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The Gas–Solid Interface
The Interaction of Argon, Xenon and Sulfur Hexafluoride with Rhombic Sulfur

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Summary. Further theoretical calculations have been carried out for the adsorption potentials of Ar on the (011) face of rhombic sulfur, and for Xe and SF_6 on the (011) and (111) faces. By using the same sites for the three molecules and pair-potentials of the *Lennard-Jones* type, specific scaling factors were found. These are constant within 5–10%, for each adsorbate, and therefore the distribution curves of the adsorption potentials of simple molecules on crystalline sulfur are related in a simple way. The influence of the size of the molecule and the local geometry of the surface is also discussed.

1. Introduction. – The present series of investigations [1] [2] is concerned with the interaction of simple gases with the surface of crystalline sulfur. The choice of sulfur was dictated by the fact that it is a molecular solid, with only one atomic species, and which has a well defined structure. Unlike graphitic surfaces, a traditional source of informations in the field of gas-solid interactions, sulfur has a heterogeneous surface, as a consequence of its more complex structure [2]. It is therefore a useful intermediate in the systematic investigation of adsorption forces and potentials, although more complicated cases have already been dealt with. The adsorption energy of neopentane in a zeolite of the NaX type has for example been calculated by *Kiselev et al.* [3], but the method which was used involves a number of assumptions which are related to the geometrical and chemical complexity of the system. Informations about geometrical factors only, can therefore be obtained from systems like the present ones, or from the adsorption of rare gases on xenon [4] [5], for example.

The interaction between a gas molecule and a surface is the sum of intermolecular pair-potentials. These consist of an attractive part, which prevails at relatively large distances, and of a repulsive part which occurs at small distances. The pair-potential goes through a minimum at an intermolecular distance close to the sum of the molecular radii of the particles. Various theoretical approaches exist for the calculation of intermolecular energies [5–9], and they are periodically reviewed [10] [11].

Quantum mechanical calculations have been used successfully for the pair-potentials of rare gases [10] [11], but prospects for accurate results with larger molecules still seem bleak. In the case of the gas-solid interface, on the other hand, the adsorption of He, Ne and Ar on solid Xe has been dealt with successfully from the point of view of quantum mechanics [5].

The problem of adsorption potentials can be treated on various levels of sophistication, depending on the approach and on the system which are chosen. It is our opinion, that the choice depends essentially on the use to be made of the model, and on the comparison with experimental data.

In the traditional approach, it is convenient to consider the various possible contributions to the intermolecular pair-potential $\varphi(r)$. If dispersion forces are

present only, the so-called *Lennard-Jones*- or (6-12)-potential [5–9] may be used with a good approximation,

$$\varphi(r) = -C\,[1/r^6 - r_0^6/2r^{12}]. \qquad (1)$$

It is a two-parameter equation, where r_0 represents the intermolecular distance corresponding to the minimum of the potential, and C is a constant depending on the nature of the particles.

More terms can be added, if necessary, for specific interactions involving dipoles and multipoles. The so-called *6-exponential* potential [6–9], containing 3 parameters, as well as more elaborate versions of it, have been used by authors like *Kiselev* [9] for the calculation of adsorption potentials. It would also be possible to use the refined pair-potentials proposed in the past few years, and reviewed by *Maitland* & *Smith* [11]. However, in the case of simple systems like the ones reported here, the use of a potential like (1) seems preferable. Firstly because no specific interactions are to be expected with sulfur, and secondly because of the limited number of independent parameters required for the *ab-initio* calculations of the potentials. This approach is also justified by the good agreement found previously between the experimental and calculated values for the adsorption potentials of argon on sulfur [2].

2. Argon and the (011) face of α-sulfur. – According to *Niggli* [12], the most common faces of rhombic sulfur are (111), (001), (113), (011) and (110). The first two and the fifth have already been investigated, and found to be heterogeneous [2]. A study of the (011) face will therefore complete the picture. As before, the elementary surface limited by one unit cell was divided into an array of equidistant adsorption sites (308), corresponding to patches of 1 Å^2. For each site, the adsorption potential of argon $\Phi(Z)$ and its minimum were calculated by direct summation of the pair potential (1) over the nearest 120–140 sulfur atoms

$$\Phi(Z) = -\sum_j C\,[1/r_j^6 - r_0^6/2r_j^{12}]\,. \qquad (2)$$

As before, the expression of *Kirkwood-Müller* was used for C. Fig. 1 shows the distribution of the minima of the adsorption potentials, Φ_0, for the 308 sites of the (011) face. As before, intervals of 1 kJ/mol were used. The distribution is similar to the one found for the (001) face, which also has a maximum near −5 kJ/mol.

The choice of adsorption sites of 1 Å^2 is quite sufficient for a good sampling of the surface: if one uses only every second site, or even one in three, the distribution still resembles the one given in the figure. This is also true for the other faces. By considering an increasing number of sulfur atoms around a given site, for the summation of type (2), the nearest 100–150 atoms are quite sufficient. The values of $\Phi(Z)$ show virtually no increase beyond the first 100 atoms. Typical adsorption potentials for argon on the (011) and (111) faces of rhombic sulfur are shown in Fig. 2. They were

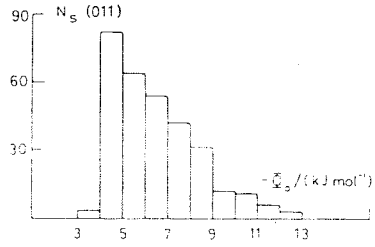

Fig. 1. *Distribution of adsorption energies (Ar) on the (011) face*

computed at intervals of 0.2 Å along Z, the normal to the sites considered, and starting at 6 Å from the plane. It is seen that deep potentials correspond to a closer approach to the surface, and even to a slight penetration into the solid in a few cases. This behaviour is in full agreement with the calculations of *Steele & Ross* [5] [13] for the adsorption potentials over different sites, in the case of a simple cubic lattice.

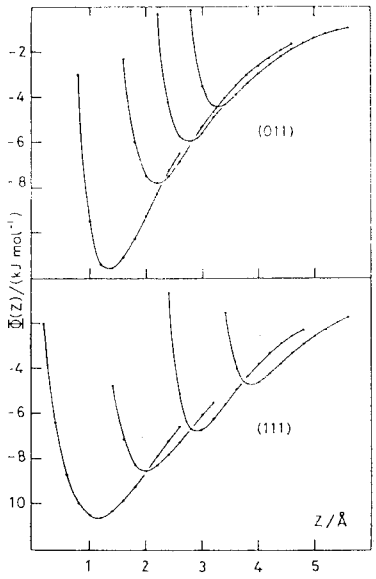

Fig. 2. *Typical adsorption potentials of Ar on the (011) and (111) faces*

3. Extension to other simple molecules. – The general procedure was repeated for xenon and sulfur hexafluoride on the (011) and (111) faces, by using the same sites as before. The two faces were selected in view of their different energy distributions (maxima near −5 and −9 kJ/mol respectively, for Ar). Xe and SF_6 are also larger than argon [14] [7], with r_o values of 4.12 and 4.90 Å for the pair-potentials with sulfur, against 3.78 Å for Ar [2].

On both faces, the pattern found for Ar was followed locally by Xe and SF_6, with specific scaling factors for Φ_o. These factors showed variations around the average values given in the Table. The fluctuations were larger for SF_6 than for Xe, and this reflects the influence of the size of the molecule and of the local geometry, on the direct lattice summations. The comparison of the adsorption energy maps for the different molecules clearly shows that the gradients are smoother for SF_6 than for Xe and Ar, in the case of neighbouring sites with strong differences. It is also found that the high-energy sites are reduced, as the size of the adsorbate increases. This means that the solid appears to be slightly more homogeneous in the case of large molecules, which is consistent with the larger equilibrium distances from the surface. This effect has also been found for the simple cubic lattice [5]. As a result, the energy distribution function for SF_6 is slightly curtailed on the high-energy side, with respect to argon. The relatively low adsorption energies found for sulfur hexafluoride are consistent with the weak adsorption of this gas by sulfur, as found experimentally at 228 K [1].

The local deviation from the average values of the scaling factors tend to cancel for the whole surface, with the exception of the high-energy sites. The energy distribution curves of Ar, Xe, SF_6, and other simple molecules on the various faces of sulfur are related by straightforward transformations (scaling factors along the Φ_0 axis, and constant areas under the curves).

The scaling factors, relative to Ar, may be compared with the predictions for a continuous and flat solid, having a uniform density of ϱ atoms per unit volume. This is the simplest possible case, corresponding in fact only to graphite-like surfaces. For such a model, the minimum of the adsorption potential is the same everywhere for a particle A [6] [8],

$$\Phi_{0\,A} = -\varrho\pi C_A/9\ Z_{0A}^3 \tag{3}$$

where $Z_{0A} = 0.765\ r_{0A}$ [6]. C_A is a specific constant for the interaction between A and the solid, which can be calculated by the *Kirkwood-Müller* equation [2] [6] [8] or by similar relations. For two particles, A and B, eq (3) leads to the ratio

$$\Phi_{0A}/\Phi_{0B} = (C_A/C_B)\,(r_{0B}/r_{0A})^3\ . \tag{4}$$

The scaling factors relative to argon, calculated by (4), are given in the Table. They are slightly larger than the values obtained from the direct lattice summations, which is not surprising in view of the simplicity of the model. However, there appears to be some consistency between the two methods.

Table. *Scaling Factors for Φ_0 on Sulfur, relative to Argon*

	(011)	(111)	eqn (3)
Xe	1.68 ± 0.04	1.68 ± 0.07	1.83
SF_6	0.93 ± 0.07	0.92 ± 0.11	1.10

It is hoped that the present results for the adsorption energy distributions can be compared at a later stage with the experimental results from adsorption by selected faces of crystalline sulfur.

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