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**The Effect of the Topography of Surfaces on Adsorption of Gases at Supercritical
Temperatures on Heterogeneous Solid Surfaces**

Wpływ topografii powierzchni heterogenicznej na adsorpcję gazów
w temperaturach superkrytycznych

Влияние топографии энергетически неоднородных поверхностей на величину адсорбции
в суперкритических температурах

INTRODUCTION

Surface heterogeneity is generally described by an expression giving the differential distribution of adsorption sites as a function of their adsorption energy. This function, however, is a satisfactory description of this distribution only in case of an ideal adsorbed phase. In cases where any departure from ideal behaviour of the adsorbed phase exists, the differential distribution of adsorption energies is only a global description of surface heterogeneity.

In such a case another property of the system which will influence the behaviour of heterogeneous adsorption is the topography of solid surfaces. It can be argued that the spatial distribution of sites with various adsorption energies over an adsorbent surface should influence the global distribution function in some way. The role of this topographical distribution of adsorption sites has not been given much considera-

tion in the past. Most publications have assumed a patchwise energy distribution [1] with no attempt being made to consider the role of the real topography of surfaces studied in physical adsorption.

The alternative topographical model, proposed by Hill [2] for the case of localized adsorption, assumes that adsorption sites of different energies are distributed randomly over an adsorbent surface. This model was subsequently used by Tompkins [3] to analyze the behaviour of a two-dimensional van der Waals gas on heterogeneous surfaces.

Steele [4] was the first to make an attempt at discriminating between these two topographical models using a virial description, but some details of his computations were criticized by Adamson [5].

Obviously, a real solid surface always exhibits some moderate topographical correlation of adsorption sites and lies between the two extremes described above. Recently, Rudziński [6] and Ripa and Zgrablich [7] have studied this spatial correlation using virial formalism. This approach is limited to the region of low coverage and no investigation has been reported of high-coverage adsorption on surfaces with a moderate degree correlation of sites of equal adsorption energies.

The purpose of this work is to investigate the role of surface topography for a surface with a moderate spatial correlation of sites of equal adsorption energies at the region of medium coverage.

I. TOPOGRAPHICAL DISTRIBUTION OF SITES

The overall adsorption isotherm, $v(p)$ for a patchwise model of heterogeneous surfaces is given by

$$v(p) = \int_{\Omega} \theta(p, \epsilon) X(\epsilon) d\epsilon \quad 1.1$$

where $\theta(p, \epsilon)$ is the local isotherm on a surface patch having adsorption energy equal to ϵ . $X(\epsilon)$ is the differential distribution of adsorption energy, and Ω is the range of possible variations of ϵ .

Various analytical approximations for $X(\epsilon)$ have been proposed [8-16]. We can argue that the topography of the surface has no effect on the adsorption process until the mutual interactions between adsorbed molecules start to play a significant role. This is in range of relatively moderate and higher coverages of surface.

In this range we define a new function $X(\tau, \epsilon)$ as the differential distribution of the nearest neighbouring sites among various adsorption energies τ with respect to an adsorption site with an adsorption energy ϵ . $X(\tau, \epsilon)$ can then be looked at as a local distribution. In case of the ideally patchwise topographical distribution, $X(\tau, \epsilon)$ is just a Dirac delta function.

$$X(\tau, \epsilon) = \delta(\tau - \epsilon) \quad 1.2$$

For the fully random topographical distribution, $X(\tau, \epsilon)$ should be independent of ϵ . Thus

$$X(\tau, \epsilon) = X(\tau) \quad 1.3$$

We are interested here in an intermediate case for which we propose the following function

$$X(\tau, \epsilon) = \frac{1}{\rho} \frac{\exp\left(\frac{\tau - \epsilon}{\rho}\right)}{\left[1 + \exp\left(\frac{\tau - \epsilon}{\rho}\right)\right]^2} \quad 1.4$$

This is a bell-shaped function centered at $\tau = \epsilon$ with a width of the order of ρ . In general, ρ will be dependent on ϵ , but here we only consider the simple case where ρ is independent of ϵ .

The potential of an average force acting on an admolecule from its nearest neighbouring admolecules is given by $4kT_c \Lambda(\rho)$, where $\Lambda(\rho)$ denotes the relative coverage of the nearest neighbours sites of a given admolecule. However, Λ will, in general, differ from both v and θ . In a first-order approximation $\Lambda(\epsilon, \rho)$ can be represented by

$$\Lambda(\varepsilon, \rho) = N(\varepsilon) \int_0^{\infty} \frac{1}{\rho} \theta(\rho, \tau) \frac{\exp\left(\frac{\tau - \varepsilon}{\rho}\right)}{\left[1 + \exp\left(\frac{\tau - \varepsilon}{\rho}\right)\right]} d\tau \quad 1.5$$

where $N(\varepsilon) = 1 + \exp\left(-\frac{\varepsilon}{\rho}\right)$ is a normalization coefficient of the local distribution function (1.4). Using the same expansion for Fermi-Dirac integrals we can evaluate $\Lambda(\varepsilon, \rho)$ with any desired accuracy. For the case of an intermediate topographical distribution, it should be sufficient to retain only the first three terms in this expansion. Hence,

$$\Lambda(\varepsilon, \rho) = \theta(\varepsilon, \rho) + 2(\ln 2)\rho \frac{\partial \theta(\rho, \varepsilon)}{\partial \varepsilon} + \frac{\pi^2}{6} \rho^2 \frac{\partial^2 \theta(\rho, \varepsilon)}{\partial \varepsilon^2} \quad 1.6$$

where θ is the local isotherm. In this work we use the Fowler-Guggenheim isotherm as given below:

$$\theta(\rho, \varepsilon) = \left[1 + \frac{k'}{\rho} \exp\left(\frac{\varepsilon + 4kT_c \theta}{-kT}\right) \right]^{-1} \quad 1.7$$

Equation (1.6) is obtained assuming that $N(\varepsilon) = 2$. This last approximation was accepted because we want the truncated series (1.6) to fulfill the necessary condition

$$\lim_{\rho \rightarrow 0} \Lambda(\varepsilon, \rho, \rho) = \theta(\varepsilon, \rho) \quad 1.8$$

The equation for the overall adsorption isotherm $v^{(M)}(p)$ can now be written in the following form:

$$v^{(M)}(p) = \int_0^{\infty} \frac{r}{kT} e^{-\frac{r\varepsilon}{kT}} \left[1 + \frac{k'}{\rho} \exp\left(\frac{\varepsilon + 4kT_c \Lambda(\varepsilon, \rho)}{-kT}\right) \right]^{-1} d\varepsilon \quad 1.9$$

Equation (1.9) can be integrated by parts

$$v^{(M)}(p) = v_1(p) + v_2(p) \quad 1.10$$

where

$$v_1(p) = \left[1 + \frac{K'}{p} \exp \left(\frac{\xi + 4kT_c \Lambda}{-kT} \right) \right]_{\xi=0}^{-1} \quad 1.11$$

and

$$v_2(p) = \int_0^{\infty} \exp \left(-\frac{r\xi}{kT} \right) d\theta \quad 1.12$$

We shall introduce the following transformation

$$\xi + 4kT_c \Lambda(\xi) = t + t_0 \quad 1.13$$

$$\frac{K'}{p} \exp \left(\frac{-t_0}{kT} \right) = \exp \left(\frac{\mu}{kT} \right) \quad 1.14$$

$$t_0 = 4kT_c [\Lambda(p, \xi)]_{\xi=0} \quad 1.15$$

Thus, θ takes now the form of a Langmuir equation

$$\theta(t, \mu) = \left[1 + \exp \left(\frac{\mu - t}{kT} \right) \right]^{-1} \quad 1.16$$

In terms of the new variable t , $v_2(\mu)$ has the form of a Fermi-Dirac integral

$$v_2(\mu) = \frac{1}{kT} \int_0^{\infty} \phi(t, \mu) \frac{\exp \left(\frac{\mu - t}{kT} \right)}{\left[1 + \exp \left(\frac{\mu - t}{kT} \right) \right]^2} dt \quad 1.17$$

where

$$\phi(t, \mu) = \exp \left[-\frac{r}{kT} (t + t_0 - 4kT_c \Lambda) \right] \quad 1.18$$

Expanding $\phi(t)$ around $t = \mu$, we obtain

$$\phi(t, \mu) = \sum_{n=0}^{\infty} \frac{(t - \mu)^n}{n!} \left[\frac{\partial^n \phi}{\partial t^n} \right]_{t=\mu} \quad 1.19$$

Introducing the new variable $x = \frac{t-\mu}{kT}$ we can write

$$V_2(\mu) = \sum_{n=0}^{\infty} \frac{(kT)^n}{n!} \left[\frac{\partial^n \phi}{\partial t^n} \right]_{t=\mu} * \int_{-\frac{\mu}{kT}}^{\infty} \frac{x^n}{(1+e^x)(1+\bar{e}^x)} dx \quad 1.20$$

We shall now apply a further approximation to the integrals appearing in Equation (1.20).

According to Equations (1.14) and (1.15) we have

$$\frac{-\mu}{kT} = \ln \left[\frac{\theta(\rho, \epsilon)}{1-\theta(\rho, \epsilon)} \right]_{\epsilon=0} \quad 1.21$$

Furthermore, we are interested in the region of moderate and higher coverages of the surface, where interactions between ad molecules play an important role and the effects of surface topography become important. Thus, when evaluating the integrals in Equation (1.20), we shall accept that in this region of overall surface coverages, the sites with the smallest adsorption energy are half-covered. The integration limits are then from zero to plus infinity, and we have [18]

$$\int_0^{\infty} \frac{x^n dx}{(1+e^x)(1+e^{-x})} = n! B_n \quad 1.22$$

where B_n is expressed by Riemann's zeta functions $Z(n)$

$$B_n = (1-2^{1-n})Z(n) \quad 1.23$$

i.e., $B_n = 1/2, \ln 2, \pi^2/12, \dots$ for $n = 0, 1, 2, \dots$ respectively.

This approximation immediately limits the range of application to moderate coverage, the region where the main interest of this publication lies. For $\theta = 0.5$, the surface is half covered at zero energy. The change of integration limit involves no error. However, for $\theta = 0.8$ the integral in Equation 1.20 gives roughly about 0.29, 0.20 and 0.10 between $\chi = 0.0$ and 1.4 for $n = 0, 1$ and 2, respectively. These values, which represent the errors introduced by the change of limit are compared with the total values (integration limits from 0 to ∞)

of 0.50, 0.69 and 1.64. Furthermore, because of the symmetrical nature of the integrals for $n = 0$ and 2, the errors introduced by the limit change for $\Theta = 0.2$ will be of the same magnitude as those for $\Theta = 0.8$. Thus, a significant error may result if Θ is greater than 0.7 or less than 0.3.

Retaining only the first three terms of Equation 1.23 we obtain

$$V_2(\mu) = \left[1/2 \phi(t) + kT \ln 2 \frac{\partial \phi(t)}{\partial t} + (kT)^2 \frac{\pi^2}{12} \frac{\partial^2 \phi(t)}{\partial t^2} \right]_{t=\mu} \quad 1.24$$

Combining Equation (1.11) and (1.24) we finally get

$$V^{(M)}(p) = \left[\theta^{(M)}(p, \xi) \right]_{\xi=0} + \frac{1}{2} \left(\frac{p}{kT} \right)^r \exp \left[2\xi r \left(1 + \frac{p}{kT} \frac{\ln 2}{1-\xi} \right) \right] * \\ * \left\{ 1 - 2 (\ln 2) r (1-\xi) \left[1 + \frac{\pi^2}{12} \frac{p}{kT} \frac{\xi}{(1-\xi)^4} \left(\frac{p}{kT} + 1 - \xi \right) \right] + \right. \\ \left. + \frac{\pi^2}{6} [r(1-\xi)]^2 \left[1 + \frac{\pi^2}{12} \left(\frac{p}{kT} \right)^2 \frac{\xi}{(1-\xi)^4} \right]^2 \right\} \quad 1.25$$

In the limit $p \rightarrow 0$, $\chi(\tau, \xi)$ is the Dirac delta function $\delta(\tau - \xi)$ and Equation (1.25) reduces correctly to the isotherm equation of ideally patchwise surfaces.

$$V^{(P)}(p) = \left[\theta^{(P)}(p, \xi) \right]_{\xi=0} + \frac{1}{2} \left(\frac{p}{kT} \right)^r e^{2\xi r} \cdot \\ \cdot \left[1 - 2 (\ln 2) r (1-\xi) + \frac{\pi^2}{6} r^2 (1-\xi)^2 \right] \quad 1.26$$

Furthermore, in the limit $\xi = T_c/T \rightarrow 0$ the isotherm of $v^{(M)}$ or $v^{(P)}$ reduces to equation

$$v = \left[1 + \frac{K'}{p} \right]^{-1} + \left(\frac{p}{K'} \right)^r \sum_{n=0}^{\infty} (-1)^n B_n r^n \quad 1.27$$

which is the exact form of $v(p)$, obtained for Langmuir local isotherm. Thus, when the mutual interaction between molecules vanishes, the topography of surface has no effect on adsorption data.

If there is no spatial correlation between adsorption sites of equal adsorption energy, the distribution of adsorption sites

among different adsorption energies is exactly the same as for the whole heterogeneous surface. With the superscript (R) denoting the random topographical distribution of adsorption energies, the local isotherm $\theta^{(R)}(\xi, p)$ has the form:

$$\theta^{(R)}(\xi, p) = \left[1 + \frac{K}{p} \exp\left(\frac{\xi + 4kT_c \sqrt{r}}{-kT}\right) \right]^{-1} \quad 1.28$$

and the corresponding overall isotherm $v^{(R)}(p)$ is, then, given by

$$V^{(R)}(p) = \left[\theta^{(R)}(\xi, p) \right]_{\xi=0} + \frac{1}{2} \left(\frac{p}{K} \right)^r \exp\left(\frac{4T_c r v^{(R)}}{T}\right) \cdot \left[1 - 2(\ln 2)r + \frac{\pi^2}{6} r^2 \right] \quad 1.29$$

II. THE ISOSTERIC HEAT OF ADSORPTION

Since the total coverage v is a function of p and T therefore, at constant v , we shall write the equation for the isosteric heat of adsorption Q_{st} in the following form:

$$Q_{st}(p, T) = k \frac{[\partial v(p, T) / \partial (1/T)]_p}{[\partial v(p, T) / \partial (\ln p)]_T} \quad 2.1$$

Using equation (2.1) we may calculate the isosteric heat of adsorption for the three theoretical isotherms, $v^{(P)}$, $v^{(M)}$, $v^{(R)}$, developed for the different topographical models of surface.

(a) Isosteric heat of adsorption on ideally patchwise heterogeneous surfaces $Q_{st}^{(P)}$ is

$$Q_{st}^{(P)}(p, T) = kT \left\{ \theta(1-\theta) Q^{(P)} / \eta + r \left[(v^{(P)} - \theta) Q^{(P)} - \ln \frac{\theta}{1-\theta} \right] + \frac{1}{2} e^{2\xi r} \left(\frac{p}{K} \right)^r \left(2 \ln 2 - \frac{\pi^2}{3} r(1-\xi) \right) \right\} / \left[\theta(1-\theta) / \eta + r(v^{(P)} - \theta) \right] \quad 2.2$$

where

$$Q^{(P)} = \frac{5}{2} + \frac{\xi_0}{kT} + 4\xi\theta \quad 2.3$$

$$\eta = 1 - 4\xi\theta \quad (1 - \theta) \quad 2.4$$

and

$$\theta = \left[\theta^{(R)}(p, \xi) \right]_{\xi=0} \quad 2.5$$

(b) Isotheric heat of adsorption on fully random heterogeneous surfaces $Q_{st}^{(R)}$ is

$$Q^{(R)}(p, T) = kT \left\{ \theta(1-\theta) Q^{(R)} + r \left[(v^{(R)} - \theta) \left(Q^{(R)} - \ln \frac{\theta}{1-\theta} \right) + \frac{1}{2} e^{-4r\xi} v^{(R)} \left(\frac{p}{kT} \right)^r \left(2 \ln 2 - \frac{\pi^2}{3} r \right) \right] \right\} / \left[\theta(1-\theta) + \right. \quad 2.6$$

$$\left. + r(v^{(R)} - \theta) \right] \quad 2.6$$

where

$$Q^{(R)} = \frac{5}{2} + \frac{\xi_0}{kT} + 4\xi v^{(R)} \quad 2.7$$

and

$$\theta = \left[\theta^{(R)}(p, \xi) \right]_{\xi=0} \quad 2.8$$

(c) Isotheric heat of adsorption on heterogeneous surfaces exhibiting moderate topographical correlation of sites $Q_{st}^{(M)}$ is

$$Q_{st}^{(M)}(p, T) = kT \left\{ \frac{1}{T} \frac{\partial \theta}{\partial (1/T)} + r(v^{(M)} - \theta) \left(Q^{(M)} - \ln \frac{\theta}{1-\theta} + 2 \ln 2 \right) \frac{p}{kT} \frac{\xi}{(1-\xi)^2} + \frac{1}{2} \exp \left[2\xi r \left(1 + \frac{p}{kT} \frac{\ln 2}{1-\xi} \right) \right] \cdot \left(\frac{p}{kT} \right)^r \cdot \left[2 \ln 2 \left(1 + \frac{\pi^2}{12} \frac{p}{kT} \frac{\xi}{(1-\xi)^4} \left(\xi^2 - \frac{p}{kT} (2+\xi) - 1 \right) - \frac{\pi^2}{3} r(1-\xi) \left(1 + \frac{\pi^2}{12} \left(\frac{p}{kT} \right)^2 \frac{\xi}{(1-\xi)^4} \left(1 - \frac{\pi^2}{12} \left(\frac{p}{kT} \right)^2 (2+\xi) \frac{\xi}{(1-\xi)^4} \right) \right) \right] \right\} / \left[\frac{\partial \theta}{\partial \ln p} + r(v^{(M)} - \theta) \right] \quad 2.9$$

where

$$\frac{\partial \theta}{\partial (1/T)} = T \frac{\theta(1-\theta) Q^{(M)}}{1-4\xi\theta(1-\theta)} \frac{\partial \Delta}{\partial \theta} \quad 2.10$$

$$\frac{\partial \theta}{\partial \ln p} = \frac{\theta(1-\theta)}{1-4\xi\theta(1-\theta)} \frac{\partial \Delta}{\partial \theta} \quad 2.11$$

$$\frac{\partial \Delta}{\partial \theta} = 1 + 2 \ln 2 \frac{\rho}{kT} \frac{1-2\theta}{\eta} + \frac{\pi^2}{6} \left(\frac{\rho}{kT} \right)^2 \frac{1}{\eta} \left\{ (1-2\theta)^2 + \right. \quad 2.12$$

$$\left. + 2\theta(1-\theta) [4\xi(3\theta^2 - 3\theta + 1) - 1] \right\} \quad 2.12$$

$$Q^{(M)} = \frac{5}{2} + \frac{\xi\theta}{kT} + 4\xi \left[\theta + 4 \ln 2 \frac{\rho}{kT} \frac{\theta(1-\theta)[1-2\xi\theta(1-\theta)]}{\eta^2} + \right. \quad 2.13$$

$$\left. + \frac{\pi^2}{12} \cdot \left(\frac{\rho}{kT} \right)^2 \frac{\theta(1-\theta)(1-2\theta)}{\eta^2} \right]$$

and

$$\theta = \left[\theta^{(M)}(p, \xi) \right]_{\xi=0} \quad 2.14$$

In the limit $T_c/T \rightarrow 0$, $Q_{st}^{(P)} = Q_{st}^{(M)} = Q_{st}^{(R)}$, and if $\rho \rightarrow 0$, we have $Q_{st}^{(M)} \rightarrow Q_{st}^{(P)}$.

III. RESULTS AND DISCUSSION

First, we shall discuss the behaviour of the overall adsorption isotherms; $v^{(P)}$, $v^{(R)}$, and $v^{(M)}$. All these isotherms can be written in the following general form

$$v^{(i)}(p) = \theta^{(i)}(p, \xi_0) + \alpha^{(i)} \left(\frac{\rho}{kT} \right)^r \quad 3.1$$

where $i = P, R, M$, and $\alpha^{(i)}$ is, in general, some function of (T_c/T) , r and (ρ/RT) . In other words, every overall isotherm

equation is a linear combination of the appropriate local isotherm for a homogeneous surface with the most probable value of adsorption energy* ξ_0 , and a Freundlich isotherm function of the form $\left(\frac{p}{K}\right)^r$.

The last term $\alpha^{(i)} \left(\frac{p}{K}\right)^r$ in Equation (3.1) illustrates the limitations which arise from the several approximations accepted here. It is clear that our equations can only be applied in the region of moderate surface coverages, in which region the Freundlich isotherm can be applied in the absence of interactions between adsorbed molecules. Thus, although we present our numerical results over the whole region of surface coverages, we should remember that at very low and very high coverages our results are not quantitative.

We can now discuss the role of surface topography by comparing the overall adsorption isotherms for the two extreme cases of surface topography: the patchwise, and the random topography of adsorption sites. Furthermore, we shall confine ourselves to the region of supercritical temperatures.

Taking $(T_c/T) = 0.5$, we have evaluated $v^{(P)}(p)$ and $v^{(R)}(p)$, for three different values of the dimensionless heterogeneity parameter r : $r = 0.01$, $r = 0.1$ and $r = 0.3$. The results are shown in Fig. 1. In Fig. 2 another comparison is made between these curves, evaluated now at the constant value $r = 0.1$ and various values of (T_c/T) : $(T_c/T) = 0.1$, $(T_c/T) = 0.5$ and $(T_c/T) = 0.75$.

A general conclusion, which can be drawn from these two figures, is as follows: surfaces with random topography of sites behave more like homogeneous surfaces than surfaces characterized by patchwise topography. In other words, the patchwise topography exaggerates the effects of surface heterogeneity. It also appears that at low surface coverages, adsorption on surfaces with random topography is smaller than on those having a patchwise topography. This relationship becomes reversed at high overall coverages of surface. The explanation for this observation is as follows:

For high values of ξ , in general, $\theta(p) > v(p)$. Thus, at small adsorbate pressures when adsorption is occurring mainly

*In case of the exponential distribution function, the lowest energy ξ_0 is simultaneously the most probable energy.

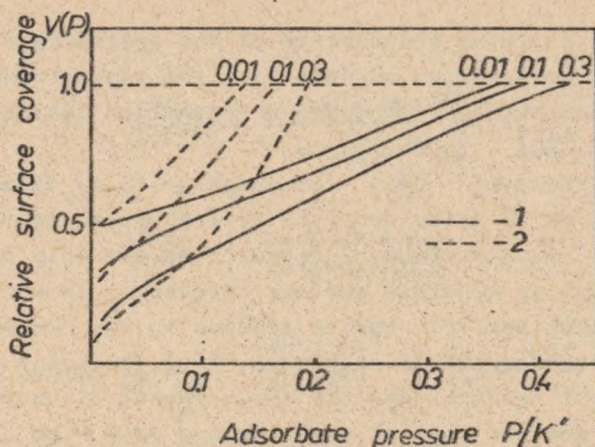


Fig. 1. Calculated overall isotherms; 1 - $v^{(P)}(p)$, 2 - $v^{(R)}(p)$, at $(T_c/T) = 0.5$ for three values of the dimensionless heterogeneity parameter r^H .

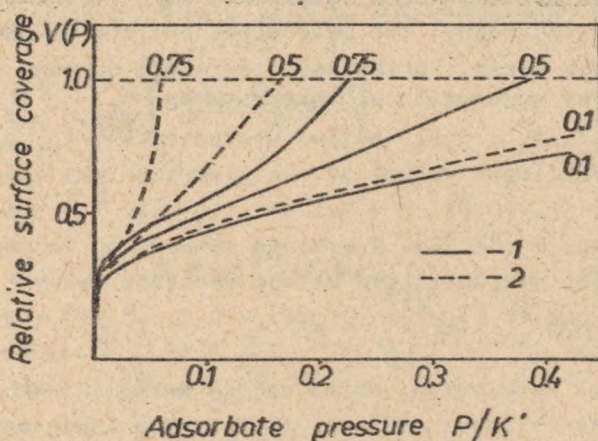


Fig. 2. Calculated overall isotherms; 1 - $v^{(P)}(p)$ and 2 - $v^{(R)}(p)$, evaluated for $r = 0.1$, and for three values of (T_c/T) .

on highly energetic sites, adsorption on surfaces with random topography will be smaller than on those with patchwise topography. An opposite effect will be observed at high coverages, where adsorption will occur mainly on low-energy sites where $e(p) < v(p)$.

Figure 3 shows some limitations of Eq. (2.25), arising from cutting the expansion (1.6) after the third term. Values of (P/RT) higher than 0.4 could not be accepted since $v^{(M)}(p)$

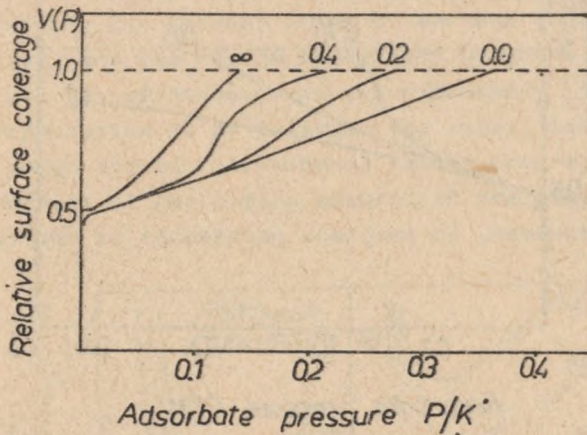


Fig. 3. Calculated overall isotherms $v^{(M)}(p)$, evaluated at $r = 0.01$ and $(T_c/T) = 0.5$ for three different values of (P_c/RT) ; in case of $(P_c/RT = \infty)$ the curve was evaluated from eq. 2.2

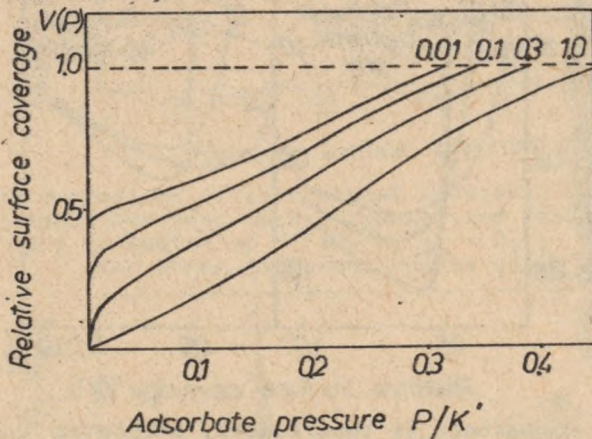


Fig. 4. Calculated overall isotherms $v^{(M)}(p)$ at $(P_c/RT) = 0.1$ and $(T_c/T) = 0.5$ for three values of "r"

would then exceed the values of $v^{(R)}(p)$ at higher adsorbate pressures. Obviously, the highest acceptable value of (P_c/RT) depends on both r and (T_c/T) . This limitation can be removed as far as necessary by taking higher terms of the expansion (1.6) into account. Fig. 4 shows how the overall surface heterogeneity affects the shape of the overall adsorption isotherm in systems with some moderate spatial correlation of sites. The next figure, Fig. 5, provides a similar illustra-

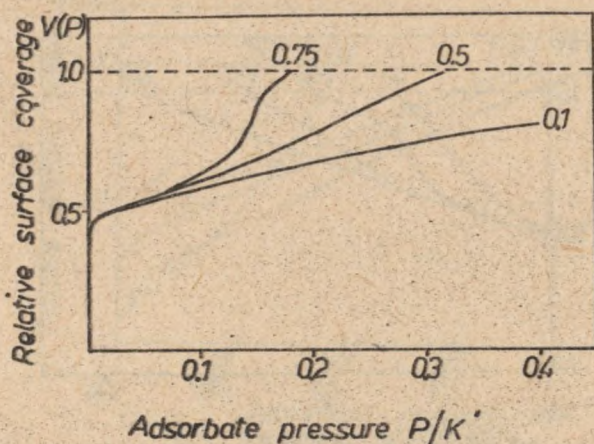


Fig. 5. Calculated overall isotherms $v^{(M)}(p)$ at $(P/RT) = 0.1$ and $r = 0.01$ for three different values of (T_c/T)

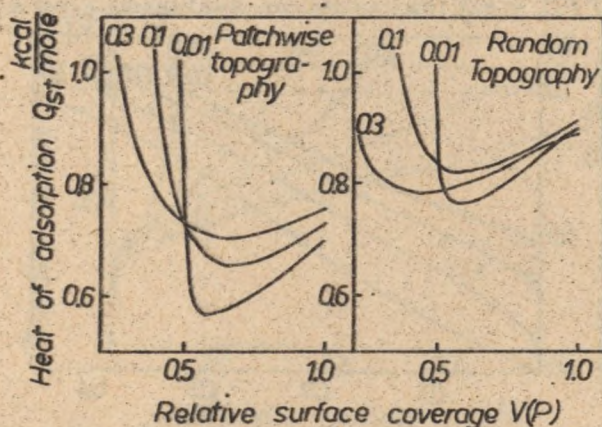


Fig. 6. The comparison of theoretical, isosteric heats of adsorption between surfaces with patchwise and random topography of sites; all curves were evaluated at $T = 100^\circ\text{K}$, $\epsilon_0 = 0.0$ and $(T_c/T) = 0.5$ for three values of ϵ_n

tion of the effect when the value of (T_c/T) changes.

Figures 6-10 show the effect of surface topography in the isosteric heats of adsorption. All these curves have been evaluated for the temperature $T = 100^\circ\text{K}$. The reason for these figures is that isosteric heats of adsorption are probably the most extensively investigated adsorption characteristics next to the isotherms themselves. In various publications, heats of adsorption are commonly presented as a function of surface coverage in the way we present them here.

Figure 6 shows the comparison of the isosteric heats of adsorption for the two extreme cases of surface topography: for the patchwise, and the random topography of sites. Curves such as shown here are often observed experimentally [19-23], and their interpretation is as follows: the first, decreasing branch of these curves, corresponds to the coverage region in which the effect of decreasing adsorption energies prevails over the effect of increasing energies of interaction between

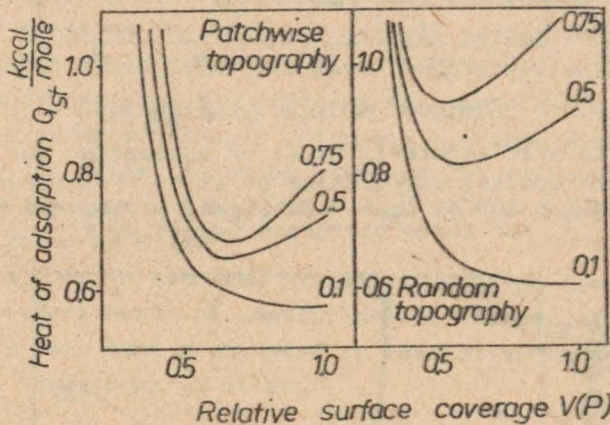


Fig. 7. The comparison of theoretical isosteric heats of adsorption between surfaces with patchwise and random topography; all curves were evaluated at $T = 100^\circ\text{K}$, $\epsilon_0 = 0.0$, and $r = 0.1$ for three different values of (T_c/T)

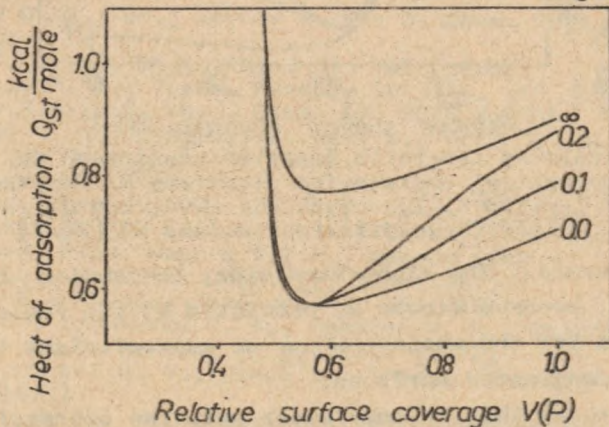


Fig. 8. Calculated isosteric heats of adsorption for surfaces of moderate spatial correlation of sites; all curves were evaluated at $T = 100^\circ\text{K}$, $\epsilon_0 = 0.0$, $r = 0.01$, and $(T_c/T) = 0.5$ for three different values of (P/RT)

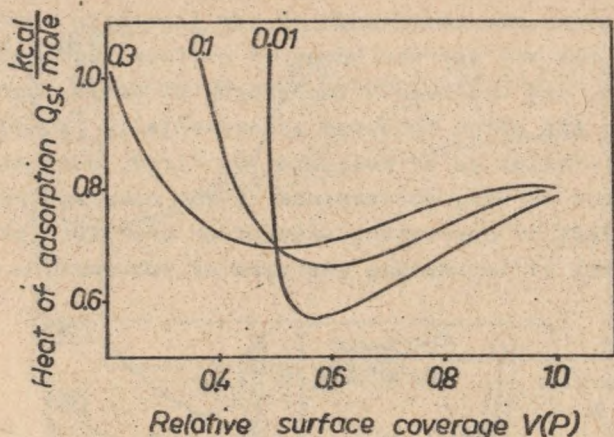


Fig. 9. Calculated isosteric heats of adsorption for surfaces with moderate spatial correlation of sites. All curves were evaluated at $T = 100^{\circ}\text{K}$, $\epsilon_0 = 0.0$, $(T_c/T) = 0.5$, and $(P/RT) = 0.1$ for three different values of r

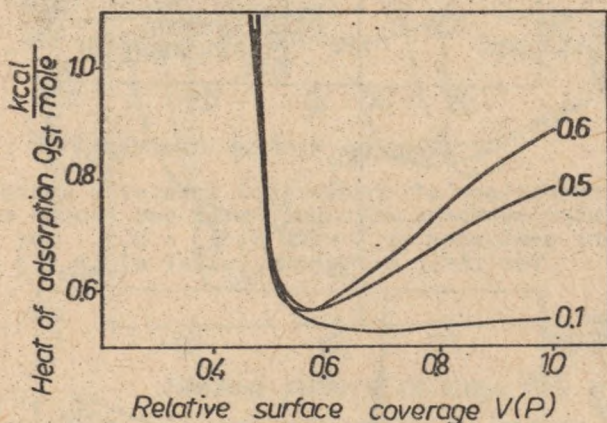


Fig. 10. Calculated isosteric heats of adsorption for surfaces with moderate spatial correlation of sites. All curves were evaluated at $T = 100^{\circ}\text{K}$, $\epsilon_0 = 0.0$, $r = 0.01$, and $(P/RT) = 0.1$ for three different values of (T_c/T)

adsorbed molecules. The right-hand side, increasing branch of these curves, becomes linear as predicted by the Fowler-Guggenheim equation for the whole region at supercritical temperatures and on homogeneous surfaces.

Figure 7 shows that in some cases only the decreasing branch of the isosteric heat of adsorption will be found. Since such curves are sometimes used as an approximate estimate of the

overall distribution of adsorption energy we see how risky this procedure can be.

Figures 8-10 illustrate the behaviour of the isosteric heats of adsorption in various physical situations, in systems with some mediate topographical correlation of sites.

CONCLUSION

By introducing some approximations, analytical expressions have been obtained for both the overall adsorption isotherms and for the overall isosteric heats of adsorption; in adsorption at supercritical temperatures for three basic topographical models of heterogeneous surfaces: surfaces with patchwise topography of sites, surfaces with spatial correlation of sites of equal adsorption energies, and for surfaces with a random topography of sites.

We find that in both the overall adsorption isotherms and the theoretical heats of adsorption the effects of surface heterogeneity are most pronounced in case of surfaces with a patchwise topography of sites.

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STRESZCZENIE

Rozważono konsekwencje przyjęcia trzech różnych modeli topografii powierzchni (płatewego, random i pośredniego) w zjawiskach adsorpcji na powierzchniach heterogenicznych w obszarze temperatur superkrytycznych. Badania przeprowadzono w oparciu o tzw. całkowity formalizm opisu izoterm adsorpcji globalnej, przyjmując do opisu adsorpcji lokalnej model Fowlera-Guggenheima. Przy pewnych uproszczeniach o charakterze matematycznym otrzymane zostały analityczne wzory dla izoterm adsorpcji i całkowitych izosterycznych ciepł adsorpcji. Stwierdzono, że na powyższe wielkości termodynamiczne największy wpływ ma niejednorodność powierzchni o topografii płatewej.

Резюме

В данной работе рассуждены результаты применения трех разных моделей топографии поверхности (лоскутной, случайной и серединной) в теоретических исследованиях адсорбции на энергетически-неоднородных поверхностях. Исследования проведены на основании интегрального формализма описания изотермы общей адсорбции. В качестве локальной изотермы адсорбции принято уравнение Фовлера-Гуггенгейма. При некоторых математических упрощениях получено аналитические формулы для изотерм адсорбции и общих изостерических теплот адсорбции. Установлено, что самое большое влияние на эти термодинамические величины имеет неоднородность поверхности с лоскутной топографией.