

distributed completely at random. In other words, the adsorption system must be treated here as a thermodynamic entity. Except for adsorption on polycrystalline surfaces, it is difficult to judge a priori which model of surface topography should be accepted for the particular adsorption system under consideration. So, it is a mystery, why, most of the authors writing on adsorption on heterogeneous surfaces, always assume the patchwise model.

In addition to further development of experimental techniques which could decide which is the proper model of surface topography - theoretical studies should be developed to describe the effect of surface topography on various thermodynamic quantities. In this work we are going to demonstrate, how the surface topography influences the behaviour of differential heats of adsorption, in both mobile and localized adsorption.

THEORY

Effects of surface topography arise from the interactions between adsorbed molecules; in the absence of these interactions, (Langmuir model or ideal 2D gas), the topography of heterogeneous surfaces has no effect on the behaviour of adsorption systems. The contribution from the mutual interactions between molecules to the thermodynamic properties of an adsorption system increases, as the temperature of the system decreases. It should, therefore, be expected, that the effects of surface topography will be demonstrated mainly in the low-temperature region.

This is a fortunate circumstance from the point of view of a possible theoretical description. In the low-temperature region we can safely use the Condensation Approximation, which we already used in our previous work.

In CA (Condensation Approximation), the adsorption is assumed to run in a stepwise fashion; this means, that adsorption sites are covered gradually, in the sequence of decreasing adsorption energies ϵ . In other words, the local adsorption on the sites having adsorption energy ϵ , is described by the following local "condensation" isotherm:

$$\theta_c(p, \epsilon) = \begin{cases} 0, & p < p_c(\epsilon, T) \\ 1, & p \geq p_c(\epsilon, T) \end{cases} \quad (1)$$

At a constant pressure "p" and temperature "T", the adsorption on sites of different adsorption energy is given by:

$$\theta_c(p, \epsilon) = \begin{cases} 0, & \epsilon < \epsilon_c(p, T) \\ 1, & \epsilon \geq \epsilon_c(p, T) \end{cases} \quad (2)$$

The overall adsorption isotherm $v(p, T)$ is, according to equ. (2), given by:

$$v(p, T) = \int_{\epsilon_c}^{\infty} \chi(\epsilon) d\epsilon \quad (3)$$

where $\chi(\epsilon)$ is the differential distribution of sites among various adsorption energies. This function is usually called the "adsorption energy distribution". The upper integration limit is taken just as a mathematical convenience, and the form of the function $\epsilon_c(p, T)$ is found appropriate, exact form of the adsorption isotherm governing adsorption on the sites having adsorption energy ϵ . Some simple variational considerations lead us to the condition [2]:

$$\theta_c(p, \epsilon_c) = \frac{1}{2} \quad (4)$$

Similarly, as in our previous publication, we consider here the monolayer adsorption with nearest-neighbour interactions between admolecules. Both in case of localized and mobile adsorption, we shall accept the simplest, mean-field approximation for the effect of the mutual interactions between adsorbed molecules. In case of localized adsorption, it leads us to the well-known, Fowler-Guggenheim isotherm which, for the patchwise heterogenous surfaces, takes the form [3]:

$$\theta^{(p)}(\epsilon, p, T) = \left\{ 1 + \frac{K_1}{p} \exp \left[\frac{\epsilon + 2 kT_c \theta^{(p)}}{-kT} \right] \right\}^{-1} \quad (5)$$

whereas, for the random topography we have:

$$\theta^{(r)}(\xi, p, T) = \left\{ 1 + \frac{K_1}{p} \exp \left[\frac{\xi + 4 k T_c v}{-kT} \right] \right\}^{-1} \quad (6)$$

Above K_1 is the Langmuir constant and $T_c = (z \cdot n / 4k)$, where n is the number of the nearest-neighbours, adsorption sites, and z is the interaction energy between two molecules adsorbed on nearest neighbour sites. In case of patchwise topography, T_c is the real, 2D critical temperature of the 2D condensation of the Bragg-Williams lattice gas on homogenous patches. In case of surfaces with the random topography of sites, T_c is only a measure of interactions between adsorbed molecules.

Let $\xi_c^{(p)}$ and $\xi_c^{(r)}$ denote the function $\xi_c(p, T)$, for the patchwise, and the random topography, respectively. From eqs. (4), (5) and (6), we obtain:

$$\xi_c^{(p)} = -kT \ln \frac{p}{K_1} - 2 k T_c \quad (7)$$

$$\xi_c^{(r)} = -kT \ln \frac{p}{K_1} - 4 k T_c v \quad (8)$$

For the purpose of some model investigations, we shall assume the widely accepted, right hand widened gaussian distribution

$$\chi(\xi) = 2 B \xi \exp(-B \xi^2) \quad (9)$$

which is related to the Dubinin-Radushkevitch overall behaviour of adsorption systems. The resulted, overall adsorption isotherms $v^{(p)}(p, T)$ and $v^{(r)}(p, T)$ are given as:

$$v^{(p)}(p, T) = \exp \left[-B (\xi_c^{(p)})^2 \right] \quad (10)$$

$$v^{(r)}(p, T) = \exp \left[-B (\xi_c^{(r)})^2 \right] \quad (11)$$

After solving these equations with respect to $\ln p$, we obtain:

$$\ln p = \frac{-1}{k \sqrt{B} T} \left[\ln \frac{1}{v^{(p)}} \right]^{1/2} + \ln K_1 - 2 \frac{T_c}{T} \quad (12)$$

$$\ln p = \frac{-1}{k\sqrt{B}T} \left[\ln \frac{1}{v(r)} \right]^{1/2} + \ln K_1 - 4 \frac{T_c}{T} v(r) \quad (13)$$

The isosteric heat of adsorption is found from the relation:

$$Q_{st} = \left[\frac{\partial \ln p}{\partial \left(\frac{1}{T}\right)} \right]_v \quad (14)$$

From (12) - (14), we obtain:

$$\frac{Q_{st}^{(p)} - Q_{st}^{(o)}}{kT} = \frac{1}{k\sqrt{B}T} \left[\ln \frac{1}{v(p)} \right]^{1/2} + \frac{2 T_c}{T} \quad (15)$$

$$\frac{Q_{st}^{(r)} - Q_{st}^{(o)}}{kT} = \frac{1}{k\sqrt{B}T} \left[\ln \frac{1}{v(r)} \right]^{1/2} + 4 \frac{T_c}{T} v(r) \quad (16)$$

where $Q_{st}^{(o)}$ is the non-configurational contribution:

$$Q_{st}^{(o)} = \left[\frac{\partial \ln K}{\partial \left(\frac{1}{T}\right)} \right] \quad (17)$$

Coming to the mobile adsorption, we shall consider the 2D analogue of the Van der Waals gas. In case of the patchwise topography, this yields the well-known, Hill-deBoer isotherm:

$$\ln \frac{p}{K_m} = - \frac{\mathcal{E}}{kT} + \ln \frac{\theta}{1-\theta} + \frac{\theta}{1-\theta} - \frac{27}{4} \frac{T_c}{T} \quad (18)$$

where T_c is the 2D critical temperature of the 2D Van der Waals gas, on an ideally homogeneous surface (homogeneous patches of surface). In case of the random topography we have the well-known, Tompkin's isotherm equation [4]:

$$\ln \frac{p}{K_m} = - \frac{\mathcal{E}}{kT} + \ln \frac{\theta}{1-v(r)} + \frac{\theta}{1-v(r)} - \frac{27}{4} \theta - \frac{27}{4} v(r) \quad (19)$$

but this time θ is defined as the ratio of the molecules occupying surface regions of adsorption energy \mathcal{E} , to (α/b) , where α is the surface area and b is the area occupied by one admolecule.

Cerofolini has shown [2] that replacing $(1/2)$ by other constant has no essential meaning in the Condensation Approximation, and we have already explained in our previous publication [1], why, the constant $(1/2)$ is also an appropriate value in case of the surfaces, characterized by a random topographical distribution. Thus, in case of the random topography, we obtain the following pressure-energy relation:

$$\mathcal{E}_c^{(r)} = -kT \ln \frac{p}{K_m} + \ln \frac{1}{2} - \ln(1 - v^{(r)}) - \frac{27}{16} \frac{T_c}{T} - \frac{27}{8} \frac{T_c}{T} \quad (20)$$

which, for surfaces with the patchwise topography, reduces to the following, simpler one:

$$\mathcal{E}_c^{(p)} = -kT \ln \frac{p}{K_m} - \frac{27}{8} \frac{T_c}{T} \quad (21)$$

From eqs. (18) - (21), we obtain:

$$\frac{Q_{st}^{(r)} - Q_{st}^{(o)}}{kT} = \frac{1}{k\sqrt{B}T} \left[\ln \frac{1}{v^{(r)}} \right]^{\frac{1}{2}} - \ln \frac{1}{2} + \ln(1 - v^{(r)}) + \frac{27}{8} \frac{T_c}{T} + \frac{27}{4} \frac{T_c v^{(r)}}{T} \quad (22)$$

$$\frac{Q_{st}^{(p)} - Q_{st}^{(o)}}{kT} = \frac{1}{k\sqrt{B}T} \left[\ln \frac{1}{v^{(p)}} \right]^{\frac{1}{2}} + \frac{27}{4} \frac{T_c}{T} \quad (23)$$

The discussion of the eqs. (15) - (16), and (22) - (23) is given in the next section.

NUMERICAL RESULTS AND DISCUSSION

From the above we can see, that, investigating the behaviour of the isosteric heats of adsorption in low temperatures, can be the source of very interesting information about the nature of adsorption systems. At low temperatures, the isosteric heats of adsorption are related in a very simple way to the heterogeneity and the interaction parameters, as well as, to the surface topography. To discuss this in a more detail, we have performed some illustrative numerical calculations which are shown in Figs. 1 - 4.

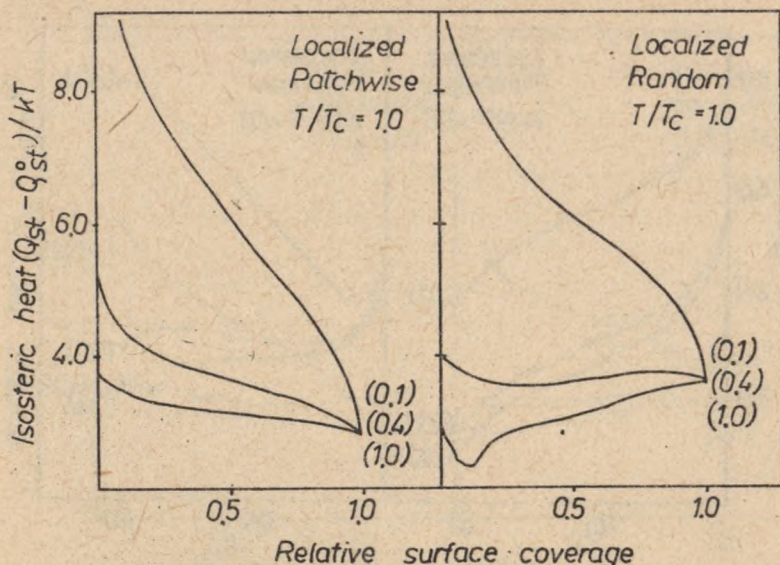


Fig. 1. Localized adsorption, Bragg-Williams approximation. The isosteric heat of adsorption as the function of the overall surface coverage, when $T/T_c = 1.0$, for various values of the heterogeneity parameter $kTB^{1/2}$, given in the brackets at appropriate curves

Let us remember, that these figures show the behaviour of the isosteric heat of adsorption in the zero-temperature limit; only in this limit adsorption runs in a fully stepwise fashion, assumed in Condensation Approximation. It was generally assumed till now, that at this temperature limit, the function $(\partial v / \partial Q_{st})$ is identical with the true energy distribution $\chi(\mathcal{E} = Q_{st})$.

It was, therefore, assumed [5] that extrapolating of the experimental data for $Q_{st}(v)$, to the zero-temperature limit, leads to the true energy distribution for a given adsorption system. Now, we can see that the validity of this conclusion is limited, to surfaces with patchwise site topography. For this case, the heterogeneity parameter B^* can be found from the relation Q_{st} vs. $[kT \ln \frac{1}{v}]^{1/2}$, and that the interaction parameter T_c does not affect this estimation. In case of surface with random topography, however, we must know a priori the parameter T_c , in order to estimate correctly the heteroge-

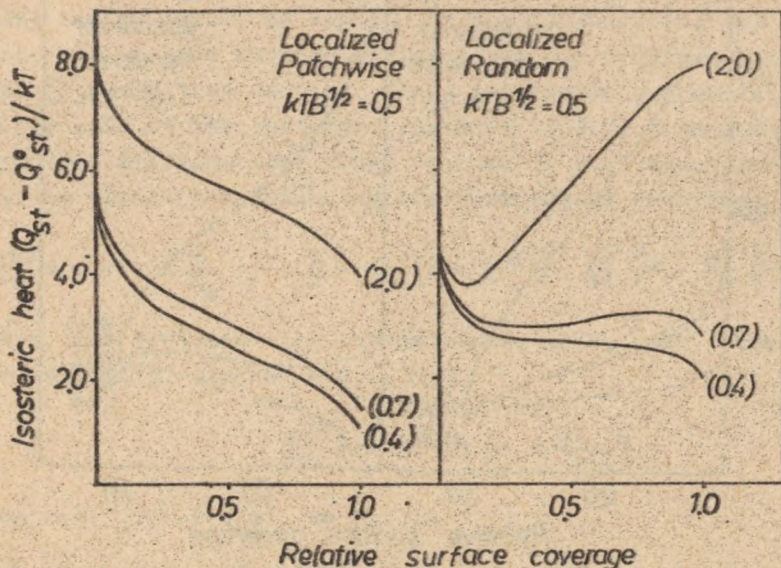


Fig. 2. Localized adsorption, Bragg-Williams approximation. The isosteric heat of adsorption as the function of the overall surface coverage, when $kTB^{1/2}=0.5$, for various values of the interaction parameter T/T_c given in the brackets at appropriate curves

neity parameter B . In other words, the very popular procedure of Drain and Morrison [5] does not apply in this case.

Now, let us consider yet the case of localized adsorption in more detail. In Fig. 1, the function $Q_{st}(v)$ is shown when $(T_c/T) = 1.0$, for three values of the heterogeneity parameter B . The form of $Q_{st}(v)$ presented here is very often found in the experiment. For example, the curves; (1A), (2A), (3A), and 1B are similar to those for argon, nitrogen and oxygen on rutile [6,7]; CH_3OH on silica gel [8]; nitrogen on carbon blacks [9], etc. The shape of the curve (2B) is also very interesting. Such curves were observed in the systems; CH_3OH on activated carbon [8] or, nitrogen on oxidized (110) copper [10].

In Fig. 2, we show the form of the function $Q_{st}(v)$ for three values of the interaction parameter (T_c/T) , taking every time $kTB^{1/2}=0.5$. Here, in addition to the already discussed forms of $Q_{st}(v)$, we have a new form (1B). This form is very often observed in the experiment [10].

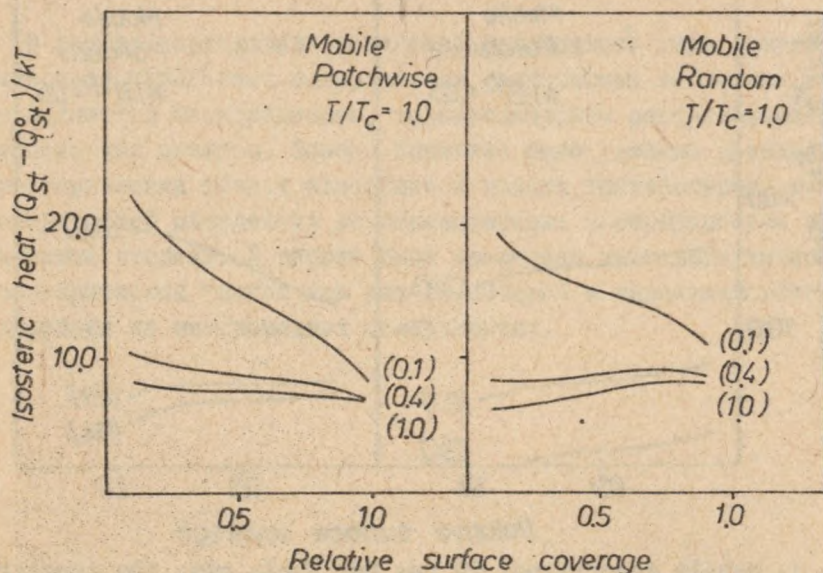


Fig. 3. Mobile adsorption, 2D Van der Waals gas. The isosteric heat of adsorption as the function of the overall surface coverage when $T/T_c = 1.0$ for various values of the heterogeneity parameter $c_{kTB}^{1/2}$ given in the brackets at appropriate curves

Now, let us discuss the mobile adsorption on heterogeneous surfaces exhibiting the Dubinin-Radushkevich distribution of adsorption energies. The behaviour of $Q_{st}(v)$ for such systems is presented in Fig. 3 - 4. In fact, there is no essential difference between the shape of the curves in Figs. 3 - 4, and those, presented in Figs. 1 - 2. Thus, the differential heat of adsorption is not very sensitive to the mobility of adsorbed phase. It seems also that, in case of mobile adsorption, the differential heat of adsorption is also less sensitive to surface topography, than it is in localized adsorption. Further investigation along these lines will be continued.

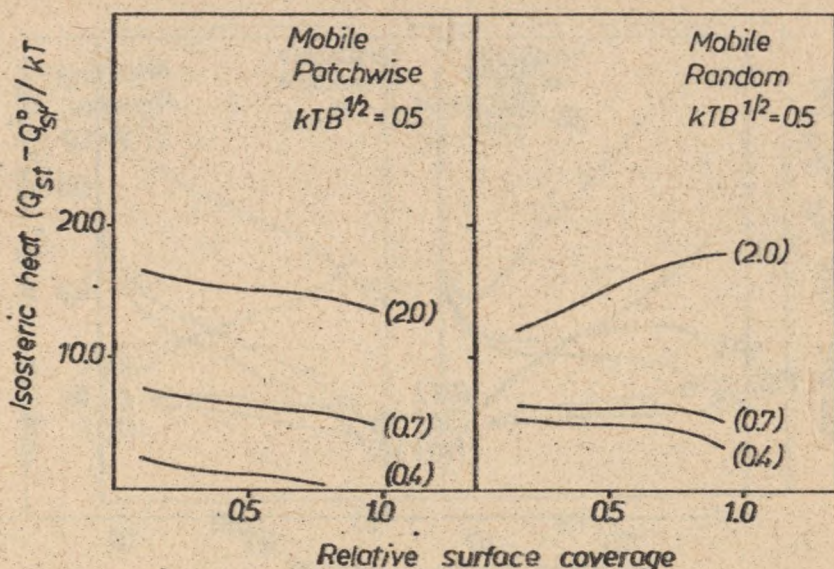


Fig. 4. Mobile adsorption, 2D Van der Waals gas. The isosteric heat of adsorption as the function of the overall surface coverage, when $kTB^{1/2}=0.5$, for various values of the interaction parameter T/T_c given in the brackets at appropriate curves

REFERENCES

1. Rudziński W., Łajtar L., Patrykiewicz A.: *Surface Sci.* **67**, 195, (1977).
2. Cerofolini G.: *Surface Sci.* **47**, 469 (1975).
3. Hill T. L.: *J. Chem. Phys.* **17**, 762 (1949).
4. Tompkins F.C.: *Trans. Faraday Soc.* **46**, 569 (1950).
5. Drain L.E., Morrison J. A.: *Trans. Faraday Soc.* **48**, 316 (1952).
6. Drain L. E., Morrison J. A.: *Trans. Faraday Soc.* **48**, 1 (1952).
7. Drain L. E., Morrison J. A.: *Trans. Faraday Soc.* **49**, 1 (1953).
8. Kiselev A. V.: *Vest. Moscov. Univ. Khim. Series* **1-3** (1962).
9. Joyner L. G., Emmet P. H.: *J. Am. Chem. Soc.* **70**, 2353 (1948).
10. See for the data collected by Gregg S. S.: *Physical Surfaces*. Chapman and Hall Ltd. London 1961.

STRESZCZENIE

Ważnym czynnikiem determinującym adsorpcję na powierzchniach heterogenicznych jest, poza oddziaływaniami między zaadsorbowanymi cząsteczkami oraz stopniem mobilności, topografia powierzchni. Dotychczas tym zagadnieniem nie zajmowano się dokładnie. Podjęto badania wpływu rozkładu miejsc adsorpcyjnych na izosteryczne ciepła adsorpcji, które dokładniej niż izotermy adsorpcji odzwierciedlają wpływ topografii powierzchni. Przeprowadzono modelowe obliczenia izosterycznych ciepła adsorpcji dla zlokalizowanej i mobilnej adsorpcji gazów na powierzchniach o płaskiej i przypadkowym rozkładzie miejsc adsorpcyjnych.

Резюме

В работе исследовано поведение решеточного газа Брегга-Вильямса на гетерогенных поверхностях, обладающих лоскотным, а также полностью беспорядочным, топографическим распределением адсорбционных центров. Особое внимание было уделено поведению изостерических теплот адсорбции в низких температурах, в случае поверхностей обладающих экспоненциальным распределением адсорбционной энергии. В работе были проведены модельные вычисления изостерических теплот для локализованной и нелекализованной адсорбции на неоднородных поверхностях.

