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The Gas-Solid Interface
The Adsorption of Nitrogen, Argon, Neopentane, Sulfur Dioxide, Carbon Dioxide and Sulfur Hexafluoride on Rhombic Sulfur

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Summary. Physical adsorption of the title compounds on rhombic sulfur of 0.4 to 0.5 m^2/g is reported. The isotherms are of type II for N_2, Ar and C_5H_{12}, of type III for SO_2 and CO_2, and linear for SF_6. There is no hysteresis. The method of *Ross & Olivier* shows that the surface is relatively heterogenous ($\gamma = 17$). Isosteric heats of adsorption and c values of the B.E.T. equation are also reported.

1. Introduction. – Physical adsorption of gases on sulfur has received little attention in the past, and only the adsorption of nitrogen near 78 K has been reported so far [1]. Sulfur has a non-conducting surface of low energy, with adsorption properties resembling those of molecular solids and certain polymers. In the present paper, we wish to report on general properties of this surface, corresponding to relative pressures p/p_0 between 0.05 and 0.8 approximately. Adsorption at low pressures will be dealt with later, in connection with studies of the morphology of the surface.

2. Experimental. – The adsorption measurements were carried out volumetrically, as described earlier [2], and with gases of high purity. The main adsorbent was rhombic sulfur (S_F) obtained by sublimation (*Siegfried* AG, Zofingen, $> 99.8\%$). The solid was ground manually in a mortar and passed through a nylon mesh of 60μ. This type of solid contains mainly rhombic sulfur S_α, and some amorphous forms such as S_μ, S_λ and S_ω [3]. Samples of higher crystallinity (S_C) were also prepared at a later stage, by recrystallisation in CS_2 (*Merck*, p.a. $> 99.5\%$) between $+30$ and $-30°$, followed by drying under vacuum for 100 h and manual grinding.

In view of the low surface area of the solid (0.4–0.5 m^2/g), samples of 25–30 g had to be used. They were initially outgassed at room temperature (10^{-4} to 10^{-5} Torr) for 3 days before a series of runs, and for 24–48 h between runs. No retention of gases was observed in the course of the adsorption measurements described below. The gases released by the surface during outgassing in the range of 10^{-2} to 10^{-4} Torr, were analysed in a mass-spectrograph and shown to have the same composition as atmospheric air. No volatile sulfur compounds were found.

In order to prevent contamination of the solid by mercury, a low-viscosity silicon oil with a vapour pressure of 10^{-9} Torr was used as an intermediate between the solid and the manometer.

A slight contamination became visible only after 10–15 days. At a later stage, *Pirani* and transducer gauges were used exclusively, in order to avoid the use of mercury. The same results were found under these conditions, as before.

3. Results and discussion. – The various isotherms for adsorption on S_F are shown in Fig. 1–5. They are of type II for nitrogen, argon and neopentane, of type III for sulfur dioxide and carbon dioxide, and almost linear for sulfur hexafluoride. The results for SO_2 and CO_2 are especially surprising, and reminiscent of water adsorption on graphite.

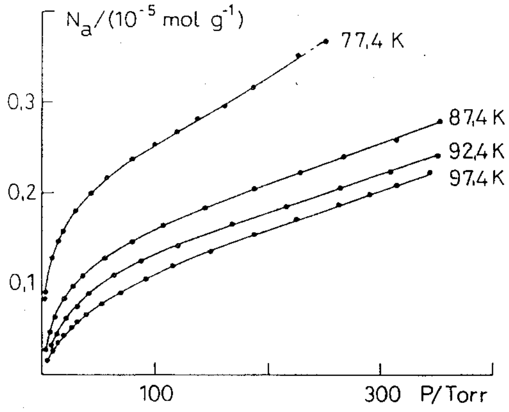

Fig. 1. *Adsorption of nitrogen on rhombic sulfur* S_F

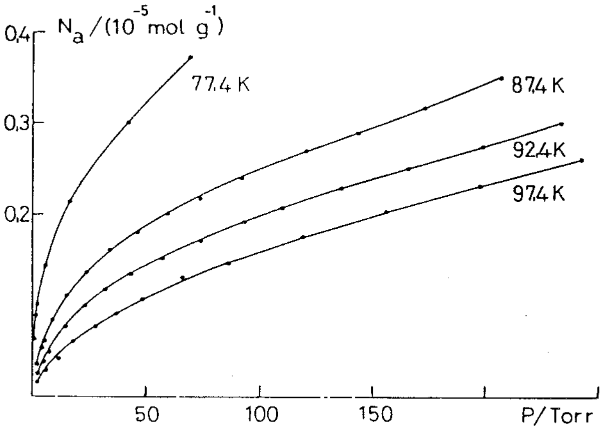

Fig. 2. *Adsorption of argon on rhombic sulfur* S_F

For a particular sample, the B.E.T. surface area was found to be $S_m = 0.40$ m²/g, assuming a molecular surface area fo 16.2 Å² for nitrogen near 78 K. This value leads to molecular surface areas of 13.8 and 46 Å² for argon and neopentane, at 78 and 273 K respectively. These results are consistent with other determinations [4].

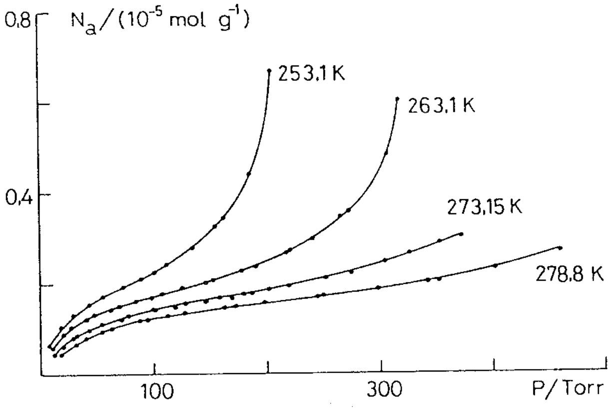

Fig. 3. *Adsorption of neopentane on rhombic sulfur* S_F

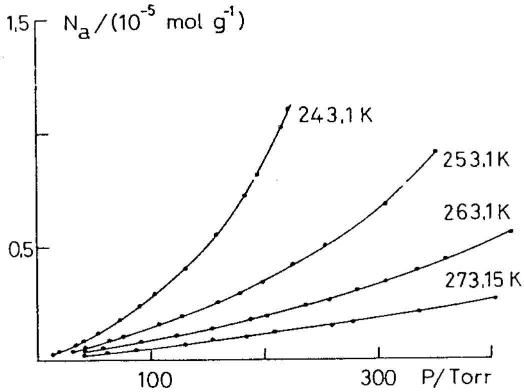

Fig. 4. *Adsorption of sulfur dioxide on rhombic sulfur* S_F

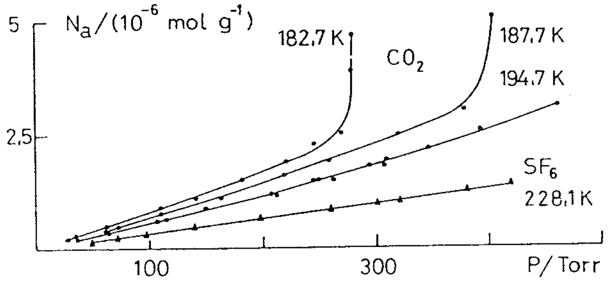

Fig. 5. *Adsorption of carbon dioxide and sulfur hexafluoride on rhombic sulfur* S_F

The average values of constant c of the B.E.T. equation [5] for adsorption on S_F are given in Table 1. The same value was found for N_2 on S_C, and the two reduced isotherms for 77.4 K agree, as expected.

Table 1. *c values of the B.E.T. equation* (Adsorption on S_F)

adsorbate	N_2	Ar	neopentane	SO_2	CO_2	SF_6
c (average)	60	35	22	1.4	3.5	1.4

The isosteric heats of adsorption Q^{st} [2] on S_F are shown in Fig. 6 and 7, as functions of the degree of surface coverage. The similarity between the results for nitrogen and argon is remarkable, and it probably reflects the absence of contributions from the nitrogen quadrupole to the adsorption potential. In view of the low adsorption of CO_2 and SF_6, no reliable estimates could be obtained for their heats of adsorption.

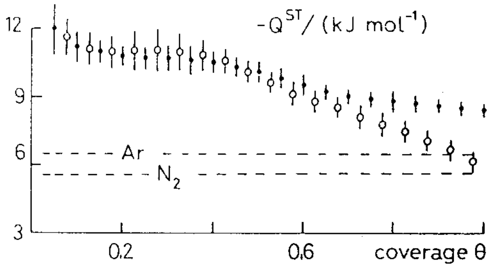

Fig. 6. *Isosteric heats of adsorption of nitrogen* (○) *and argon* (●) *on rhombic sulfur S_F*

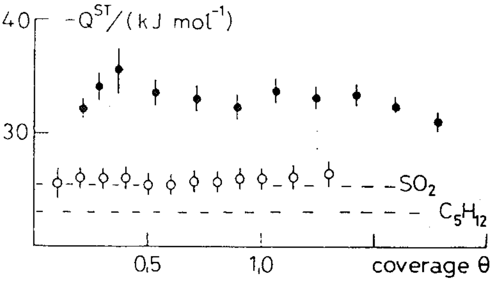

Fig. 7. *Isosteric heats of adsorption of neopentane* (●) *and sulfur dioxide* (○) *on rhombic sulfur S_F*

From entropy calculations for the adsorbed state [2] [5], it is found that the mobility on the surface increases in the order neopentane, sulfur dioxide, nitrogen and argon, for the range $0.2 < \theta < 0.7$. This justifies the use of *Ross* & *Olivier*'s method for the determination of the surface heterogeneity [5] [6] in the case of N_2 and Ar. The method is based on two assumptions:

a) the adsorbate behaves like a two-dimensional gas following the *Hill-de Boer* equation [7], and

b) the surface of the solid consists of patches of various adsorption potentials U, with a gaussian distribution around a value U_0'.

The first requirement is fulfilled for argon and nitrogen, and the second assumption is certainly a reasonable one, for a first investigation of the surface of sulfur.

The graphical method of *Ross & Olivier* yields U_0' and the width 2r of the gaussian, corresponding to half the surface. The surface is frequently characterized by the quantity γ, related to r by

$$r = 477\,\gamma^{-1/2}. \qquad (1)$$

U_0' can also be estimated from the isosteric heat of adsorption at $\theta = 0.4$. In the case of gases which loose one degree of translational freedom, the approximate relation is

$$U_0' = -Q^{st}(\theta = 0.4) - (3/2)R\overline{T} - 0.8(\alpha/\beta) \qquad (2)$$

where $\overline{T}$ is the average temperature in the determination of Q^{st}, and α and β are the constants of the two-dimensional *Van der Waals* equation. They are related to the three-dimensional equation by

$$\alpha = a(9\pi/256\,b)^{1/3}, \quad \beta = 2b(9\pi/256\,b)^{1/3}. \qquad (3)$$

Table 2 gives the values of $U_0' \pm r$ for argon and nitrogen at 77.4 K, obtained by the method of *Ross & Olivier*, and the values derived from the heats of adsorption by eq. (2). (The experimental error is about ±0.5 kJ/mol.)

Table 2. *Adsorption potentials U_0' on rhombic sulfur*

adsorbate	$[U_0' \pm r$ (graphical)	U_0' (eq. 2)]/kJmol^{-1}
argon	8.5 ± 0.5	8.0 ± 0.5
nitrogen	7.7 ± 0.5	6.6 ± 0.5

The value of r = 0.5 kJ/mol (or $\gamma = 17$) means that the surface of rhombic sulfur has a degree of heterogeneity comparable to that of the carbon black P-33 quoted by *Ross & Olivier*, which had been partly graphitized at 1000 K. The relative heterogeneity of sulfur is certainly due to the structural complexity of the surface, as suggested by a molecular model of the unit cell [3]. This problem is actually under investigation.

The B.E.T. monolayer capacities and the values obtained from the method above [6], agree within 2% for argon and nitrogen at 77.4 K.

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