# 252. The Gas-Solid Interface Physical Adsorption of Simple Molecules in Slot-Like Micropores

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*Summary.* Adsorption potentials of simple molecules on various active carbons have been calculated directly from GSC. measurements, by using the procedure of *Hansen et al.* The model of slot-like micropores developed earlier, and based on a 3–9 adsorption potential, leads to consistent results. It reveals the existence of micropores having widths between 6.5 and 7.5 Å, in agreement with other methods.

**1. Indroduction.** – A method has recently been proposed for the calculation of pore-widths in active carbons, from the adsorption potentials of simple molecules [1]. It was found, by comparison with adsorption on graphitized carbon blacks, that the width of slot-like micropores was between 5 and 8 Å, in agreement with X-ray determinations [2]. In the present paper, we wish to report further results and refinements which lead to more accurate values, for different types of active carbons.

Previously, the adsorption potentials $\Phi_0$ were calculated from the limiting heats of adsorption $Q_0^{st}$, which involve a correction for the changes in translational and vibrational degrees of freedom on adsorption. In the present investigation, we used the treatment of *Hansen & al.* [3], also applied more recently by *Boucher & Everett* [4]. The method is based on the virial approach to adsorption [5], and on the fact that the net retention volume of GSC. ($V_R$), can be equated to the so-called excess volume of the high temperature adsorption theory [3] [4] [6]. In the case of a continuous and flat solid, the adsorption potential $\Phi(Z)$ takes the form [1] [4]

$$\Phi(Z) = -a/Z^3 + b/Z^9 \qquad (1)$$

where a and b are constants depending on the gas and the solid. Potential (1) can be used for the single surface (graphitized carbon blacks, for example) and for slit-shaped pores of the same material [1]. With the 3–9 potential (1), the excess volume can be written in the form [3] [4]

$$\ln (V_R/T^{1/2}) = \ln A Z'_0 (2\pi k/27\varepsilon^*)^{1/2} - \varepsilon^*/kT - 0.8102\,kT/\varepsilon^* + 1.1733\,(kT/\varepsilon^*)^2 + \dots \qquad (2)$$

A is a surface area ($m^2/g$), and $\varepsilon^*$ is the minimum of the adsorption potential, which occurs at the distance $Z'_0$ from the wall of the pore. It is equal to $-\Phi_0$, since the adsorption energy is a negative quantity and $\varepsilon^*$ is positive.

With eq (2) it is therefore possible to obtain directly the minimum of the adsorption potential. The limiting heat of adsorption, on the other hand, can be obtained from a plot of ln ($V_R/T$) against 1/T [4]. The difference between $Q^{st}$ and $\Phi_0$ is equal

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to RT/2 for mobile adsorption [4], and in the present investigation it was found to be slightly smaller.

**2. Experimental.** – The experiments were carried out in a *Perkin-Elmer* chromatograph of type F-11 (hot wire detector), with helium as carrier gas. The steel column (diameter 0.6 cm and length 15 cm) was packed with 3–4 g of activated carbon as supplied (grains of 1–2 mm), and the same procedure was followed for all the samples. The solids were outgassed for 24 h near 400°, with a flow rate of 100 ml/min. The retention volumes of the various gases (Ar, Kr, Xe, $N_2$, $CH_4$) were determined at intervals of 20–30° in the range of 50–400° approximately. Samples of 0.05 $cm^3$ STP were used, with Neon as a marker gas. This gas was found to have the same retention time in helium, as helium in nitrogen under the same conditions. The flow rate of the carrier gas (measured at the exit of the column) was always kept at 5 ml/min, and the correction of *Martin & James* for the pressure drop across the column was equal to unity.

The samples were activated carbons of mineral and vegetable origin, with micropore volumes $W_0$ between 0.4 and 0.7 $cm^3/g$. A carbon molecular sieve (M-5), with $W_0 = 0.30$ $cm^3/g$ and with a majority of pores in the range of 5–6 Å, was also investigated. All the gases, supplied by *Air Liquide* SA, had a stated purity of 99.9% at least.

**3. Results and discussion.** – The values of $\Phi_{0A}$ for the various active carbons, derived from eq(2), are given in the table. The results of *Hansen & al.* [3] and *Boucher & Everett* [4] (Columbia L and coconut shell carbons, respectively) are also given for comparison. These values were compared with the corresponding adsorption potential minima $\Phi_{0G}$ of the gases on standard graphitized carbon blacks quoted by *Everett* [7]. They also correspond to the 3–9 potential (1).

As shown earlier [1], the ratio $\Phi_{0A}/\Phi_{0G}$ is a function of $L/Z_0$, where L represents the width of the slot-like pore and $Z_0$ is the equilibrium distance for the adsorption on the flat single surface. From our tabulated values, and from the distances $Z_0$ of the different gases [3] [4], it is possible to calculate L. The table shows that all the results are consistent, and they are mostly in the range of 6.5–7.5 Å for the simple molecules considered here. These results also agree with investigations of *Everett* [8] on other active carbons, when the 3–9 potential is used. We also investigated two impregnated carbons, which gave the same range of pore-widths.

The quantity A in eq(2) should represent the surface area of the solid, but it is generally found that it is smaller than the corresponding B.E.T. value [4]. It also depends on the nature of the gas and on the method of calculation used [5]. One other reason, however, may be the fact that eq(2) implies a type of pore which is not necessarily representative for the whole solid, except for the case of a very narrow pore-size distribution. It has also been pointed out [7] that even for very homogeneous surfaces, there are still uncertainties in the calculation of the surface area from *Henry's* law.

The pore-widths of 6.5–7.5 Å found from GSC. measurements correspond to the slots in which the adsorption potential is the highest, for the molecules considered. This value does not have to coincide with the maximum of the real pore-size distribution in the solid. (For larger molecular probes, such as $SF_6$ for example, one may expect larger values of L from the present method, which is based on the limiting adsorption potentials).

It must also be pointed out, that mathematically the model which has been used here, also allows in all cases a solution L ≃ 5.5 Å. This is due to the fact that the

Table. *Adsorption of simple gases by various active carbons.* Calculated pore-widths L.

| Gas | $-\Phi_{0A}/(\text{kJ mol}^{-1})$ | $\Phi_{0A}/\Phi_{0G}$ | $L/Z_0$ | L/Å |
|---|---|---|---|---|
| Columbia L [3] | | | | |
| Ar | 15.98 | 1.67 | 2.30 | 6.72 |
| $N_2$ | 17.56 | 1.78 | 2.24 | 6.80 |
| $CH_4$ | 21.39 | 1.73 | 2.26 | 7.00 |
| Activated coconut shell [4] | | | | |
| Ar | 16.14 | 1.68 | 2.30 | 6.72 |
| Kr | 21.15 | 1.77 | 2.24 | 6.72 |
| Xe | 31.57 | 1.98 | 2.04 | 6.49 |
| $N_2$ | 17.03 | 1.73 | 2.26 | 6.87 |
| $CH_4$ | 21.31 | 1.72 | 2.26 | 7.00 |
| U—O 2 (mineral origin) | | | | |
| Kr | 18.25 | 1.52 | 2.44 | 7.32 |
| Xe | 25.21 | 1.58 | 2.38 | 7.56 |
| $N_2$ | 14.21 | 1.44 | 2.50 | 7.60 |
| $CH_4$ | 18.21 | 1.47 | 2.48 | 7.68 |
| F—O 2 (coconut shell) | | | | |
| Ar | 13.04 | 1.36 | 2.60 | 7.60 |
| $N_2$ | 13.82 | 1.40 | 2.55 | 7.75 |
| $CH_4$ | 18.18 | 1.47 | 2.48 | 7.68 |
| C—O 2 (mineral origin) | | | | |
| Kr | 17.54 | 1.46 | 2.49 | 7.47 |
| Xe | 24.48 | 1.53 | 2.42 | 7.69 |
| $N_2$ | 14.45 | 1.47 | 2.48 | 7.53 |
| $CH_4$ | 17.79 | 1.44 | 2.53 | 7.81 |
| M-5 (molecular sieve carbon) | | | | |
| Ar | 16.59 | 1.73 | 2.27 | 6.62 |
| Kr | 20.95 | 1.75 | 2.26 | 6.78 |
| Xe | 28.87 | 1.81 | 2.22 | 7.05 |
| $N_2$ | 17.35 | 1.76 | 2.25 | 6.84 |
| $CH_4$ | 21.15 | 1.74 | 2.28 | 7.06 |

function $\Phi_{0A}/\Phi_{0G}$ also decreases (very rapidly) for $L < 2Z_0$. Pores of 5.5 Å may be present in the solids under investigation, but it is likely that they are really dominant only for active carbons like M-5 or of the 'Saran' type which have small structural constants B in the *Dubinin-Radushkevich* equation [9]. In the case of sample M-5, it was found independently that there also exists a system of pores in the range of 6–7 Å, which is probably located behind the main system of 5 Å. The results of the table are therefore not surprising.

As shown previously [1], the use of a 4–10 adsorption potential leads to pore-widths which are about 10% larger, and is not possible to decide between the two sets of results. On the other hand, the model of *Gurfein et al.* [10], for cylindrical pores, leads to radii which are in the region of 4–5 Å. Structural considerations and molecular-sieve effects observed with molecules of different sizes and shapes [11] tend to favour the model of slot-like micropores.

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## 253. Über die selektive katalytische Reduktion von substituierten Anilinen zu substituierten Cyclohexylaminen und von Benzol- bzw. Phenyl-alkan-sulfonsäuren zu Cyclohexan- bzw. Cyclohexylalkan-sulfonsäuren

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*Zusammenfassung.* Bei Verwendung von Rh-Alox-Katalysatoren lassen sich *p*-Aminophenyl-2-hydroxyäthyl-äther unter sorgfältig definierten Bedingungen ohne starke Hydrogenolyse zu *cis-/trans*-(4-Aminocyclohexyl)-(2-hydroxyäthyl)-äthern reduzieren; durch selektive Reduktion erhält man 4-Benzyl-cyclohexylamin aus 4-Benzylanilin sowie 1-(4-Aminocyclohexyl)-2-phenyläthan aus 1-(4-Aminophenyl)-2-phenyl-äthan.

Rh- und Ru-Katalysatoren sind imstande, die bisher als nicht hydrierbar geltenden Methyl-, Amino- und Hydroxy-benzolsulfonsäuren *quantitativ* in die Methyl-, Amino- und Hydroxy-cyclohexansulfonsäuren überzuführen. Die Hydrierparameter werden ausführlich diskutiert.

Wie sich aus $^{13}$C-NMR.-Daten herleiten lässt, entstehen bevorzugt die *cis*-Stereoisomeren. Die 4-Methyl-cyclohexansulfonsäure liegt bei Raumtemperatur zu $>90\%$ in der Konformation mit axialer $CH_3$- und äquatorialer $SO_3^{\ominus}$-Gruppe vor (als Na-Salz in $D_2O$ gemessen).

Seit der Einführung von bequem handhabbaren Ruthenium- und Rhodiumkatalysatoren ist die katalytische Reduktion von aromatischen Verbindungen unter relativ milden Bedingungen möglich geworden[2]). Unter den besonderen Eigenschaften dieser neuen Katalysatoren fallen dem Praktiker vor allem auf: eine geringe Neigung zu Hydrogenolysen [7] [8] und eine stark pH-abhängige Hydriergeschwindigkeit [9][3]). Ferner hängt die Reduzierbarkeit eines aromatischen Substrates stark von Natur, Anzahl und Stellung der Substituenten ab.

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[1]) Aus der Dissertation *R. Egli* [1].
[2]) Zusammenfassungen: *Freifelder* [2], *Rylander* [3], *Augustine* [3], *Zymalkowski* [5], *Gilman & Cohn* [6].
[3]) Teilweise auf das Trägermaterial zurückzuführen.