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237. The Gas-Solid Interface Heats of Adsorption of Simple Molecules on Microporous Carbons and on Graphitized Carbon Blacks, at Low Surface Coverage

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(20. VI. 74)

Summary. The heats of adsorption of nitrogen, argon, xenon, pentane, cyclohexane and benzene on a typical microporous carbon have been measured by gas-solid chromatography. An overall comparison of the limiting heats of adsorption on active carbons and on graphitized carbon blacks shows a ratio of 1.6 between them. This is also the value of the ratio of the minima of the adsorption potentials. This result is discussed in terms of simple models for the shape of the micropores. Slot-like pores give a better agreement.

1. Introduction. – Physical adsorption of gases on graphitized carbons has received considerable attention, and good correlations have been found between the limiting heats of adsorption and adsorption potentials [1–4]. In the case of microporous (or active) carbons, the heats of adsorption at low coverage of the surface can be obtained from static isotherms or from gas-solid chromatography (GSC.) measurements [5–10]. The latter method presents several advantages, but it is limited to simple molecules, in view of the relatively high temperatures needed (about 550 K for benzene). Enough results are now available, to justify a comparison between the two types of carbon.

2. Experimental Part. – The GSC. experiments were carried out in two chromatographs, of the *Philips* PV 4000 and the *Hewlett-Packard* 7620 A types, with short columns (diameter 0.6 cm and length 5 cm) packed with the adsorbent (20–30 mesh). A typical microporous carbon of the '*Pittsburgh*' type was used, with helium as a carrier gas (flow rates of 5–15 ml/min) and hydrogen as a reference. Static measurements with nitrogen at 78 K gave the structural constant $B = 1.07\ 10^6$ and a micropore volume $W_0 = 0.54\ cm^3/g$ for the *Dubinin* equation [10]. Before runs, the samples were prepared by heating to 300° in a stream of hydrogen or helium, for a minimum of 24 h.

The limiting heats of adsorption q_{0A}^{st} were derived from plots of $\ln V_R/T_C$ against $1/T_C$, where T_C is the temperature of the column and V_R the retention volume defined [7] as

$$V_R = f \cdot t_R' \cdot j \cdot T_C/T_0; \qquad 5(1)$$

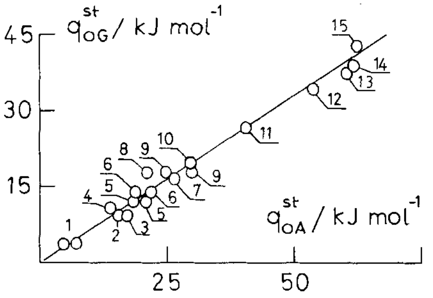
f is the flow rate measured at the temperature of the flow meter, T_0, at the outlet of the column, t'_R the retention time of the adsorbed gas less the time for the marker gas, and j the column pressure gradient correction factor of *Martin & James,* close to 1 in our experiments (negligible pressure drop in the column). The pure adsorbates were injected as supplied, in samples of about 0.05 cm³ S.T.P. for gases, and 1–5 µl for liquids.

3. Results and discussion. – Table 1 gives the limiting heats of adsorption at the average temperature $\overline{T}$. The values for N_2, Ar and Xe agree with the results found for various active carbons [5–8]. Fig. 1 shows the relation between the limiting heats of adsorption of 15 simple gases on graphitized carbon blacks, q_{oG}^{st}, and on active carbons, q_{oA}^{st}. The values of q_{oG}^{st} were determined by GSC. and static methods [1] [4], the two being usually in good agreement. In the case of q_{oA}^{st}, all the results [5–9], including our own, were obtained from GSC. measurements.

Limiting heats of adsorption q_{oA}^{st} measured by GSC. (sample of activated 'Pittsburgh' coal)

adsorbate	N_2	Ar	Xe	C_5H_{12}	C_6H_6	C_6H_{12}
$\overline{T}/K$	485	485	485	543	563	553
q_{oA}^{st}/kJ mol^{-1}	17.3	17.5	26.3	61.9	62.1	60.4

According to the figure, there is a linear relationship, the limiting heats of adsorption on the activated carbons being on the average 1.6 times larger than on the graphitized carbon blacks. The comparison is possible, owing to the relatively small variation of q_o^{st} with temperature, in the case of graphite-like surfaces [1] [4] [11]. However, the most reliable comparison should come from pairs of measurements carried out on the same samples of graphitized and activated carbons, and at the same average temperature for a given adsorbate. No such systematic investigation has been reported yet.



Comparison of the limiting heats of adsorption on graphitized carbon blacks q_{oG}^{st} [1] [4], *and on active carbons q_{oA}^{st}* (including our own results for a *'Pittsburgh'* coal)

1: Ne [5] [8], 2: Ar [5] [8], 3: N_2 [6–8], 4: O_2 [7] [9], 5: CH_4 [6–8], 6: Kr [5] [7] [8], 7: Xe [8], 8: CO_2 [7], 9: C_2H_4 [6] [7], 10: H_2O [7], 11: C_3H_8 [7], 12: C_4H_{10} [6], 13: c-C_6H_{12}, 14: C_5H_{12}, 15: C_6H_6 (this work).

It is known from small angle X-ray analysis that the effective radius of the micropores is between 5 and 7 Å, for typical active carbons [12]. (The effective radius is either equal to the radius of cylindrical pores, or to the width of slot-like pores.) *Wolff* [13] suggested that the micropores of active carbons were slits of 6–8 Å in width, which agrees with experiments on the adsorption of molecules of various shapes and sizes [14]. The limiting heats of adsorption given above can also be used to draw conclusions as to the shape of these micropores, by using different theoretical models.

The limiting heat of adsorption q_o^{st} and the minimum of the adsorption potential on a given surface, $\Phi(Z_o)$, are related by [2–4]

$$q_o^{st} = -\Phi(Z_o) + \Delta E_{tr} + \Delta E_{rot} + RT - E_{vibr} \tag{2}$$

where ΔE_{tr} and ΔE_{rot} are the changes in translational and rotational energy on adsorption, and E_{vibr} represents the vibrational energy of the adsorbed molecule, at the distance Z_o from the surface. $-\Phi(Z_o)$ is the leading term in the right-hand side of eq. (2), and if we assume that the adsorption is mobile (loss of one translational degree of freedom only),

$$-\Phi(Z_o) = q_o^{st} - (3/2)RT. \tag{3}$$

This is a good approximation in the case of graphitic surfaces, where the term (3/2)RT represents only 10–15% of q_o^{st} [4] [11]. Let us suppose that the experimental values of q_o^{st} measured on our microporous adsorbent are mainly caused by the adsorption potential in a micropore and that those found on graphitized carbon black measure the adsorption potential of a flat surface. Using these experimental data, their ratio has been calculated and found to be close to 1.6. The problem has been investigated theoretically by *Steele & Halsey*, who assumed a simple hard-sphere adsorption potential of the $3:\infty$ type [15]. For cylindrical pores of radius r, the ratio of 1.6 leads to $r/D = 1.2$, where D is the hard-sphere diameter of the adsorbate. In the case of slot-like pores, the model leads to a width of $L = 2.5$ D. For simple molecules, D is near 3 Å, as calculated from adsorption data on carbons of the '*Saran*' type [15] [16]. (This value should also include the normal alkanes, if they are treated as chains of spherical segments.) Consequently, $r = 3$–4 Å for cylindrical pores, and $L = 6$–8 Å for parallel-walled pores. The comparison with the experimental values shows that the simple model of *Steele & Halsey* gives better agreement for micropores considered as slits between parallel graphitic planes. This conclusion is also reached by considering more elaborate potentials.

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238. The Gas-Solid Interface Calculations of Adsorption Potentials in Slot-Like Pores of Molecular Dimensions

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Summary. Two theoretical models are presented for the calculation of adsorption potentials in slot-like pores of molecular dimensions, with respect to the adsorption by a single flat surface. The cases of continuous and layer-like solids are considered, with interatomic pair-potentials of the 6:12 type, and for pore widths ranging from two to four times the equilibrium distance of adsorption. Both models give good results for the adsorption of simple molecules by microporous carbons and graphitized carbon blacks.

1. Introduction. – A theoretical model for the adsorption of single molecules in cylindrical pores of molecular dimensions has recently been presented by *Gurfein et al.* [1].

Based on an intermolecular pair-potential of the *Lennard-Jones* type of eq. (1), the model gives the ratio of the adsorption potentials in the pore and on a flat surface, as a function of the radius of the capillary and the diameter of the molecule. We wish to present similar models for the case of slot-like pores, and to compare them with experimental results for the adsorption of simple molecules on graphitized and activated carbons [2]. The models are all improvements on earlier calculations of *Steele & Halsey* [3], who used hard-sphere potentials for the adsorption in cylindrical and parallel-walled pores.

2. The models. – Let us assume an intermolecular pair-potential of the *Lennard-Jones* type [4] [5],

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

where C and B are constants for the attractive and repulsive parts of the potential, and r represents the distance between the particles (atoms or molecules).

The potential is often expressed in the equivalent form

$$\varphi(r) = \varepsilon[(r_0/r)^{12} - 2(r_0/r)^6], \tag{2}$$