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Studies on Pore Systems in Catalysts

VIII. The Adsorption of Krypton and of Nitrogen on Graphitized Carbon

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The deviation between the S_t and the S_{BET} values found with the graphitized carbon blacks, in Article VI of this series, is caused by the homogeneity of the graphitized carbon blacks, as is clear from the comparison of the behavior of adsorbed krypton and adsorbed nitrogen. A monolayer capacity is derived from the krypton isotherm and compared with the figure derived from the S_t value of the nitrogen isotherm. If the molecular area of a nitrogen molecule is fixed as to be 16.3 Å^2, the krypton value seems to be between 15.3 and 15.45 Å^2.

1. THE PROBLEM OF THE GRAPHITIZED CARBONS

In Part VI of this series (*1*) we reported a deviation between the values of the surface areas of graphitized carbon blacks, when measured with our t method (*2*), and the values obtained by means of the BET equation. For all three graphitized carbons, which we investigated, the values from the V_a-t plots (S_t) are 10% higher than the BET values (S_{BET}). In the same article we offered, tentatively, three possible explanations of the difference, the first being based on the supposition that the first adsorbed layer is more or less localized and arranged according to the pattern of the graphite cells, while with following layers it is assumed to return to the normal packing, a possibility already forwarded by Pierce and Ewing (*3*); the second being based on the loss of one freedom of rotation of the adsorbed nitrogen molecules, regaining this freedom with the adsorption of the second layer, a suggestion which would quantitatively explain the 10% difference; and a third explanation based on stepwise adsorption caused by the homogeneity of the surface. In the present article we shall indicate that this latter explanation may be considered to be the right one.

2. THE CHOICE OF KRYPTON AS AN ADSORBENT

If the homogeneity of the surface is responsible for the effect, the deviation of the experimental points lying under the theoretical t curve, between the relative pressures, $p/p_0 \sim 0.1$ and $p/p_0 \sim 0.3$, has to be ascribed to the retention of the two-dimensional supercritical fluidization of the second adsorbed layer of adsorbed nitrogen molecules. A similar effect in the first adsorbed layer cannot be noticed in the normal measurements, because of the very low relative pressures of this phenomenon in the strongly adsorbed first layer.

In order to study these phenomena we decided to use krypton as an adsorbate instead of nitrogen, because at our measuring temperature (—196°C) krypton is below its two-dimensional critical tem-

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perature, while nitrogen is above its two-dimensional critical temperature [these temperatures being assumed to be half the absolute three-dimensional critical temperatures, if no polarization phenomena interfere (*4*)]. As Singleton and Halsey (*5*) had already measured the adsorption of krypton on a graphitized carbon (Sterling F.T.), which might be identical with one of the samples which we used for our nitrogen adsorption measurements, we chose this sample, originating from Godfrey L. Cabot, Inc., Boston, Massachusetts.

3. EXPERIMENTAL

The apparatus for the measurement of the krypton adsorption isotherm was built after the design of Tomlinson (*6*). For the details of the measuring procedure we refer to the report, cited under (*6*). The krypton gas was furnished by Philips Gas Co., it was of a very high purity and it could be used without further purification.

Samples and the measuring part of the apparatus were degassed very carefully at room temperature with the aid of an oil-diffusion pump fitted with a molecular-sieve trap to prevent contamination of the system with vapors from the pumps. Evacuation was continued until the pressure in the system was less than 10^{-6} mm Hg, as measured by a Penning manometer.

During adsorption measurements the sample tube was held immersed in liquid nitrogen, the level of which was kept constant automatically. Special care was taken to ensure the establishment of equilibrium, which took from several hours to several days at high relative pressures. For each sample the adsorption of krypton

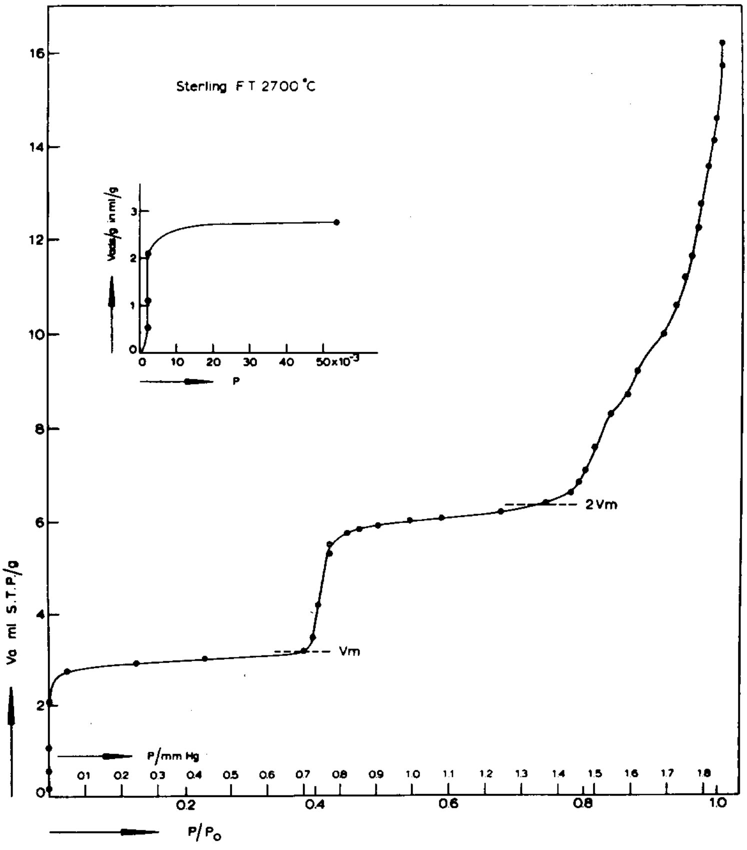

FIG. 1.

up to the saturation pressure of solid krypton at liquid nitrogen temperatures, as well as the desorption, was determined twice. The sample was evacuated between successive runs to check upon possible leakage.

4. RESULTS

Figure 1 gives the adsorption isotherm of krypton on our graphitized carbon Sterling F.T. The pressure axis gives, apart from the figures for the krypton pressures, also the relative pressures, p/p_0. The saturation pressure p_0, is separately determined and corresponds to the pressure of solid crystalline krypton at our measuring temperature.

Our curve is practically identical with the isotherm given by Singleton and Halsey, who also used the same p/p_0 scale. It is, therefore, clear that the sample of graphitized carbon which we used has the same high degree of homogeneity, showing at least three successive phenomena of two-dimensional condensation, in the first, second, and third adsorbed layers, respectively. We are, therefore, allowed to ascribe the "dips" in the V_a–t plot of Fig. 4 of our previous paper (*1*), between the t values of 3 and 5 Å and in the t–p/p_0 plot of Fig. 5 of the same paper, between the p/p_0 values 0.1 and 0.3, as to be caused by the two-dimensional densification to a two-dimensional supercritical fluid of the adsorbed nitrogen in the second layer.

It will be clear from these results that the supercritical "dip" in the nitrogen adsorption curve yields values too low for a reliable use of a BET plot. We may, therefore, assume the S_t value of our previous article (*1*) to give the right value of the surface area. We may then disregard the two first-mentioned possibilities of our previous article for the explanation of the difference between the S_t and S_{BET} values. The adsorbed nitrogen molecules, therefore, may be considered as behaving as two-dimensional gas molecules above the two-dimensional critical temperature. This is also in accordance with the conclusion drawn in former work (*7*) where from the comparison of the entropy of adsorbed nitrogen on charcoal, calculated from adsorption measurements between 77.4° and 90.2°K by Brunauer and Emmett (*8*), it could be concluded that even at these low temperatures there is only a certain restriction of the free translation of the adsorbed nitrogen molecules over the surface. The rotation of the adsorbed molecules is not hindered and there is no mutual orientation.

5. ESTIMATION OF THE VALUE FOR THE MONOLAYER FROM THE KRYPTON ISOTHERM

The monolayer capacity of the krypton adsorption may not be estimated—as Singleton and Halsey (*5*) did—from the sharp bend in the first part of the isotherm. This sharp bend indicates the end of the spontaneous condensation in the first layer; the first layer, however, is not completely filled at that point. The degree of saturation depends on the strength of the forces between adsorbent and adsorbate (adsorption forces) and of the strength of the forces between the adsorbate molecules mutually (intermolecular forces), as is given by the expression (*9*)

$$\frac{p}{p_0} = k_2 \frac{\theta}{1-\theta} \exp \frac{\theta}{1-\theta} \exp -k_1\theta$$

In this equation, which is given in its reduced form, θ is the degree of occupation, while k_1 and k_2 are dimensionless constants, of which k_1 contains the intermolecular forces and k_2 the adsorption forces. At the bend after the sharp rise due to the two-dimensional condensation in the first adsorbed layer (inset in Fig. 1), θ is substantially lower than unity. If, e.g., $k_1 = 10$ and $k_2 = 0.1$, the value of θ at this point is less than 0.9.

The part of the isotherm from the sharp bend to higher relative pressures partly gives a further uptake of adsorbed molecules in the uncompleted condensed monolayer and, secondly, adsorption of single molecules in the second layer as individual two-dimensional gas molecules, adsorbed on the condensed part of the first layer. This goes on until the second layer, in itself, shows the condensation to a two-dimensional liquid layer, etc.

We may, however, obtain a close approximation of the capacity of the monolayer when we measure the difference in uptake between two corresponding points of the straight condensation jumps in the first and in the second layer. As corresponding points we took the middle of the straight upward parts. At the middle of the straight part of the second jump 4.5 ml Kr(STP) was taken up per gram of adsorbent; at the middle of the straight part of the first jump this amount was 1.3 ml Kr(STP)/g. We may, therefore, take the difference, hence 3.2 ml Kr(STP)/g as the capacity of the monolayer, and we may consider this figure to be a minimum figure, as the θ value of the chosen point of the second layer will be lower than that of the chosen point of the first layer.

6. COMPARISON OF THE MONOLAYER CAPACITY OF Kr WITH THAT OF N_2

The S_t value of 13.3 m^2/g given in our previous article (*1*) corresponds with a monolayer capacity of 3.04 ml(STP) nitrogen per gram. We may compare this figure with the monolayer capacity of 3.2 ml(STP) krypton found above.

If we assume the molecular area of nitrogen which we use, 16.27 Å^2 per molecule (*10*), to be right (*11*), we can calculate the molecular area of krypton and we find:

$$(3.04/3.2) \times 16.27 = 15.4_5 \text{ Å}^2$$

We may compare this figure with the molecular area of krypton calculated from the three-dimensional condensed states at 77.2°K. The molar volume of solid krypton at this temperature, interpolated from the data of Dobbs (*12*) is 28.4^5 cm^3/mole, from which a molecular area of 14.3 Å^2 would follow. The molar volume of supercooled liquid krypton at 77.2°K may be extrapolated from data (*13*) of Matthias *et al.* to a value between 31 and 32 cm^3/mole, from which a molecular area between 15.1 and 15.3 Å^2 would follow. Our figure is somewhat higher than these last figures. As we may consider our adsorbed krypton to be in a condensed close-packed two-dimensional state, where every molecule (atom) is surrounded by six neighbors, we may expect the molecular area to be higher than the figure derived from the close-packed condensed three-dimensional state, where every molecule is surrounded by 12 neighbors.

On the other hand, as stated at the end of Section 5, our monolayer capacity may be somewhat higher than 3.2 ml Kr, which would lead to a somewhat lower figure for the molecular area; 15.4^5 Å^2 may, therefore, be considered as a maximum figure.

The molecular area of adsorbed molecules has often been identified with the two-dimensional van der Waals constant b_2. The b_2 value of krypton is 15.7 Å^2, hence larger than the molecular area of 15.4^5 Å^2 which we derived above from the krypton isotherm. The equality of b_2 and the molecular areas derived from the liquid state is, as was stated before (*14*), rather incidental and certainly not a rigourous one.

7. SUMMARY

(a) One of the graphitized carbon blacks, mentioned in Article VI of this series, where a deviation between the S_t value and the S_{BET} value was found, has been used as an adsorbent for krypton.

(b) The krypton isotherm which we found is identical with the isotherm published by Singleton and Halsey, and shows two-dimensional condensation steps.

(c) The "dips" in the isotherms and in the t plots of nitrogen on the graphitized carbon blacks, described in Article VI of this series, may, therefore, be ascribed to supercritical two-dimensional densification bends.

(d) The S_{BET} values do not, therefore, give the right surface areas, the S_t values, however, do.

(e) From the krypton isotherm a monolayer capacity may be derived, which is, probably, still a minimum figure.

(f) Taking the nitrogen molecular area as fixed at 16.3 Å^2, the krypton molecular area is 15.4^5 Å^2 or somewhat smaller, while from the density of the close-packed supercooled liquid krypton at 77.2°K a value somewhat higher than 15.1 to 15.3 Å^2 may be derived.

(g) The true value, based on that of nitrogen, may, therefore, be estimated between 15.3 and 15.4^5 Å^2, which is lower than the b_2 value (15.7 Å^2).

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