. The deviation of the experimental data from the theoretical curve is shown by dotted lines. In Table 1 the results of the curve-fitting are presented in the form of surface heterogeneity parameter γ , mean adsorption potential of the solid ϵ'_0 , and theoretical monolayer volume $V_{m(\text{theo})}$.

For multilayer adsorption of N_2 on non-porous adsorbents, *viz.* the data reported by Brunauer *et al.*,¹³⁾ the experimental values of monolayer volume, $V_{m(\text{expt})}$, were determined from BET plots. For N_2 adsorption on microporous adsorbents¹⁵⁾ $V_{m(\text{expt})}$ was determined from the slope of Dubinin —

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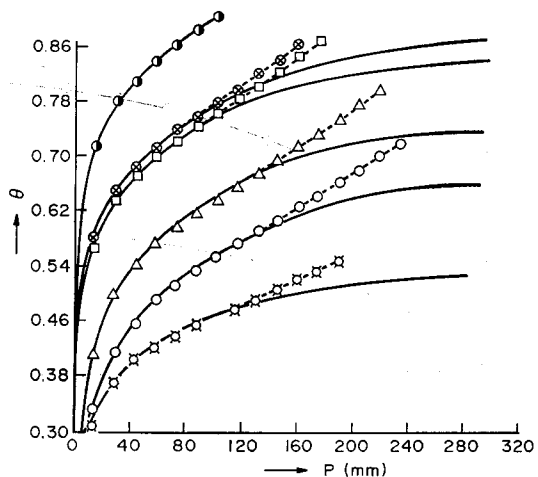


Fig. 1. Experimental points and theoretical isotherms for N_2 on several adsorbents¹² at 80 K.

- | | |
|---------------------------|------------------|
| ●● Silica gel | △△ Unpromoted Fe |
| ⊗⊗ Fe- Al_2O_3 | ○○ Fused Cu |
| □□ Fe- Al_2O_3 - K_2O | ⊠⊠ Chromia gel |

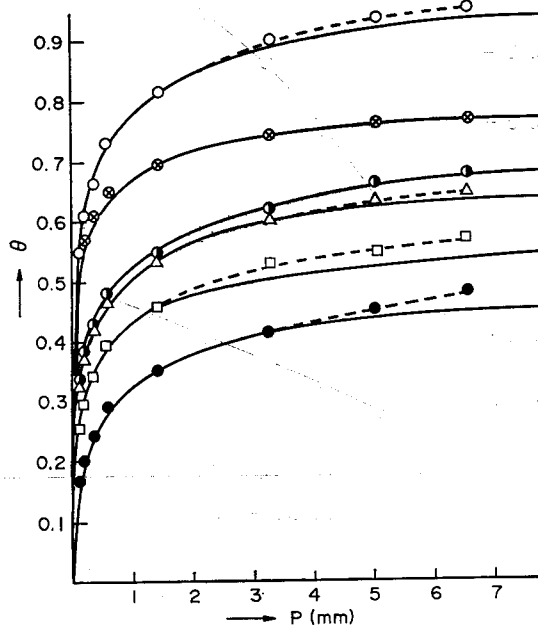


Fig. 2. Experimental data and theoretical isotherms for N_2 adsorption on several adsorbents¹³ at 77 K and 90 K.

- | | |
|-----------------------------|-----------------------------|
| ○○ Coconut charcoal at 77 K | □□ Silica gel S-204 at 90 K |
| ⊗⊗ Charcoal skt at 77 K | ●● Silica Aerogel at 77 K |
| ●● Silica gel S-200 at 77 K | — Theoretical Isotherm |
| △△ Silica gel S-204 at 77 K | ⋯⋯ Experimental Isotherm |

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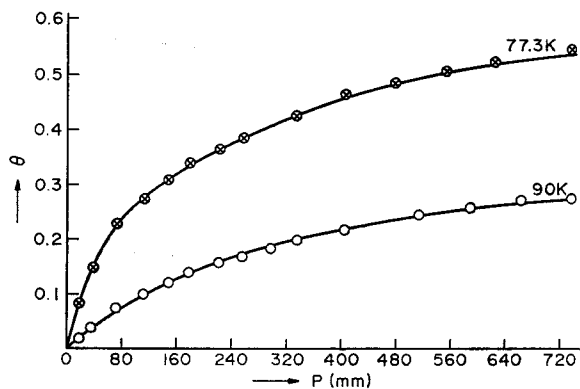


Fig. 3. Experimental points and theoretical isotherms for H_2 adsorption on Al_2O_3 promoted Fe catalyst.

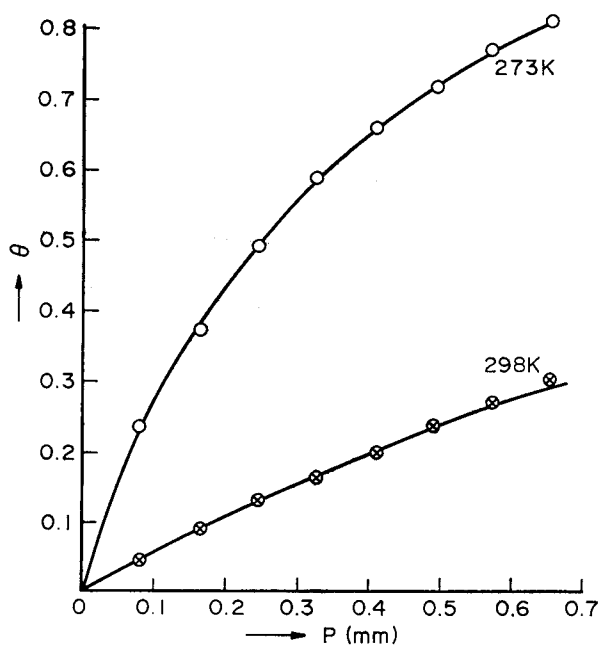


Fig. 4. Experimental points and theoretical isotherms (solid lines) for benzene Adsorption on graphite.

Radushkevich (DR) plots. Moreover, for all N_2 adsorptions the monolayer volume was estimated from the master t -curve of N_2 adsorption at 90 K¹⁸. All these values of monolayer volume ($V_{m(BET)}$, $V_{m(DR)}$ and $V_{m(t)}$) are presented

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TABLE 1. Surface heterogeneity parameter, monolayer volume and mean adsorption potential for different gas-solid systems as obtained from curve-fitting

System	$T^{\circ}\text{K}$	γ	$V_{\text{m}(\text{theo})}$	$V_{\text{m}(\text{expt})}$	$V_{\text{m}(t)}$	ϵ_0' cal/mol
1. N ₂ -Unpromoted Fe ^a	80	3	251.9	146.4**	147.0	1579.2
2. N ₂ -1.5% Al ₂ O ₃ -Fe ^a	80	7	163.9	113.6**	130.8	1634.4
3. N ₂ -1.3% Al ₂ O ₃ -1.59% K ₂ O-Fe ^a	80	3	44.2	30.0**	34.6	1782.4
4. N ₂ -Fused Cu ^a	80	3	57.9	29.8**	27.9	1457.6
5. N ₂ -Cr ₂ O ₃ gel ^a	80	1	136.9	57.7**	91.4	1342.4
6. N ₂ -SiO ₂ gel ^a	80	100	87.1	69.6**	78.6	1737.6
7. N ₂ -Active carbon from coal ^b	78	1	8.75	8.28*	—	2825.2
8. N ₂ -SiO ₂ gel S 204 ^b	77	1	5.94	5.11*	5.05	2100.6
9. -Do- ^b	90	1	6.05	4.88*	4.58	1941.9
10. N ₂ -SiO ₂ Aerogel ^b	77	1	5.00	3.58*	3.38	1746.4
11. N ₂ -SiO ₂ gel S 200 ^b	77	1	8.00	6.84*	6.96	1965.8
12. N ₂ -coconut charcoal ^b	77	1	13.87	17.15*	17.10	2485.6
13. N ₂ -charcoal SKT ^b	77	1	17.45	15.93*	15.65	2470.2
14. H ₂ -1.5% Al ₂ O ₃ -Fe ^a	77	500	11.5	8.9***	—	935.6
15. -Do- ^a	90	50	11.2	8.9***	—	687.2
16. C ₆ H ₆ -graphite ^b	273	1	5.36	3.80*	—	—
17. -Do- ^b	298	1	4.76	3.76*	—	—

a Monolayer volume in ml (STP)

b Monolayer volume in mmol-g⁻¹

** From BET plot

* From Dubinin-Radushkevich plot

*** From point B

in Table 1 along with the theoretical monolayer volumes, $V_{\text{m}(\text{theo})}$.

(Since the temperature of N₂ adsorption in the cases considered here is mostly 77-80 K, the values of $V_{\text{m}(t)}$ derived from the t -curve would be approximate. Nevertheless, it would serve as an indication of the agreement of experimental monolayer volume with the value obtained theoretically.)

An examination of Table 1 would reveal that in all cases except for N₂ adsorption on coconut charcoal at 77.1 K, the theoretical monolayer volume is higher, sometimes to a large extent, than the experimental monolayer volume. In case of N₂-coconut charcoal system, however, $V_{\text{m}(\text{theo})}$ is much lower than $V_{\text{m}(\text{expt})}$. The difference between the two monolayer volumes ($V_{\text{m}(\text{theo})}$ and $V_{\text{m}(\text{expt})}$) occurs in spite of a rather satisfactory fitting of the experimental adsorption data with the theoretical isotherms upto a

moderate coverage of $\theta=0.5-0.8$. In this connection it should be mentioned that, in general, $V_{m(t)}$, *i. e.*, V_m obtained from t -curve, agrees with $V_{m(\text{BET})}$ or $V_{m(\text{DR})}$ within $\pm 10\%$. (Table 1).

The technique of curve-fitting for multiple heterogeneity⁹⁾ could not be applied to the present systems because even for the single heterogeneity parameter the deviation of $V_{m(\text{theo})}$ from $V_{m(\text{expt})}$ is so large that any further fitting of residual data with a curve of higher heterogeneity parameter would add to the already-calculated $V_{m(\text{theo})}$ and make the difference from $V_{m(\text{expt})}$ still larger. Moreover, it is reasonable to assume that for such porous and microporous adsorbents a local coverage of more than unity, that is, condensation of the adsorbate, occurs, even when the overall coverage is 0.5-0.8. Since the theory of Ross and Olivier is valid for sub-monolayer coverage, the on-set of condensation within the pores may be responsible for the deviations of experimental data from the theoretical isotherms at moderate values of surface coverage and above.

Table 1 also indicates that in case of a large number of adsorbents,¹⁵⁾ particularly those having micropores, the curve-fitting indicates a heterogeneity parameter of $\gamma=1$ only, implying a very high heterogeneity of the surface. However, for N_2 adsorption on silica gel at 80.1 K¹³⁾ the surface appears to be nearly homogeneous with $\gamma=100$ (Fig. 1 and Table 1).

The results of curve-fitting nitrogen adsorption at 80.1 K on three different samples of ammonia synthesis catalysts¹³⁾ present some interesting observations (Fig. 1 and Table 1).

Usually it may be expected that more is the number of components in a catalyst, other things remaining same, more would be the heterogeneity of the surface. Thus, the unpromoted iron catalyst should have the least heterogeneity, followed by the singly promoted, then by the doubly promoted samples. But from Table 1 and Fig. 1 it is observed that the unpromoted and the doubly promoted samples have the same heterogeneity parameter, namely, $\gamma=3$, while the singly promoted sample exhibits less heterogeneity with $\gamma=7$.

Of course, the mean adsorption potential, ϵ'_0 , increases gradually from the unpromoted iron catalyst (1579.2 cal/mol) to Al_2O_3 -promoted sample (1634.4 cal/mol) and finally to doubly promoted sample (1782.4 cal/mol.)

In contrast to the adsorption of N_2 , the fitting of adsorption data for H_2 at 77.3 and 90.1 K on Al_2O_3 -promoted iron¹⁴⁾ is excellent (Fig. 3). The heterogeneity parameters, estimated therefrom, indicate a considerably homogeneous surface with $\gamma=500$ at 77.3 K and $\gamma=50$ at 90.1 K (Table 1). Incidentally, the same surface appeared to be considerably heterogeneous

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($\gamma=3$) when N_2 was adsorbed on this surface at 80.1 K.

Lastly, the agreement of adsorption data¹⁷ for benzene on graphite with the theoretical curve is shown in Fig. 4. It is observed that the experimental data collected under low pressure for graphite at 273 and 298 K have fitted fairly well into the standard isotherm for $\gamma=1$, indicating a high degree of heterogeneity of the surface. Like other results discussed above, the quantity of adsorbate required for monolayer formation is 5.363 m-mol g⁻¹ and this is much higher than the experimental monolayer requirement of 3.800 m-mol g⁻¹.

Regarding the results of curve-fitting for benzene adsorption on other adsorbents such as active carbons¹⁶ and BN,¹⁷ not a single experimental isotherm could be fitted with any theoretical isotherm. This is in sharp contrast with the results discussed so far. Similar break-down of the theory has been noticed for N_2 adsorption data¹⁶ obtained on chabazite at 77.3 K as the data could not be fitted with any theoretical isotherm drawn for nitrogen at that temperature.

Discussions

It may be mentioned that there is no direct way to verify the results obtained from the applications of Ross and Olivier's theory. But the nature of fitting of the experimental isotherm data with the theoretical isotherms and the agreement of the monolayer volume derived thus with the values obtained by other methods like point B, BET, *t*-curve, etc. may be taken as indirect evidences in support of the assumptions behind the theory and the heterogeneity parameters obtained thereof.

As with the present systems of study, an analysis of the results¹⁹ of Ross and Olivier would reveal a higher monolayer volume invariably in all cases; but the differences, though a bit large in some cases, for example, rutile and Linde 13 X, are not of such magnitude as in the present work. Moreover, as it has been observed for N_2 and H_2 adsorption on Al_2O_3 -promoted iron at 80.1 and 77.3 K, respectively, a heterogeneity parameter of 3 and 500, respectively, several results of Ross and Olivier¹⁹ indicate that for the same solid surface, a different heterogeneity parameter is obtained with a change in adsorbate, N_2 showing a lower heterogeneity parameter than the other inert gases.

This suggests that, after all, there may be some interactions, however small, between the adsorbate and the solid surface, this being minimum with inert gases. In other words, the contribution to surface heterogeneity does not come from *a priori* heterogeneity alone; a part of it, however small,

comes from the self-interaction of the adsorbate and the adsorbate-adsorbent interactions.

Due to low polarizability ($0.79 \times 10^{-24} \text{ m}\ell$) and low self-interaction energy (108 cal/mol) of H_2 in comparison with those of N_2 ($1.76 \times 10^{-24} \text{ m}\ell$ and 645 cal/mol, respectively), the interaction of hydrogen with iron is very low at 77.3–90.1 K. A theoretical estimate of metal-gas interaction energy at 80 K by Kirkwood-Müller formula²⁰ has yielded values of 257 cal/mol and 2,777 cal/mol for H_2 -Fe and N_2 -Fe systems, respectively. Though the quantities are not exactly same as the mean adsorption potential of the solid, the order is nearly same (Table 1) and the interaction energy of hydrogen with iron is definitely much less than that of nitrogen in conformity with the observed nature of curve-fitting.

In case of N_2 on Fe, an added factor may be the interaction between the quadrupole moment of N_2 with the net magnetic moment of Fe which may be appreciable even at such low temperatures.

In the microporous adsorbents, the proximity of adsorbed nitrogen molecules within pores causes considerable self-interaction and, consequently, a high heterogeneity of the surface is noticed in the form of $\gamma=1$. This self-interaction along which the interaction between adsorbate and adsorbent may be quite high for N_2 adsorption on chabazite at 77.3 K¹⁵ due to strong electrostatic field within the pores, and, though small, but a definite quadrupole moment of N_2 .

The same explanation, that is, considerable interaction during the process of adsorption, may hold true for non-fitting of other adsorption data with the theoretical isotherms, such as benzene on BN and activated carbons^{16,17} in the temperature range of 273–298 K.

The result with BN is somewhat contradictory with that arrived by Pierotti *et al*¹⁷ on the basis of an analysis of second gas-solid virial coefficient. According to these authors¹⁷ the adsorption potential of BN is 8,720 cal/mol and that of graphite, 9,840 cal/mol. Also, a theoretical estimate of adsorption potential for benzene-BN system by a procedure which is exactly analogous to that of Kiselev and Poshkus²¹ yielded a value of 8,400 cal/mol.²⁰ Consequently, the graphite surface is supposed to be a little more heterogeneous than the hexagonal BN. But as it has been observed earlier, the experimental adsorption data for benzene on graphite agree fairly well with the theoretical isotherms drawn on the basis of mobile monolayer model without interaction (Hill-de Boer), while the same for BN do not at all agree with the theory.

A consideration of bonding in two materials — BN and graphite —

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reveals that graphite, after sp^2 hybridization, is covered by a uniform ring of six delocalized π -electrons. In hexagonal BN, after similar hybridization, each nitrogen atom is left with two unshared electrons and there is no excess electron on the boron atoms. This introduces a degree of heterogeneity on the surface of BN in comparison with graphite. Moreover, BN has more surface area ($18.3 \text{ m}^2 \text{ g}^{-1}$), hence more micropores, than graphite ($11.7 \text{ m}^2 \text{ g}^{-1}$). Since benzene has a very high self-interaction energy (4,170 cal/mol) a small difference in the percentage of micropores may result in a considerable difference in surface heterogeneity.

Finally, to show that a better fit of experimental data may be achieved if interactions are taken into consideration while drawing the theoretical isotherms, a set of such curves was constructed on the basis of localized monolayer formation with lateral interaction (Fowler-Guggenheim isotherm) as the model of local adsorption. These curves have been presented in Fig. 5.

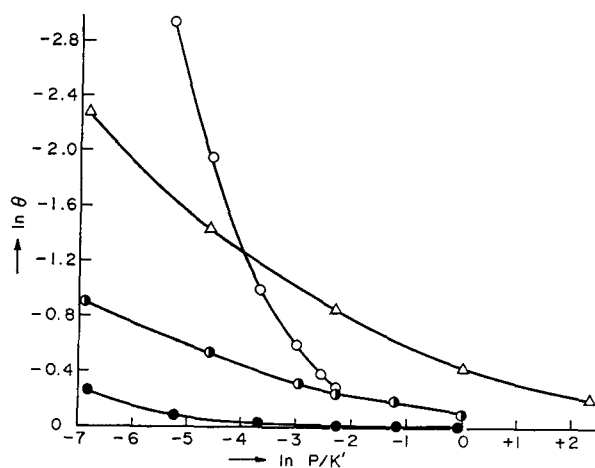


Fig. 5. Standard isotherms on the basis of fowler-guggenheim model.

$$Z' = \frac{Z\omega}{RT}$$

$\triangle-\triangle-\triangle$	$Z' = 2.92$ ($T = 84 \text{ K}$)	$\circ-\circ-\circ$	$Z' = 5.74$ ($T = 273 \text{ K}$)
$\bullet-\bullet-\bullet$	$Z' = 8.76$ ($T = 84 \text{ K}$)	$\bullet-\bullet-\bullet$	$Z' = 11.47$ ($T = 273 \text{ K}$)

It is apparent from Fig. 5 that with increasing values of Z' (a parameter which is proportional to the product of adsorbate coordination number in the adsorbed state and adsorbate-adsorbate interaction energy), the slope of the curve changes to a large extent. At high values of Z' the calculated curve assumes a shape that is completely compatible with that of the experimental isotherms for benzene at 273–298 K on active carbons and BN, and for nitrogen on chabazite at 77.3 K.

Earlier, Adamson *et al.*²⁰ suggested the site energy distribution to be independent of the model of local adsorption, but their observations were based on the analysis of data for relatively homogeneous systems. The same may not hold true in case of 'real' gas-solid systems where considerable interaction may occur during adsorption.

In conclusion, it may, therefore, be suggested that the theoretical isotherms drawn on the basis of Ross and Olivier's theory may serve as a simple yard-stick to assess the relative surface heterogeneity vis-a-vis the extent of interaction in a number of samples obtained by different methods of preparation. Whereas the fitting of the experimental adsorption data would indicate the surface heterogeneity parameter, the deviations would indicate the extent of interactions.

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