

VARIATION OF ADSORPTION HEAT OF RARE GAS ATOMS  
ON ALKALI HALIDE CRYSTALS\*

BY J. M. ROGOWSKA AND K. F. WOJCIECHOWSKI

Institute of Experimental Physics, University of Wrocław\*

(Received October 5, 1976)

An attempt to explain the experimentally observed variation of adsorption heat of rare gas atoms on a distorted alkali halide crystal (100) face is given. The adsorption heat is calculated taking into account the non-additivity of dispersive forces and different distributions of adatoms on the substrate, depending on the coverage. Some models of adsorption layer are considered and the calculations of the adsorption heat dependence on coverage for the Ar-NaCl system are given. Good agreement with experiment was obtained.

## 1. Introduction

Adsorption of rare gases in ionic crystals is a subject of interest for many authors [1-8]. The dependences of the adsorption heat on the coverage  $\theta$ ,  $q^{\text{st}} = q^{\text{st}}(\theta)$ , — have a very similar shape for all systems investigated until now. Especially typical is the initial decrease of the adsorption heat for  $\theta < 0.3$  and the existence of a distinct maximum for  $\theta = 1$ , (c. f. experimental data of Jackson and Davis [4], obtained for sublimated and double heated NaCl crystals, represented by the full curve in Fig. 4). In many works [2-7], attempts to calculate the dependence  $q^{\text{st}}(\theta)$  were undertaken, but until now the reasons for the initial decrease of the adsorption heat in the investigated systems have not explained. Assuming the interaction energy between an adatom and crystal  $X_m$  to be independent of  $\theta$ , the reasons of this decrease should be searched either in the inhomogeneity of adsorbent surfaces [4, 5] or in interactions between adatoms [2, 3, 6, 7]. The good agreement between the calculated and measured values of the adsorption heat  $q_0^{\text{st}}$  for  $\theta = 0$  [8, 9] suggests, that the initial decrease of the adsorption heat is caused mainly by the change of the adatom interaction energy  $V$  with changing coverage  $\theta$ .

We have calculated the  $\theta$ -dependence of the adsorption heat taking into account the following affects: surface relaxation of NaCl [10], the Sinanoglu and Pitzer non-addi-

---

\* This work was supported by the Institute of Physics of the Polish Academy of Sciences.

\*\* Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Cybulskiego 36, 50-205 Wrocław, Poland.

tivity of dispersive forces [11], and different distributions of adatoms on the substrate depending on  $\theta$ . The surface relaxation was taken into consideration in calculating the energy  $X_m$  of adatom interaction with the crystal in the same way as in [8]. This energy was calculated for four adatom positions  $A$  — above the centre of a lattice cell,  $B$  — above the centre of a lattice edge,  $C$  and  $D$  — above the positive and negative ion, respectively. The adatom interaction energy  $V$  was, according to [11], expressed as a sum Buckingham potential  $V_{6-\text{exp}}$ , and of third-order interaction energy  $V_3$ , connected with the presence of the crystal surface

$$V = V_{6-\text{exp}} + V_3. \quad (1)$$

Let us consider some models of the adsorption layer and calculate the dependence  $q_{\text{st}}(\theta)$ , for the Ar–NaCl system, as an example.

## 2. Method of calculation the adsorption heat

The isosteric heat of adsorption may be represented in the following form [12]:

$$-q^{\text{st}} = E^{\text{G}} - \frac{d}{d\theta} [\theta(X_m + E_{\text{tr}} + E_{\text{vib}} + \frac{1}{2} V)] + kT, \quad (2)$$

where:  $E^{\text{G}}$  — atom energy in the gaseous phase,  $E_{\text{tr}}$  and  $E_{\text{vib}}$  — adatom translational and vibrational energies, respectively,  $k$  — Boltzmann's constant,  $T$  — temperature. Assuming  $E_{\text{vib}}$  and  $E_{\text{tr}}$  be independent of  $\theta$  it may be shown [9], (see Appendix), that:

$$E^{\text{G}} - E_{\text{tr}} - E_{\text{vib}} + kT \simeq 0, \quad (3)$$

so

$$q^{\text{st}}(\theta) = \frac{d}{d\theta} [(X_m + \frac{1}{2} V)\theta], \quad (4)$$

for  $\theta \rightarrow 0$ :

$$q_0^{\text{st}} = X_m. \quad (5)$$

The interaction energy of an adatom and crystal  $X_m$  is a sum of dispersive energy  $X_m^{\text{d}}$ , repulsive energy  $X_m^{\text{r}}$  and electrostatic energy  $X_m^{\text{es}}$  (see e. g. [8]). We assume that  $X_m^{\text{d}}$  and  $X_m^{\text{r}}$  do not depend on  $\theta$ . According to (4) and (5) we have

$$q^{\text{st}} = q_0^{\text{st}} - X_m^{\text{es}}(\theta = 0) + \frac{d}{d\theta} [(X_m^{\text{es}}(\theta) + \frac{1}{2} V(\theta))\theta]. \quad (6)$$

Assuming the crystal electrostatic field  $F$  be constant in the adatom volume, we obtain the following expressions for  $X_m^{\text{es}}(\theta = 0)$  and  $X_m^{\text{es}}(\theta)$ :

$$X_m^{\text{es}}(\theta = 0) = -\frac{1}{2} \alpha F^2, \quad (7)$$

where  $\alpha$  is the adatom polarizability, and

$$X^{es}(\theta) = -\mu(\theta)F. \quad (8)$$

where  $\mu(\theta)$  is the induced dipole moment of an adatom.

To determine  $V(\theta)$  given by (1) we assumed

$$V_{6-\text{exp}} = \sum_i [CR_i^{-6} + B \exp(-bR_i)], \quad (9)$$

where  $R_i$  is the distance between interacting adatoms,  $C, B, b$  — constants of the Buckingham potential, taken after [13]. The magnitude  $V_3$  is, according to [11], equal to:

$$V_3 = V_{es} + V_{fl}, \quad (10)$$

where  $V_{es}$  denotes the electrostatic energy, and  $V_{fl}$  — the third-order fluctuation interaction energy.

Sinanoglu and Pitzer gave the following expression for  $V_{fl}$ :

$$V_{fl} = \sum_i SR_i^{-3}, \quad (11)$$

for

$$S = \frac{\Delta_0 \alpha}{4} |X^d(\bar{z})| (1 - 3 \cos^2 \varphi), \quad (12)$$

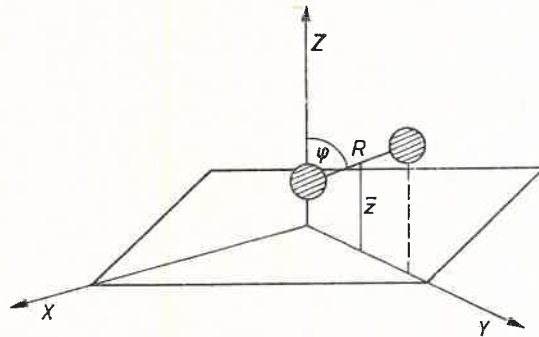


Fig. 1. Scheme of the adatom arrangement over the crystal surface, defining the variables in formula (12)

where  $\Delta_0$  is about 1.5, and the quantities  $\bar{z}$  and  $\varphi$  are defined in the Fig. 1. The constant  $S$  was calculated taking into account the mobility of adatoms in the following way. The localized adatoms, adsorbed on centres of the same type, have equal equilibrium distances from the crystal surface  $z_s$ , and equal energies of dispersive interactions with the crystal, so:  $\bar{z} = z_s$ ,  $X^d(\bar{z}) = X_m^d(z_s)$ . For the adatoms in the same layer  $\varphi = 90^\circ$  and the expression (12) takes the following form:

$$S = \frac{\Delta_0}{4} \alpha |X_m^d(z_s)|, \quad (13)$$

In order to estimate the constant  $S$  we assumed the mean distance between the interacting adatom pairs and surface to be constant (this permits one to take  $\varphi \simeq 90^\circ$ ) and the mean dispersional energy of mobile adatoms to be equal to  $\langle X_m^d \rangle$ . The value  $\langle X_m^d \rangle$  was calculated by averaging the adatom dispersional energy over all adsorption centre types. We assumed herewith, that the number of adatoms in the centres of a given type is proportional to the number of these centres on a unit area of the crystal surface. With these assumptions the constant  $S$  for the mobile adatoms, denoted by  $\langle S \rangle$ , may be calculated as

$$\langle S \rangle = \frac{A_0 \alpha}{4} |\langle X_m^d \rangle|. \quad (14)$$

The electrostatic interactions  $X_m^{es}$  and  $V_{es}$  will be considered together. Denoting by  $F_w$  the sum of  $z$ -components of the crystal electrostatic field and the field  $F_d$  generated by the dipole moments  $\mu$  (induced in the adatoms by the field  $F_w$ ) it may be written

$$\mu(\theta) = \alpha F_w(\theta), \quad (15)$$

$$F_w(\theta) = F - F_d(\theta). \quad (16)$$

In the centre of any adatom being in the given adatom layer the field intensity  $F_d(\theta)$  is

$$F_d(\theta) = \mu(\theta) \sum_{i=1}^{M\theta} R_i(\theta)^{-3}. \quad (17)$$

where  $M$  is the number of available adsorption centres in the first layer. From the above equations it follows:

$$F_w(\theta) = F [1 + \alpha \sum_{i=1}^{M\theta} R_i(\theta)^{-3}]^{-1}. \quad (18)$$

So the adatom electrostatic energy in the field  $F_w$  is

$$-\frac{1}{2} \alpha F_w^2 = X_m^{es}(\theta = 0) [1 + \alpha \sum_{i=1}^{M\theta} R_i(\theta)^{-3}]^{-2}. \quad (19)$$

The electrostatic interactions are taken into account only in the case of adsorption localized in  $C$  centres. When the most favourable are  $A$  centres, the values  $X_m^{es}$ , and thereby also  $V_{es}$ , are equal to zero [9]. This results from the fact, that the crystal electrostatic field in  $A$  centre (and similarly in  $B$  centre) equals zero. Also for the mobile layers, assuming that the number of adatoms in equally numerous  $C$  and  $D$  centres is the same, the mean electrostatic interaction energy is close to zero, because the crystal field intensity in centres  $C$  and  $D$  is nearly equal, but having opposite directions. For the mobile layers the adsorption heat was calculated with the help of the formula

$$q^{st}(\theta) = \langle q_0^{st} \rangle + \frac{d}{d\theta} (\frac{1}{2} V(\theta) \cdot \theta), \quad (20)$$

where  $q_0^{st} = \langle X_m \rangle$  is the initial adsorption heat, equal to the adatom-crystal energy averaged over all adsorption centres in the same way as  $\langle X_m^d \rangle$ .

### 3. Models of adsorption layers

#### A. Model of pseudolocalized ordered layer

In the pseudolocalized layers the adatoms are placed in the adsorption centres. On the (100) face of a NaCl crystal these centres form a square lattice of constant  $a\sqrt{2}$ . Model A is based on the assumption, that adatoms form a square lattice of "lattice constant"  $a^*$ , dependent on the coverage in the following way:

$$a^*(\theta) = \frac{a\sqrt{2}}{\sqrt{\theta}} \quad (21)$$

The lattices of centres and of adatoms are related to the coordinate systems  $(m, n)$  and  $(\alpha, \beta)$ , respectively, where the unit in both coordinates systems is the appropriate lattice constant. The coordinate systems  $(m, n)$  and  $(\alpha, \beta)$  have a common origin. In the lattice of constant  $a^*(\theta)$  the distance  $R_i$  between the adatoms having coordinates  $(0, 0)$  and  $(\alpha, \beta)$  is

$$R_i = a^*(\theta)r_i \quad (22)$$

where

$$r_i = \sqrt{\alpha^2 + \beta^2}; \quad \alpha, \beta = 0, \pm 1, \pm 2 \dots \quad (23)$$

except  $(\alpha, \beta) = (0, 0)$ .

The lattice constant for adatoms is equal to  $R_1$  which is the distance between the adatom at the point with coordinates  $(0, 0)$  and its nearest neighbour

$$R_i = a^* = \frac{a\sqrt{2}}{\sqrt{\theta}} \quad (24)$$

On the other hand,  $R_1$  in the system  $(m, n)$  is described by the following expression:

$$R_1 = a\sqrt{2} \sqrt{m^2 + n^2}; \quad m, n = 0, \pm 1, \pm 2 \dots \quad (25)$$

except  $(m, n) = (0, 0)$ .

By comparing (24) with (25) it can be seen, that the adatom lattices coherent with the centres lattice exist only in the case when  $\theta$  takes the following discrete values:

$$\theta = (m^2 + n^2)^{-\frac{1}{2}} \quad (26)$$

For low coverages we assumed the transitions between the subsequent values  $\theta(m, n)$  given by (26) to be continuous. With these assumptions it follows from (9)-(11) and (19) that

$$\begin{aligned} X^{\text{cs}}(\theta) + \frac{1}{2} V(\theta) &= -\frac{1}{2} C \left(\frac{2}{\theta}\right)^{-3} \sum_i r_i^{-6} + \frac{1}{2} B \sum_i \exp\left[-ba \left(\frac{2}{\theta}\right)^{\frac{1}{2}}\right] \\ &+ \frac{1}{2} S \left(\frac{2}{\theta}\right)^{-\frac{3}{2}} \sum_i r_i^{-3} + X_m^{\text{cs}}(\theta = 0) \left[1 + \alpha a^{-3} \left(\frac{2}{\theta}\right)^{-\frac{3}{2}} \sum_i r_i^{-3}\right]^{-2}, \end{aligned} \quad (27)$$

where constants  $C$  and  $S$  are expressed in units of  $a$ .

The sums appearing in (27) were computed numerically for 3600 adatoms what corresponds to the limit value  $\alpha, \beta = 30$ . These sums are defined by the following expressions:

$$\frac{1}{4} \sum_i r_i^{-6} = \sigma_3 = 1.165, \quad (28)$$

$$\frac{1}{4} \sum_i r_i^{-3} = \sigma_{3/2} = 2.254, \quad (29)$$

$$\frac{1}{4} \sum_i \exp(-ba^*(\theta)r_i) = \sigma \exp(\theta), \quad (30)$$

$$(1 + A\theta^{\frac{3}{2}})^{-2} - 3A\theta^{\frac{3}{2}}(1 + A\theta^{\frac{3}{2}})^{-3} = \sigma_{es}(\theta), \quad (31)$$

where

$$A = \alpha \sqrt{2} a^{-3} \sigma_{3/2}. \quad (32)$$

The sums  $\sigma_{exp}(\theta)$  and  $\sigma_{es}(\theta)$  were computed numerically, and for the considered low coverage range it may be assumed, that  $\sigma_{exp} = 0$ . The value  $\sigma_{es}(\theta)$  varies from 1 (for  $\theta = 0$ ) to 0.28 (for  $\theta = 1$ ). From (27) and (28)–(32), according to (6) the isosteric adsorption heat

TABLE I

$C$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	2904
$B \times 10^{-5}$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	2199
$b$	$[\text{\AA}^{-1}]$	3621 /
$S \times 10^{-2}$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	1147
$S \times 10^{-3}$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	9065
$w \times 10^{-2}$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	1786
$w' \times 10^{-3}$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	2196
$X_m^{es}(\theta = 0)$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	161
$X_m$	$\left[ \frac{\text{cal}}{\text{mol}} \right]$	2420

of Ar on NaCl may be calculated, which for the constants  $C$ ,  $B$ ,  $S$  and  $X_m^{\text{es}}$  given in Table I is equal to

$$q^{\text{st}}(\theta) = q_0^{\text{st}} - 3260 \theta^3 + 440 \theta^{\frac{3}{2}} + 162(\sigma_e(\theta) - 1) \left[ \frac{\text{cal}}{\text{mol}} \right]. \quad (33)$$

The dependence  $q^{\text{st}}(\theta) - q_0^{\text{st}} = \Delta q^{\text{st}}(\theta)$  is shown by the curve  $A$  in Fig. 2. The apparent small decrease of adsorption heat in the low coverage range is due to the prevailing repulsive interactions between adatoms, which form lattices of constants  $a^* < 3a$  at these coverages.

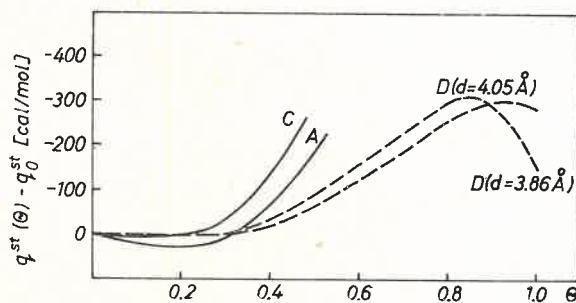


Fig. 2. Adsorption heat as a function of coverage for the Ar-NaCl system. The curves  $C$ ,  $A$  and  $D$  were obtained from the models of:  $A$  — localized, ordered layer (33),  $C$  — mobile, ordered layer (44),  $D$  — mobile, disordered layer, respectively

With increasing  $\theta$ , the attractive interactions increase faster than the repulsive ones, and the abrupt increase in  $q^{\text{st}}(\theta)$  occurs. In the range  $\theta < 0.3$  the above model is no longer valid, because with the prevailing attractive interactions the adatoms tend rather to form larger islands than the regular lattices.

### B. Model of localized, disordered layer

Similarly as in the previous model, it is assumed that adatoms are localized in favourable centres of adsorption, which form a square lattice of lattice constant  $a\sqrt{2}$ . The distribution of adatoms in centres is random. The distance  $R_i$  between the adatom having the coordinates  $(0, 0)$  and the  $i$ -th centre, expressed by  $r_i(\alpha, \beta)$  given by (23), is

$$R_i = a\sqrt{2} r_i. \quad (34)$$

The probability of finding an adatom in the  $i$ -th centre is equal to  $\theta$ , therefore

$$V(\theta) = V(\theta = 1) \cdot \theta, \quad (35)$$

and

$$F_d(\theta) = F_d(\theta = 1) \cdot \theta, \quad (36)$$

which gives

$$q^{\text{st}}(\theta) - q_0^{\text{st}} = -\frac{1}{2} C\theta\sigma_3 + S\sqrt{2}\theta\sigma_{3/2} + B\theta\sigma'_{\text{exp}} + X_m^{\text{es}}(\sigma'_{\text{es}} - 1), \quad (37)$$

where  $\sigma_3$  and  $\sigma_{3/2}$  are given by (28) and (29), while the value  $B\sigma'_{\text{exp}}$  calculated for the four nearest neighbours of an Ar adatom on the NaCl surface is

$$B\sigma'_{\text{exp}} = 4B \exp(-ba\sqrt{2}) \simeq 5002 \left[ \frac{\text{cal}}{\text{mol}} \right]. \quad (38)$$

The values  $\sigma'_{\text{es}}(\theta)$  were calculated using the formula

$$\sigma'_{\text{es}} = (1 + A\theta)^{-2} - 2A\theta(1 + A\theta)^{-3}, \quad (39)$$

with  $A$  given by (32). The values  $\sigma'_{\text{es}}(\theta)$  vary from 1 (for  $\theta = 0$ ) to 0.41 (for  $\theta = 1$ ). After putting the values from Table I to (37) we have

$$q^{\text{st}}(\theta) = q_0^{\text{st}} - 775\theta + 162(\sigma'_{\text{es}}(\theta) - 1) \left[ \frac{\text{cal}}{\text{mol}} \right]. \quad (40)$$

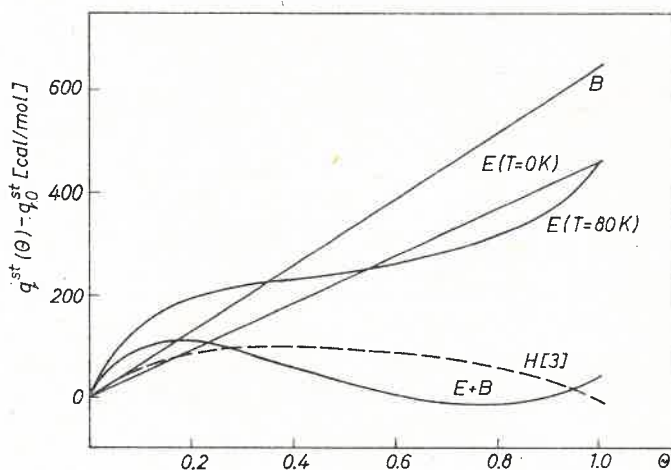


Fig. 3. Adsorption heat versus coverage for Ar-NaCl system. The curves  $B$  and  $E$  were obtained according to  $B$  and  $E$  models of the localized, disordered layer, from (40) and (58), respectively. The curve  $H$  was obtained by Hayakawa [3].

The above relation is shown by the line  $B$  in Fig. 3 the slope of which being approximately the interaction energy of an adatom with the adatom layer and crystal field. This model is valid for an ideal localized layer.

### C. Model of mobile, ordered layer

This model differs from model A only with the assumption of the mobility of adatoms. This results in a lower value of  $\langle S \rangle$  in comparison with  $S$  (cf. (13), (14) and Table I) and in neglecting the electrostatic interactions. Similarly as in model A the adatoms form now the lattice of a "lattice constant"

$$a^*(\theta) = \frac{d}{\sqrt{\theta}}, \quad (41)$$



where  $d$  is the distance between two neighbour adatoms at  $\theta = 1$  and corresponds to the effective diameter of the adatom, calculated from the density of liquid argon ( $d = 4.05 \text{ \AA}$ ). The distance  $R_i$  is

$$R_i = \frac{d}{\sqrt{\theta}} r_i, \quad (42)$$

where, on account of adatom mobility, condition (26) is not valid here any more. In a similar way as previously we obtain

$$\frac{d}{d\theta} (\theta^{\frac{1}{2}} V(\theta)) = -\frac{1}{2} C \left(\frac{d}{a}\right)^{-6} \sigma_3 \theta^3 + \frac{1}{2} \langle S \rangle \left(\frac{d}{a}\right)^{-3} \theta^{\frac{3}{2}} \sigma_{3/2} + \frac{1}{2} B \sigma_{\text{exp}}, \quad (43)$$

which for  $\theta < 0.5$  and  $\sigma_{\text{exp}} = 0$  gives  $q^{\text{st}}(\theta)$  in the form

$$q^{\text{st}}(\theta) = \langle q_0^{\text{st}} \rangle - 3890 \theta^3 + 348 \theta^{\frac{3}{2}} \left[ \frac{\text{cal}}{\text{mol}} \right], \quad (44)$$

represented by the curve  $C$  in Fig. 2. Model C, similarly like A, is valid only for low coverages, where the repulsive interactions prevail ( $V(\theta) > 0$ ). This is the condition for forming the regular adatom lattices.

#### D. Model of mobile, disordered layer

This model describes the adsorbed layer being a kind of a quasi-twodimensional gas. The adatoms are mobile, their distribution over the surface is random, and the mean distance  $\bar{R}_n$  of any adatom from its  $n$ -th neighbour is [14]

$$\bar{R}_n = d' \left( \frac{n}{\pi\theta} \right)^{\frac{1}{2}}. \quad (45)$$

Assuming, that at  $\theta = 1$  the distance between an adatom and its nearest neighbour is  $d$ , the constant  $d'$  is determined by the equation

$$\bar{R}_1(\theta = 1) = d = d' \pi^{-\frac{1}{2}}. \quad (46)$$

So

$$\bar{R}_n = d \left( \frac{n}{\theta} \right)^{\frac{1}{2}}. \quad (47)$$

In the considered model  $X_m^{\text{es}} = 0$ , then

$$\begin{aligned} \frac{1}{2} V(\theta) = & -\frac{1}{2} C \left(\frac{d}{a}\right)^{-6} \sum_n \left(\frac{\theta}{n}\right)^3 + \frac{1}{2} \langle S \rangle \left(\frac{d}{a}\right)^{-3} \sum_n \left(\frac{\theta}{n}\right)^{\frac{3}{2}} \\ & + \frac{1}{2} B \sum_n \exp\left(-bd \left(\frac{n}{\theta}\right)^{\frac{1}{2}}\right), \end{aligned} \quad (48)$$

In the above expression the first two sums are the values of Riemann's function  $\zeta(x)$  for  $x = 3$  and  $x = \frac{3}{2}$ , respectively. The last sum was computed numerically. Taking the appropriate values of constants from Table I and  $\zeta(3)$ ,  $\zeta(\frac{3}{2})$  according to [15], we obtain

$$q^{\text{st}}(\theta) = \langle q_0^{\text{st}} \rangle - 750 \theta^3 + 950 \theta^{\frac{3}{2}} + \frac{1}{2} B \sum_{\text{exp}} (\theta) \left( \frac{\text{cal}}{\text{mol}} \right), \quad (49)$$

where

$$\sum_{\text{exp}} (\theta) = \sum_n \left[ 1 + b \frac{1}{2} d \left( \frac{n}{\theta} \right)^{\frac{1}{2}} \right] \left[ \exp \left( -bd \left( \frac{n}{\theta} \right)^{\frac{1}{2}} \right) \right], \quad (50)$$

and

$$\sum_{n=1}^{\infty} n^{-3} = \zeta(3) = 1.202, \quad \sum_{n=1}^{\infty} n^{-\frac{3}{2}} = \zeta\left(\frac{3}{2}\right) = 2.612.$$

In Fig. 2 the dependence  $q^{\text{st}}(\theta) - q_0^{\text{st}}$  calculated from (49) is shown by two curves *D*: one for the value  $d$  calculated from the liquid density ( $d = 4.05 \text{ \AA}$ ) and the other where  $d$  is the equilibrium distance between free argon atoms ( $d = 3.86 \text{ \AA}$ ). The dependence (49) is characterized by a nearly stable increase of  $q^{\text{st}}(\theta)$  for  $0.3 < \theta < 0.9$ , and a small decrease for  $\theta = 1$ . The latter results from the repulsive interactions, appearing in the layer due to overlapping of the adatom electron shells. This decrease is more pronounced when the value  $d = 3.86 \text{ \AA}$  is taken (cf. Fig. 2). Equation (49) shows, how important are the third-order fluctuation repulsive interactions, which are the reason for the nearly constant value of  $q^{\text{st}}(\theta)$  in the coverage range  $0 < \theta < 0.3$ .

#### E. Model of localized, disordered layer

In the previously discussed models the number of interacting adatom pairs was estimated within the Bragg-Williams approximation. Now we shall use the quasi-chemical method in the given by Hill version [16] which assumes that adatoms are localized in the centres, forming a lattice of a constant  $a\sqrt{2}$ , and their configuration is defined only by the interactions with first and second neighbours in the layer. Let us consider the group of four centres being in edges of squares formed by the centres lattice.  $N$  adatoms are distributed in  $M$  centres in such a way, that there are  $M$  squares,  $N_i$  of which contain  $i$  adatoms (see Table II). So

$$M = N_0 + N_1' + N_2'' + N_2 + N_4, \quad (51)$$

$$4N = N_1 + 2N_2' + 2N_2'' + 3N_3 + 4N_4. \quad (52)$$

Similarly as before  $\theta = N/M$ ,  $w$  and  $w'$  denote the interaction energy of first and second neighbours. Taking  $u = \exp(-w/kT)$ ,  $u' = \exp(-w'/kT)$  and  $g(N_2', N_2'', N_3, N_4, N, M)$  equal to the number of arrangements of  $N$  molecules in  $M$  centres in such way, that there

TABLE II

Type of square	$\begin{array}{c} \cdot \cdot \\ \cdot \cdot \end{array}$	$\begin{array}{c} \odot \cdot \\ \cdot \cdot \end{array}$	$\begin{array}{c} \cdot \odot \odot \\ \cdot \cdot \end{array}$	$\begin{array}{c} \odot \cdot \\ \cdot \odot \end{array}$	$\begin{array}{c} \odot \odot \\ \cdot \odot \end{array}$	$\begin{array}{c} \odot \odot \\ \odot \odot \end{array}$
	0	1	2'	2''	3	4
Number of equivalent arrangements	1	4	4	2	4	1
Number of squares of this type	$N_0$	$N_1$	$N_2'$	$N_2''$	$N_3$	$N_4$
Energy of each square	0	0	$w$	$w'$	$2w+w'$	$4w+w'$

are  $N_2'$  squares of the type 2',  $N_2''$  squares of the type 2'',  $N_3$  squares of type 3 and  $N_4$  squares of the type 4, the grand partition function may be written in the following form:

$$\bar{E} = \sum_N \sum_{N_2'} \dots \sum_N g u^{\frac{N_2' + 2N_3 + 4N_4}{2}} u'^{N_2'' + N_3 + 2N_4} (a^0 \lambda)^N, \quad (53)$$

where  $a^0$  is a partition function of an isolated adatom and  $\lambda$  its absolute activity. Minimalization of the partition function gives the following expression for  $N_i(\theta)$ :

$$\begin{aligned} N_2' &= \frac{ct}{t+p+2s+3r-1}, & N_2'' &= \frac{-cp}{t+p+2s+3r-1}, \\ N_3 &= \frac{-cs}{t+p+2s+3r-1}, & N_4 &= \frac{cr}{t+p+2s+3r-1}, \end{aligned} \quad (54)$$

where:

$$t = 4\eta^2 u, \quad p = 2\eta^2 u^2, \quad s = 4\eta^2 u^2 u'^2, \quad r = \eta^4 u^4 u'^4, \quad c = M(1-4\theta), \quad (55)$$

and  $\eta$  being the real positive solution of the equation:

$$4\theta + 4\eta(4\theta - 1) + \eta^2(4u + 2u'^2)(4\theta - 2) + \eta^3 4u^4 u'^4(4\theta - 3) + \eta^4 u'^4(4\theta - 4) = 0. \quad (56)$$

The energy of an adatom layer calculated for one adatom is expressed in terms of  $N_i(M, \theta)$ , given by (51) in the following way:

$$\frac{1}{2} V(\theta) = \frac{1}{4M\theta} (N_2' w + N_2'' w + (2w + w') N_3 + (4w + 2w') N_4). \quad (57)$$

The adsorption heat is, according to (6) and (57), described by the expression

$$q^{\text{st}}(\theta) = q_0^{\text{st}} + \frac{d}{d\theta} \left\{ \frac{1}{4} [N_2'(\theta)w + N_2''(\theta)w' + N_3(\theta)(2w + w') + N_4(\theta)(4w + 2w')] \right\}. \quad (58)$$

The values  $w$  and  $w'$  used in the calculations are taken from Table I. In Fig. 3 the dependence (58) is shown in the form of curves labelled by  $E$ , the parameter being  $T$ . The curve  $q^{\text{st}}(\theta)$  obtained at  $T = 80$  K is similar to the dependence  $q^{\text{st}}(\theta)$  obtained by Orr [2] who based his calculations on the Wang model, taking into account only the

interactions between nearest neighbours ( $w' = 0$ ). The above model corresponds at  $T = 0$  K to an ideal localized layer described by model B. The curve  $E$  for  $T \rightarrow 0$  K tends to the straight line having the origin and end points identical with the curve  $E(T = 80$  K). Comparing this curve with the line  $B$  (Fig. 3) and bearing in mind that the slopes of these lines are the measure of the interaction energy in layers, it can be seen how large is the contribution of the interaction energy neglected in the model  $E$  between the farther neighbours to the value of  $q^{st}(\theta)$ . This energy is of the same order of magnitude as the electrostatic and third-order fluctuation energy. Therefore, the models proposed by Roberts and Orr [7], a by Hayakawa [3], where the van der Waals interactions of adatoms are calculated according to the Wang model [17], and the electrostatic interactions based on a model analogous to the presented model B, should be appreciated negatively, because these models must not be combined.

#### B+D. Model of unstable layer

As results from the above considerations none of the previously discussed models gives  $q^{st}(\theta)$  in accordance with experiment. Such accordance can be obtained assuming the following model. We suppose that when the coverage increases from zero, the layer once localized becomes more and more mobile, owing to the stronger interactions between adatoms. It leads, for the coverage increasing from zero to some critical value  $\theta_1$ , to the spontaneous transition to the mobile layer. This transition corresponds to the phase transition of the type quasi-two dimensional crystal — quasi-two dimensional gas. A detailed theoretical description of such a transition exceeds the framework of this paper, being a separate problem. Assuming however, that such a transition takes place in

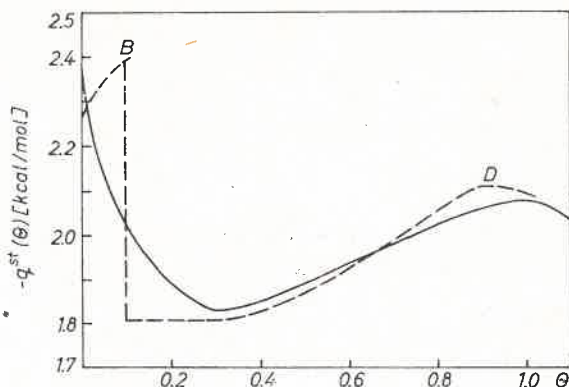


Fig. 4. Dependence of adsorption heat on coverage for Ar adsorbed on the (100) face of NaCl. The full line denotes the experimental data of Jackson [4], the dashed line — calculated according to B+D model.

the considered system, the adsorption heat for  $\theta < \theta_1$  is given by expression (37) (model B), and for  $\theta > \theta_1$  by expression (49) (model D). Thus we obtained the dependence  $q^{st} = q^{st}(\theta)$ , represented by the curve  $B$  and  $D$  in Fig. 4, where the critical value  $\theta_1$  was arbitrarily taken, because the present model is too oversimplified to estimate this value more accurately.

#### 4. Comparison of theoretical and experimental dependences of adsorption heat on coverage

None of the simple models A÷E exhibits the changes of the adsorption heat in the low coverage range, which could be compared with the experimentally observed decrease of  $300\text{--}600 \frac{\text{cal}}{\text{mol}}$ . A small decrease of 30 and  $10 \frac{\text{cal}}{\text{mol}}$  is given by models A and C, respectively (cf. Fig. 2). These models are however rather rough and hold only for  $\theta < 0.3$ . A very similar, like in model C, nearly constant value of  $q^{\text{st}}(\theta)$  for  $\theta < 0.3$  was also obtained based on model D. The mobile character of the layer in model D, where the electrostatic interactions are compensated, also explains the lack of differences in the character of adsorption on NaCl and KCl. It could not be explained by the assumption of localized adsorption, because the favourable adsorption centres on NaCl are, unlike on KCl, in the non-zero electrostatic field of a crystal.

On account of a great similarity of the considered adsorption systems, the results analogous to those obtained for Ar on NaCl may be obtained for all systems, where the adatoms adsorbed on the clean crystal surface are pseudolocalized. The decrease of adsorption heat for the unstable layer model, is equal to

$$q_0^{\text{st}} - q^{\text{st}}(\theta \simeq \theta_1) \simeq q_0^{\text{st}} - \langle q_0^{\text{st}} \rangle, \quad (59)$$

according to (5) and (20) corresponds to  $X_m - \langle X_m \rangle$ . For different adsorption systems it gives values 300 to  $500 \frac{\text{cal}}{\text{mol}}$ , which are very close to the experimental values of this decrease. This model, moreover, gives the relation  $q^{\text{st}}(\theta)$  which, compared with the experimental adsorption heat for Ar on sublimated and hence exhausted from the chemisorbed water NaCl, shows for  $\theta > 0.3$  good agreement with the experimental curve (Fig. 4). The theoretically obtained small maximum of  $q^{\text{st}}(\theta)$  at  $\theta \simeq \theta_1$  could be omitted in experiments, the accuracy of which is  $\pm 100 \text{ cal/mol}$ . According to the B+D model the maximum of this type (observed [5] for Kr on alkali chlorides) should appear for all considered systems, but its position can depend on the kind of adatom. Unfortunately we had no possibility of discussing this problem, because the majority of the experimental data concerns Argon as an adsorbate. The measurements of  $q^{\text{st}}(\theta)$  for Xe on NaCl [1] determined the adsorption heat only for  $\theta > 0.2$  and like in the majority of papers, the curve  $q^{\text{st}}(\theta)$  for low coverages is only the extrapolation of this curve for higher coverages. So the lack of experimental data does not permit one to check the above conclusions.

The validity of the B+D model could be confirmed by the experiment showing the existence of the first maximum, e. g. for Xe on sublimated iodide crystals, and stating the lack of initial rapid decay of the adsorption heat for the fluorides as adsorbents, because in the case of fluorides, where according to (59)  $X_m \simeq \langle X_m \rangle$ , such a decrease should not appear.

All the numerical calculations were performed at the Institute of Informatics of the Wrocław University on an ODRA 1204 computer. The authors wish to thank Mrs. J. Pękalska for preparing the programs.

## APPENDIX

Below the motivation of relation (3) will be given. In the case of rare gas in the temperature about 80 K and at low pressure one can assume that  $E^G = 3/2 kT$ . This allows for rewriting the relation (3) in the form:

$$E_{tr} + E_{vib} \simeq 5/2 kT. \quad (A1)$$

In the localised layers  $E_{tr} = 0$  and the vibration energy of adatom round its equilibrium position is given by [12]:

$$E_{vib} = \frac{h\nu_{\perp}}{e^{kT} - 1} + \frac{2h\bar{\nu}_{\parallel}}{e^{kT} - 1} + 1/2 h\nu_{\perp} + h\bar{\nu}_{\parallel}, \quad (A2)$$

were  $\nu_{\perp}$  and  $\bar{\nu}_{\parallel}$  are the vibrational frequencies of adatom in the adsorption centre, normal and parallel to the substrate surface, respectively. Moreover the parallel vibrations were averaged on different directions in the plane of substrate.

In the case of mobil layer  $E_{tr} = kT$ , and  $E_{vib}$  is given by:

$$E_{vib} = \frac{h\bar{\nu}_{\perp}}{e^{kT} - 1} + \frac{1}{2} h\bar{\nu}_{\perp}. \quad (A3)$$

The  $\bar{\nu}_{\perp}$  in the Eq. (A3) denotes the mean frequency of normal vibrations of adatom averaged over all adsorption centres in the rate 2:4:1:1, which determines the proportions of numbers of the centres *A*, *B*, *C* and *D* on the (100) surface of the crystal.

In order to calculate the frequencies of adatoms vibrations, we assume that the interaction energy curve of adatom with substrate one can approximate near the equilibrium position by parabola. This assumption allows to calculate the quasi-elastic force coefficient and the zeroth frequencies of vibration of adatom. The frequencies of normal vibrations of adatom in the centres *A*, *B*, *C* and *D* were computed from the interactions energy dependence on adatom to adsorbate distance. The frequencies of parallel vibrations were estimated from the crosssections of surfaces of the minimum interaction energy between adatom and crystal along some distinct directions. Such crosssections were obtained for several adsorption systems using the method described in [2, 8].

For example, for systems Ar-NaCl and Ar-KCl the following values of  $E_{vib}$  were obtained [9]:

(i). localized layer ( $E_{tr} = 0$ )

$$E_{vib_{NaCl}} \simeq 0.339 \times 10^{-13} \left[ \frac{\text{erg}}{\text{atom}} \right] \simeq 3.1kT,$$

$$E_{vib_{KCl}} \simeq 0.230 \times 10^{-13} \left[ \frac{\text{erg}}{\text{atom}} \right] \simeq 2.1kT, \quad (A4)$$

(ii). mobile layer ( $E_{tr} = kT$ )

$$E_{vib_{NaCl}} \approx 0.114 \times 10^{-13} \left[ \frac{\text{erg}}{\text{atom}} \right] \approx 1kT,$$

$$E_{vib_{KCl}} \approx 0.115 \times 10^{-13} \left[ \frac{\text{erg}}{\text{atom}} \right] \approx 1kT. \quad (\text{A5})$$

The comparison of (A4) and (A5) with (A1) shows that Eq. (A1) is fulfilled with the accuracy  $0.5 kT$ , which is about 5–10% of the isostheric adsorption heat value.

#### REFERENCES

- [1] S. Ross, H. Clark, *J. Am. Chem. Soc.* **76**, 4291 (1959).
- [2] J. W. C. Orr, *Trans. Faraday Soc.* **35**, 1247 (1939).
- [3] T. Hayakawa, *Bull. Chem. Soc. Jap.* **30**, 124, 236, 243, 332, 337 (1957).
- [4] D. J. Jackson, B. W. Davis, *J. Colloid Interface Sci.* **47**, 499 (1974).
- [5] T. Takaishi, *J. Chem. Soc. Faraday Trans. I*, **68**, 801 (1972).
- [6] D. M. Young, *Trans. Faraday Soc.* **50**, 838 (1954).
- [7] J. K. Roberts, J. W. C. Orr, *Trans. Faraday Soc.* **34**, 1346 (1938).
- [8] S. Jakubowicz, K. Wojciechowski, *Acta Phys. Pol.* **A40**, 351 (1971).
- [9] J. M. Rogowska, Doctoral dissertation Mat. Phys. Chem. Faculty, Wrocław 1976.
- [10] G. C. Benson, P. J. Freeman, E. J. Dempsey, *J. Chem. Phys.* **39**, 302 (1963).
- [11] O. Sinanoglu, K. S. Pitzer, *J. Chem. Phys.* **19**, 1279 (1960).
- [12] S. Ross, J. P. Olivier, *On Physical Adsorption*, John Wiley, Inc., York 1964.
- [13] E. A. Mason, W. E. Rice, *J. Chem. Phys.* **22**, 522, 843 (1954).
- [14] M. Kendall, P. A. Moran, *Geometrical Probabilities*, Chap. 2, Pergamon Press, London 1963.
- [15] E. Janke, F. Emde, *Tablice funkcji*, Moskwa 1949.
- [16] T. L. Hill, *J. Chem. Phys.* **18**, 988 (1950).
- [17] J. S. Wang, *Proc. Roy. Soc.* **A161**, 127 (1937).