285. The Gas-Solid Interface
The Adsorption of Nitrogen and Neopentane on Synthetic Calcium Carbonates, in Relation to Microporosity

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Summary. The adsorption of nitrogen *(78 K)* and neopentane *(253 to 273 K)* on two different samples of synthetic calcium carbonate has been used to characterize the state of their surface, with respect to microporosity. The need for well defined standards is revealed by the study of natural Ca/Mg carbonates.

1. Introduction. – Physical adsorption of gases has been used to investigate modifications in the surface properties of mechanically and thermally treated calcium carbonates [1], and to characterize the porosity of natural Ca/Mg carbonates [2]. This type of investigation requires the use of well defined reference samples, when the problem of porosity is considered. The present paper describes the adsorption of nitrogen and neopentane on two synthetic samples of $CaCO_3$, which present extreme features (a highly crystalline and open surface in one case, and an almost exclusively microporous structure in the other). This study emphasizes the care which has to be taken in the choice of suitable reference materials, in particular when meso- and microporosity have to be considered [3].

2. Experimental Part. – The two samples of high purity calcium carbonate were originally supplied by *John & E. Sturge Ltd.* (Birmingham, U.K.). The first solid, *'Grade 81'*, is a synthetic calcite of high crystallinity, as shown by transmission electron microscopy and by electron diffraction on small selected areas (the pattern consists of spots). The second sample, *'Calofort U'*, is an ultrafine precipitated calcium carbonate. It was found to consist of aggregates of microcrystallites, with a sponge-like appearance, and giving a diffraction pattern typical for polycrystalline materials (rings instead of spots). It is reasonable to expect some sort of porosity in this type of material. For this solid, our findings agree with the conclusions reached independently by *Gammage & Glasson* [4].

Adsorption measurements were carried out gravimetrically and volumetrically (metal valves only), using oxygen-free nitrogen *(Carba SA,* with a stated purity of 99.9%) and neopentane *(Fluka AG,* stated purity of 99%). The solids were originally outgassed for 70 hours under 10^{-4} to 10^{-5} Torr, and at temperatures not exceeding 130°, in order to prevent any structural damage in the samples.

3. Results and Discussion. – The adsorption isotherms are shown in Fig. 1 and 2. There is no mesoporosity in the solids under investigation, as revealed by the absence of hysteresis in all cases. From the B.E.T. plots [3] for nitrogen, surface areas of 0.37 m²/g and 19.3 m²/g were found for samples 81 and U, assuming a molecular surface area $A_m = 16.2$ Å². The neopentane adsorption isotherms at 263 K therefore

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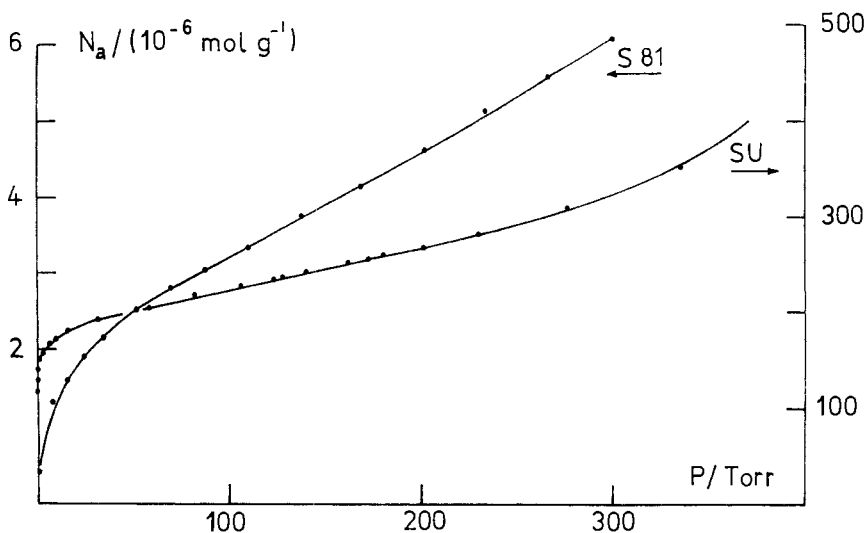[1]) Author, to whom communications should be sent.

Fig. 1. *The adsorption of nitrogen* (78 K) *on samples 81 and U* (left and right-hand side ordinates respectively)
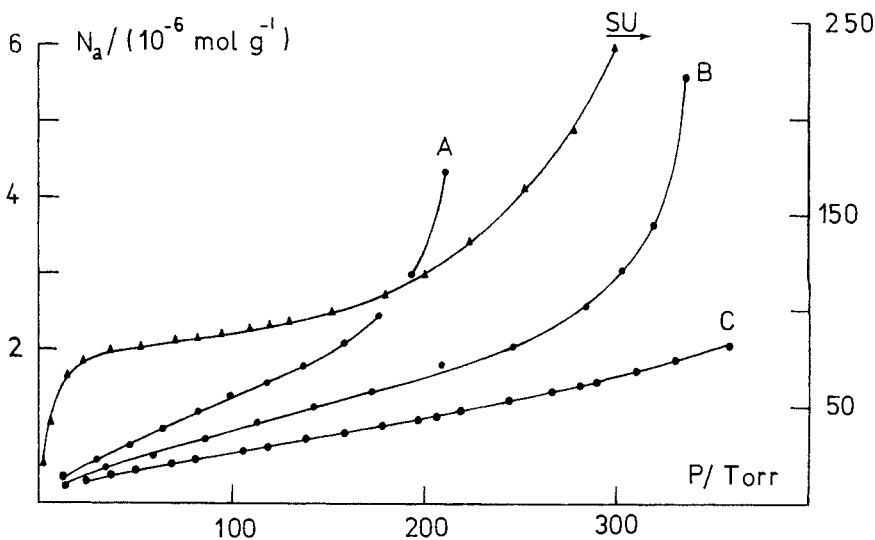
Fig. 2. *The adsorption of neopentane on samples 81* (left-hand ordinate, A = 253 K, B = 263 K, C = 273 K) *and U* (right-hand ordinate, T = 263 K)

lead to molecular surface areas for this gas which are $A_m = 70$ Å² and 42 Å² on samples 81 and U. These values are quite distinct, but they can be compared with other results for the neopentane molecule, all based on 16.2 Å² for N_2. At 273 K, for example, one finds 57 Å² on certain carbons [5], 46 Å² on sulfur [6], and 39 Å² on PVDC [7],

against 38 Å^2 as calculated [3] from the density of the liquid. It is not unusual that A_m changes, with respect to the constant value for N_2, when different solids are considered [3] [8]. In the present case, however, where the chemical nature of the adsorbent is unchanged, the observed differences suggest differences in the state of the two carbonate surface, and possibly in the adsorption mechanism. This is also suggested qualitatively by the differences in curvature for corresponding isotherms on the two solids (mathematically speaking, they are not affine). The curvature itself is related to the value of the so-called c constant of the B.E.T. theory [3],

$$c = \exp[-(E_a - \Delta H_{liq})/RT], \tag{1}$$

where E_a is the average adsorption energy and ΔH_{liq} the enthalpy of liquefaction of the adsorptive. In the case of N_2 at 78 K, it is found that c increases from 20 (sample 81) to 370 (sample U). This means that the average adsorption energy is approximately 1.5 times larger in the second case. Similar observations are made for neopentane. By analogy with the case of graphitized and activated carbons [9], one may therefore assume that sample U is microporous. This is confirmed by the good fit of the low pressure adsorption data for nitrogen ($P/P_0 < 0.01$) to the equation of *Dubinin & Radushkevich* [3] [10]

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(P_0/P)], \tag{2}$$

where W is the volume of the liquid-like adsorbate filling the pores at pressure p, W_0 represents the total micropore volume, and B and β are constants characterizing the solid and the adsorptive. The fulfilment of eq (2) is not always a proof for the presence of microporosity, since a similar analytical expression can also be used for the description of adsorption by open surfaces [3] [11] with a particular distribution of the adsorption energy [12]. However, the simultaneous enhancement of the adsorption energy and the agreement with eq. (2), as in the present case, is good evidence for the presence of microporosity in one of the two samples. Independent evidence can be given by transmission electron microscopy (see above). For sample U, it is found that $W_0(N_2, 78 \text{ K}) = 5.8 \cdot 10^{-3}$ cm^3/g, which corresponds to 17 m^2/g if the liquid is spread out. The structural constant $B = 0.41 \cdot 10^{-6}$ is relatively small, with respect to carbons [10] [13], although it depends on the chemical nature of the adsorbent, as well as on the size of the micropores. Evidence for the presence of small micropores (smallest dimension close to 6 Å) is given by the very slow rate of adsorption of neopentane at low pressures, so that no reliable test of eq. (2) could be carried out. According to *Fitzer & Kalka* [14], who worked on microporous carbons, the effective diameter of the spherical neopentane molecule is 6.3 Å, against 4.3 Å for nitrogen. The rate of desorption of N_2 itself, measured gravimetrically at 78 K, also provides useful informations. It is found that only a certain amount of nitrogen can be removed easily from the solid, when pumping on it after having preadsorbed one statistical monolayer or more. On average, $5.2 \cdot 10^{-3}$ cm^3/g of liquid-like N_2 still remain in the solid at an outgassing pressure of less than 10^{-2} Torr. This value is close to the calculated micropore volume W_0, and it suggests that the external surface of sample U is approximately 2.5 m^2/g (provided that the B.E.T. monolayer capacity is still meaningful).

The present investigation shows again that great care has to be taken in the choice of adsorption standards for a given of solid. Several samples should be tested by the methods described above, before selecting a suitable reference for the determination of the 't-plot' (thickness of the adsorbed layer as a function of p/p_0) [3]. For calcium carbonates, or isomorphous Ca/Mg carbonates, it is obvious that one should use a solid similar to sample 81, or to ground Iceland spar [1]. The present study also provides useful references for the determination of micro- and meso-porosity in natural carbonates of sedimentary origin [2]. By direct comparison, it is found that these solids contain a non-negligeable amount of microporosity which represents the lower end of a larger range of porosity. (The decrease in mesoporosity below 20 Å is frequently misinterpreted, because it does not imply a real decrease in the porosity of the material under investigation.)

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