23: 71 (100), 93 (77), 41 (70), 69 (65), 55 (57,5), 80 (34), 83 (31), 121 (27), 67 (25,5), 68 (24), 154 (M^+, 2).

24: 81 (100), 80 (86), 43 (64), 41 (52), 69 (47), 95 (44), 71 (39), 93 (38), 121 (32), 82 (32), 154 (M^+, 7).

25: 71 (100), 93 (67), 111 (62), 55 (44), 41 (38), 69 (34), 83 (33), 86 (32), 154 (M^+, 30), 58 (28).

27: 59 (100), 43 (49,5), 93 (49), 95 (43,5), 121 (43), 136 (42), 81 (32,5), 41 (23), 68 (19), 67 (18), 154 (M^+, 1).

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25. The Interaction of Argon with Sulfur Surfaces. Experimental and Calculated Variations of the Adsorption Potential with Surface Coverage

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(15. X. 74)

Summary. The adsorption potentials of argon on the (111), (001) and (110) planes of rhombic sulfur have been calculated for a total of 818 sites, using an intermolecular potential of the *Lennard-Jones* (6:12) type with the *Kirkwood-Müller* expression. Direct summation over the nearest 100–150 atoms of the solid was used. There is a good agreement between the experimental and the calculated values of the adsorption potential, as a function of the surface coverage.

1. Introduction. – Physical adsorption of various gases on rhombic sulfur has been reported recently [1]. By using the method of *Ross & Olivier* [2], it was shown that the surface was not very homogeneous. In the present communication, we wish to report on this particular aspect, by comparing the experimental adsorption potentials of argon on sulfur with theoretical calculations based on a pair-potential of the *Lennard-Jones* type. From crystallographic data and from the knowledge of frequent crystal planes, it is possible to compute the minima of the adsorption potentials on a large number of sites, by direct summation over the nearest 120–140 sulfur atoms. This approach is similar to the work of *Ricca* [3], on adsorption of noble gases on solid xenon.

2. Results and discussion. – The interaction between simple and non-polar molecules can be described by the *Lennard-Jones* (or 6:12) potential [4]

$$\varphi(r) = - C/r^6 + B/r^{12} \tag{1}$$

where C and B are constants depending on the molecules considered. This pair-potential can also be written in the form

$$\varphi(r) = - C\,(1/r^6 - r_0^6/2\,r^{12}) \tag{2}$$

where r_0 is the distance corresponding to the minimum of the potential. In the case of interactions between different particles, A and B, the corresponding value of r_0 is given with a good approximation by the combining rule

$$r_{0AB} = \tfrac{1}{2}\,(r_{0A} + r_{0B}). \tag{3}$$

Various relations have been proposed for the calculation of C [4]. One of them is the expression proposed by *Kirkwood & Müller*

$$C_{KM} = 6\,mc^2\,\alpha_A\alpha_B/(\alpha_A/\chi_A + \alpha_B/\chi_B) \tag{4}$$

where m is the mass of the electron, c the speed of light, and α and χ represent the polarisabilities and the magnetic susceptibilities of particles A and B. This relation has been used successfully for the calculation of adsorption potentials on graphite [5]. Moreover, in the case of Ar, Kr and Xe, there is a good agreement between the values of C_{KM} and the values of C derived from empirical fits (virial coefficients) to *Lennard-Jones* potentials [4] [6]. Consequently, relation (4) was retained, and argon, which had been investigated previously, was an obvious choice [1].

Using the values from standard tables, and a polarisability $\alpha = 30 \cdot 10^{-25}$ cm^3 for sulfur (derived from the value for H_2S, and in agreement with theoretical calculations [7]), it is found that $C_{KM} = 8504$ kJ/mol Å^{-6} for the argon-sulfur pair-potential. For argon the value $r_0 = 3.87$ Å [8] was chosen, against 3.69 Å for sulfur. This represents the shortest distance between two atoms of neighbouring S_8 rings in the unit cell of rhombic sulfur [9]. Relation (3) leads to a value of 3.78 Å for the argon-sulfur pair-potential.

Orthorhombic sulfur crystallizes in space group Fddd [9]. The unit cell contains 128 atoms and has dimensions a = 10.44, b = 12.85 and c = 24.37 Å. According to *Niggli* [10], the most common faces of the crystals are (111) and (001). The first is a cleavage plane and the second is a face of the unit cell. According to *Buerger* [11], the (110) plane (parallel to the S_8 rings) is also well represented, although it is only listed in fifth position by *Niggli*. It was decided to use these three planes for the calculation of adsorption potentials.

The individual planes consist of elementary surfaces, limited by the unit cells, and which are related by simple symmetry operations. Therefore, it is sufficient to consider only one such element for each plane, in order to characterize the whole plane. The portion limited by one unit cell is divided into an array of points having coordinates m and n along two sides (m, n = 0,1,2, ... Å). They define the centres of equal adsorption sites. For the planes (111), (001) and (110), there are respectively 250, 143 and 425 such sites.

The adsorption potentials were calculated by using the crystallographic data of *Abrahams* [9] and a computer (*IBM* 1130). For each site, the argon atom was first placed at a perpendicular distance $Z = 6$ Å above the surface, and all sulfur atoms to be found within a radius of 15 Å were listed (usually 100–150, within the original

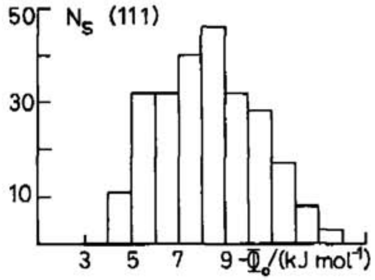

Fig. 1. *Distribution of adsorption sites on plane (111)*

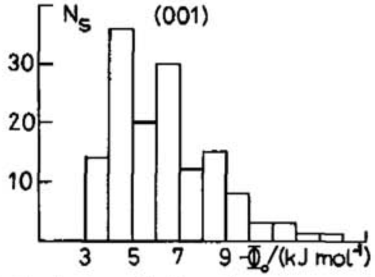

Fig. 2. *Distribution of adsorption sites on plane (001)*

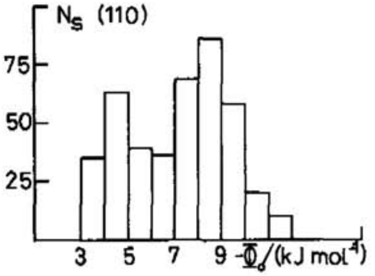

Fig. 3. *Distribution of adsorption sites on plane (110)*

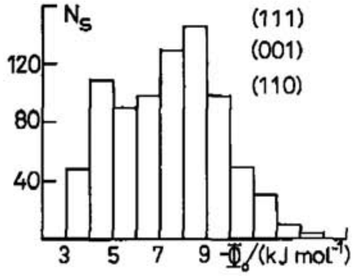

Fig. 4. *Distribution of all adsorption sites* (total of 818 sites)

unit cell and its nearest neighbours). The ad-atom was then brought closer to the surface, by steps of 0.2 Å along the normal. For each step, the adsorption potential

$$\Phi(Z) = \sum_j - C(1/r_j^6 - r_0/2\, r_j^{12}) \tag{5}$$

was computed by direct summation over the j listed atoms. Finally, the minimum value of the potential for the site, Φ_0, was obtained by interpolation. Fig. 1–3 show the distribution of the sites for the three planes, according to their adsorption energies Φ_0 (intervals of 1 kJ/mol). In view of its two distinct maxima, the distribution for plane (110) seems to be a combination of the other two. Fig. 4 gives the distribution for all 818 sites.

The variation of Φ_0 with the degree of surface coverage $\Phi_0(\theta)$ can be calculated easily, if one assumes that the surface is covered in the order of decreasing adsorption energies. This can be compared with the experimental values derived from the isosteric heats of adsorption of argon on sulfur [1]. The relation is

$$Q^{st}(\theta) = \Phi_0(\theta) - (3/2)RT + E_{lat} \tag{6}$$

if the small vibration on the surface is neglected. The lateral interaction energy between the adsorbed molecules is given by [2]

$$E_{lat} = -2\,\theta\,\alpha/\beta \tag{7}$$

where α and β are the two-dimensional equivalents of the Van der Waals constants a and b.

The method of *Ross & Olivier* gave a value of 8.5 kJ/mol for the adsorption energy on the average site, which suggests an important contribution of the (111) plane, in agreement with the classification of *Niggli* [10]. The experimental values also suggest that there is some contribution from the other two planes, which have more sites of energy in the range 3–5 kJ/mol. Fig. 5 shows the experimental values of $\Phi_0(\theta)$ and

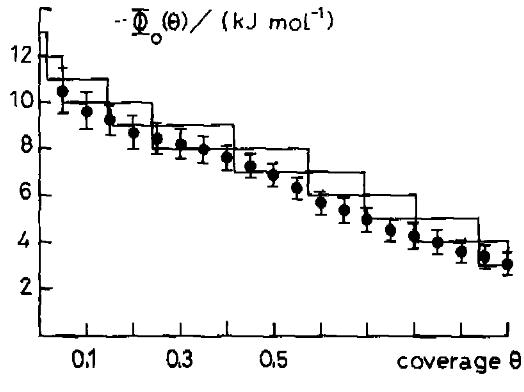

Fig. 5. *Experimental (●) and calculated adsorption potentials* (rectangles) *as functions of the surface coverage.* The calculated values include the (111), (001) and (110) planes. (total of 818 sites).

the values calculated from the 818 sites, corresponding to the three elementary surfaces (this is of course an arbitrary combination). The agreement is surprisingly good.

It is hoped that experimental results will be obtained in the future for the adsorption on selected faces of single crystals, such as the (001) plane. This will provide an even better test for the theoretical model.

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26. Crustaxanthin-tetraacetat und weitere Tetraester des Crustaxanthins

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Summary. It is shown that the acetylation of synthetic crustaxanthin with acetic anhydride in pyridine yields the tetraacetate and not the diacetate as claimed. Even more voluminous reagents such as bis-trimethylsilylacetamide, pivaloyl or 1-adamantoyl chloride give rise to tetraester. The identification of these derivatives was accomplished through spectral data.

Crustaxanthin (β,β-Carotin-3,4,3',4'-tetrol) liegt in der Natur als Tetraester vor [1]. Dem daraus durch Verseifen erhältlichen Tetrol **1** wird aufgrund seines chemischen Verhaltens und seiner physikalischen Eigenschaften eine bis-*trans*-äquatoriale Konfiguration der Hydroxylgruppen zugesprochen [1]. Das gleiche Isomere bildet auch den überwiegenden Anteil in synthetischem Crustaxanthin (siehe exper. Teil).

Trotz der Tatsache, dass das Crustaxanthin in der Natur als Tetraester vorkommt, führt die Reaktion mit Acetanhydrid in Pyridin anscheinend nur zu 3,3'-O-Diacetylcrustaxanthin (**2**), wobei die Ausbildung innermolekularer Wasserstoffbrücken für die nur partielle Acetylierung verantwortlich gemacht wird [2] [3]. Man findet in der Literatur aber auch Hinweise auf die Bildung eines Tetraacetats [4], das allerdings an

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1) Autor, an den allfällige Anfragen zu richten sind.

2) Post-doctoral fellow, *F. Hoffmann-La Roche* & Co. AG, Basel.