

Homogeneous and Heterogeneous Micropore Structures in Carbonaceous Adsorbents

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Microporous carbonaceous adsorbents obtained by moderate activation possess a rather narrow pore-size distribution, and their microporous structure may be considered to be practically homogeneous. In the case of high degrees of burn-off and of extreme activation, micropores of various sizes are formed, including large ones such as supermicropores. The distribution of the micropore volume with respect to their dimensions becomes broader, a characteristic feature of heterogeneous micropore structures. For adsorbents with homogeneous micropore structures close to carbonaceous molecular sieves, the equation of the theory of volume filling of micropores (TVFM) applies with $n = 2$ over a large range of relative pressures. In the case of slit-shaped micropores, their half-width is proportional to the inverse of the characteristic energy of adsorption, E_0 . The constant of proportionality is obtained from the molecular sieve properties of the carbonaceous adsorbents, and in the case of active carbons of industrial origin it may be regarded as a constant, with a good approximation. The development of the adsorption theory for carbonaceous adsorbents with heterogeneous micropore structures has made it possible to express the distribution of the micropore volume according to their dimensions. It is also shown that the adsorption properties of such materials can be approximated with great accuracy by a two-term equation of TVFM, with $n = 2$. A possible alternative is also considered for carbonaceous adsorbents with heterogeneous micropore structures, and for which the adsorption equation contains a term with exponent $n = 3$.

INTRODUCTION

The theory of volume filling of micropores (TVFM), which has found a wide field of applications (1), appears to be a rational basis for the description of the microporous structure in carbonaceous adsorbents.

Its fundamental equation may be expressed in two different ways. The first, originally proposed by Dubinin and Radushkevich (the D-R equation) (1, 2), reads

$$a = \frac{W_0}{v^*} \exp\{-B(T/\beta)^2 \log^2(p_s/p)\}, \quad [1]$$

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but the more general expression is the one proposed by Dubinin and Astakhov (1, 3) and known as the D-A equation,

$$a = \frac{W_0}{v^*} \exp\{-(A/\beta E_0)^n\}. \quad [2]$$

In Eqs. [1] and [2], a represents the amount adsorbed at relative pressure p/p_s and temperature T ; W_0 is the limiting volume of adsorption or the volume of the micropores, and v^* is the molar volume of the adsorbate; β is the similarity coefficient of the characteristic curves and A the change of Gibbs free energy on adsorption, defined by

$$A = -\Delta G = RT \ln(p_s/p). \quad [3]$$

The specific parameters of Eqs. [1] and [2] are respectively W_0 , E_0 , and n , where E_0 is the characteristic energy of adsorption of the reference vapor, usually benzene.

When $n = 2$, Eqs. [1] and [2] are identical and the quantities B (the so-called structural constant) and E_0 are related by

$$E_0 = 0.01915(1/B)^{1/2} \quad (\text{kJ/mole}). \quad [4]$$

The fundamental equations of TVFM, [1] and [2], which contain the fundamental parameter W_0 , are closely related to the microporous structure of the adsorbent.

Moreover, it has already been shown (4) that there exists a qualitative relation between parameter B and the dimension of the micropores. It was obvious to suggest that, during progressive activation with carbon dioxide at 900–950°C, for example, an increase of the micropore size takes place with increasing burn-off. Simultaneously, one observes an increase of parameter B or a decrease of the characteristic energy E_0 , in agreement with Eq. [4].

HOMOGENEOUS MICROPORE STRUCTURES

(1) For the majority of microporous carbonaceous adsorbents or activated carbons, Eqs. [1] and [2] (with $n = 2$) apply over a large range of relative equilibrium pressures, typically between 10^{-6} and 0.1. Judging by their molecular sieve properties, it appears that such carbons possess a rather narrow pore-size distribution. Therefore, one may consider, to some extent, that their micropore systems are practically uniform.

Typical examples are shown in Fig. 3 of Ref. (5), and in Fig. 1 of Ref. (6), giving linear representations of the D-R Eq. [1] in the form

$$W = W_0 \exp\{-By\}, \quad [5]$$

where $W = av^*$.

The quantity y , defined as

$$y = [(T/\beta) \log(p_s/p)]^2, \quad [6]$$

is a generalized coordinate, independent of the nature of the gas and of the temperature.

In these examples, B and E_0 are constant over the whole range of relative pressures and temperatures investigated by the authors, and they correspond to some characteristic average dimension x of the active carbons under investigation.

The study of small-angle X-ray scattering by carbonaceous adsorbents provides information about the linear characteristics of micropores. The experimental data are usually analyzed by applying the so-called method of the tangents, based on the equation of Guinier, linearized in the form (7)

$$\ln J = \ln J_0 - mR_i^2 \cdot \phi^2. \quad [7]$$

In Eq. [7], J represents the intensity of the beam scattered at angle ϕ , and R_i is the so-called inertia radius of the micropores, an average pore dimension. Formally, this equation is also similar to the fundamental equation of TVFM [2], which can be written as

$$\ln a = \ln a_0 - (1/E_0)^2 A^2. \quad [8]$$

From this formal analogy, one may expect R_i and $1/E_0$ to be proportional (8). A similar relationship has also been suggested in Ref. (9), for constant B .

The most plausible model for micropores, from an ideal point of view, is the one of slit-shaped micropores of half width d , between parallel disks of radius r . Good evidence for this shape is also provided by the independent work of Stoeckli (10) and of Everett and Powl (11), based on gas–solid chromatography and on the theory of intermolecular forces.

Slit-shaped micropores can result from the burning out of crystallites, or from the removal of aromatic sheets in the crystallites. Parameter d has a decisive influence on the value of the adsorption field resulting from the dispersion forces within such a micropore. Therefore, one may use this quantity as a characteristic dimension of the micropore and write that $x = d$. Table I gives the values of the inertia radii R_i and of the char-

acteristic energies E_0 , for the reference vapor benzene.

These were obtained from small angle scattering (7) and from adsorption by carbons with micropores (3) and larger micropores, i.e., supermicropores (12), using the D-A Eq. [2] with $n = 2$. It appears, to a good approximation, that the product $R_1 \cdot E_0$ is constant and equal to (14.8 ± 0.6) kJ/mole.

Generally speaking, the inertia radius R_1 does not correspond exactly to the characteristic dimension x of the micropores, but it is a function of it. (In the case of disk-shaped micropores, for example, R_1 depends on the height $2x$ and on the diameter $2r$ of the base). However, if one postulates to a first approximation that R_1 is proportional to x , it follows that

$$x = k/E_0. \quad [9]$$

This relation yields an average dimension of the micropores in the active carbon, for which Eq. [2] with $n = 2$ applies over the entire experimental range for the adsorption of benzene (usually $10^{-6} < p/p_s < 0.1$). According to Eq. [8], one observes a linear relationship between $\ln a$ and A^2 for this range, and E_0 appears to be a constant which does not depend on the filling of the micropores in the adsorbent.

(2) From the data of Table I, it appears that Eq. [9] can be used for the range of adsorption energies E_0 between 23 and 14 kJ/mole, which corresponds to adsorption in micropores as well as in supermicropores. The limits of the domain depend essentially on the highest values of E_0 for which Eq. [2] applies with $n = 2$. This problem has been dealt with in a joint work with B. A. Onusaitis, where the adsorption of benzene and carbon dioxide at 293°K was investigated in the case of carbonaceous adsorbents with fine micropores and showing therefore pronounced molecular sieve properties. These solids practically did not adsorb molecules of dimensions exceeding 0.5 nm.

Generally speaking, the molecular sieve properties of carbonaceous adsorbents may

TABLE I

Inertia Radii R_i of the Micropores and Characteristic Adsorption Energies E_0 for Benzene, Obtained for Typical Carbonaceous Adsorbents (7, 8, 12)

Ad- sorbent	Micropores			Supermicropores		
	R_1 (nm)	E_{01} (kJ/mole)	$R_1 E_{01}$	R_2 (nm)	E_{02} (kJ/mole)	$R_2 E_{02}$
D-2	0.69	20.9	14.4	—	—	—
L-8	0.71	22.7	15.4	—	—	—
D-3	0.67	21.1	14.1	1.30	11.9	15.5
E-4	0.68	22.3	15.2	1.22	12.3	15.0
E-5	0.63	22.5	14.2	1.32	11.1	14.6

be caused in two ways: either by the reduced dimensions of the entrance into the micropores, or by the small dimensions of the micropores themselves. In the first case, the dimensions of the entrance or the windows leading into the micropore system depend on the presence of long-chained radicals linked to carbon atoms on the edges of the aromatic structures. At the same time, the dimensions of the micropores themselves may be quite normal. In such cases, the characteristic energy E_0 is found in the range of 25–23 kJ/mole, and the molecular sieve properties may be lost entirely after a moderate activation in CO_2 at 950°C, for example, with a 2–3% burn-off. During the activation, the long-chained radicals are preferentially eliminated and the micropore sizes remain virtually unchanged.

On the other hand, if the molecular sieve properties are caused by the narrow size of the micropores, one observes relatively high values for the characteristic energies E_0 , but further activation, as described above, has virtually no effect on the molecular sieve properties.

For our investigations, we used the molecular sieves MSC-4A and MSC-5A of the Japanese firm TAKEDA. Since adsorption equilibrium is reached only after a long time, in particular for benzene, the desorption isotherms were determined. In the present case, it was possible to obtain equilibrium for relative pressures as low as 1.10^{-4} . For

TABLE II

Parameters of Eq. [2] for the Adsorption Isotherms on Molecular Sieves, at $T = 293^\circ\text{K}$

Adsorbent	Vapor	n	a_0 (mmole/g)	W_0 (cm^3/g)	E_0 (kJ/mole)	Range of validity for p/p_s
MSC-4A	CO_2	2	3.71	0.155	11.6	$3 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A	CO_2	2	4.55	0.191	11.5	$2 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A	CO_2	2	4.48	0.188	11.9	$2 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A (7%)	CO_2	2	4.95	0.208	11.6	$1 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A	C_6H_6	2	1.95	0.173	35.6	$1 \cdot 10^{-4} - 1 \cdot 10^{-1}$
MSC-5A (7%)	C_6H_6	2	2.50	0.222	37.0	$1 \cdot 10^{-4} - 1.7 \cdot 10^{-1}$
MSC-5A	CO_2	3	2.95	0.124	13.9	$7 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A	CO_2	3	3.00	0.126	14.4	$6 \cdot 10^{-4} - 1 \cdot 10^{-2}$
MSC-5A	C_6H_6	3	1.88	0.167	28.9	$1 \cdot 10^{-3} - 3.5 \cdot 10^{-1}$

smaller pressures, however, the adsorption data can be appreciably enhanced.

Table II lists the data obtained for the adsorption equilibria of benzene and of carbon dioxide. The micropore volumes W_0 were computed as described in Ref. (13) and by using the molar volumes $v^* = 88.5 \text{ cm}^3/\text{mole}$ for C_6H_6 and $v^* = 41.9 \text{ cm}^3/\text{mole}$ for CO_2 , at 293°K .

For the limiting values of the relative pressures p/p_s considered, the calculated data agreed within 2–3% with the experimental values.

The amount of benzene adsorbed by MSC-4A is one order of magnitude smaller than in the case of MSC-5A, since the bulk of its micropore volume is not accessible to the benzene molecules.

For MSC-5A, on the other hand, benzene fills a total volume of approximately $0.19 \text{ cm}^3/\text{g}$. A moderate activation of 7% burn-off increases perceptibly the micropore volume, but does not alter the molecular sieve properties of the material. It is also found that the characteristic energy of adsorption E_0 shows only a slight decrease in the case of benzene. It follows that the molecular sieve properties of MSC-5A depend on the small dimensions of the micropores themselves. They are directly responsible for the significantly high value of the adsorption energy E_0 of benzene, in the range of 36–37 kJ/mole for $n = 2$.

Carbon dioxide, which is less adsorbed at 293°K than benzene, is representative for the behavior of benzene at pressures lower than the experimentally accessible ones.

For carbon dioxide, as well as for benzene, the adsorption data in the range $p/p_s > 1 \cdot 10^{-4}$ are well described by Eq. [2]. The micropore volumes derived from the experimental data of CO_2 and C_6H_6 are in good agreement. The use of $n = 3$ in Eq. [2] clearly leads to lower values for the micropore volumes and to a smaller range of validity of TVFM, a feature which will be dealt with later.

(3) Relation [9] can be used for the evaluation of characteristic micropore dimensions in the case of carbonaceous adsorbents with homogeneous micropore structures. Parameter k can be derived from experimental data on the molecular sieve properties of these adsorbents. It must be stressed that the results quoted below have a preliminary character, and must be confirmed by further detailed investigations.

As pointed out earlier, molecular sieve MSC-4A practically does not adsorb benzene, unlike MSC-5A, where the entire micropore volume is filled. From the isotherm, it is found that for the latter $E_0 = 35.6 \text{ kJ/mole}$. For slit-shaped micropores one may write, to a good approximation, that $2x = 5 \text{ \AA}$ or 0.5 nm . According to Eq. [9], this leads to $k = 0.25 \cdot 35.6 = 8.90 \text{ kJ nm/}$

mole. According to the experimental data of Ref. (14), the activated adsorption of 1,3,5-triethyl benzene at 293°K on a carbon with parameter $B = 0.45 \cdot 10^{-6} \text{ K}^{-2}$ (or $E_0 = 28.5 \text{ kJ/mole}$), is similar to the adsorption of benzene by zeolite CaX (15). This is indicated by the positive temperature coefficient of the nonequilibrium adsorption process.

According to the data of monograph (16), zeolite CaX does not adsorb molecules with critical dimensions above 7.6 \AA which is close to the critical diameter of triethyl benzene (7.8 \AA). One may, therefore, accept the value $2x = 0.78 \text{ nm}$ for the energy $E_0 = 28.5 \text{ kJ/mole}$. This corresponds to $k = 11.1 \text{ kJ nm/mole}$, according to Eq. [9].

Finally, for the limiting case corresponding to the transition between supermicropores and mesopores, $x = 1.5 - 1.6 \text{ nm}$ and $E_0 = 8.56 \text{ kJ/mole}$ ($B = 5 \cdot 10^{-6} \text{ K}^{-2}$). This leads to the approximate value of $k = 13.0 \text{ kJ nm/mole}$. For the whole range of characteristic dimensions ($0.25 \text{ nm} < x < 1.6 \text{ nm}$), there exists a relationship between k and E_0 , expressed with a good approximation by Eq. [10],

$$k = (13.028 - 1.53 \times 10^{-5} E_0^{3.5}) \text{ kJ nm/mole.} \quad [10]$$

According to this equation, characteristic energies E_0 in the range of 22–14 kJ/mole (Table I) correspond to values of k between 12.5 and 12.9 kJ nm/mole. For the majority of industrial active carbons, $B > 0.75 \cdot 10^{-6} \text{ K}^{-2}$ or $E_0 < 22 \text{ kJ/mole}$, which means that k is almost constant and it can be set equal to 13 kJ nm/mole, to a good approximation. It follows that the characteristic dimension x is related to E_0 by

$$x = 13/E_0 \text{ (nm).} \quad [11]$$

For microporous adsorbents with molecular sieve properties, having characteristic energies in the range of 28.5–35.6 kJ/mole, k varies from 11.1 to 8.9 and has the average value of 10 kJ nm/mole. It follows that it is possible, to some extent, to estimate the

characteristic dimensions of micropores in the case of carbonaceous adsorbents with homogeneous micropore structures.

HETEROGENEOUS MICROPORE STRUCTURES

(1) In the case of strongly or overactivated carbons, one observes the formation of micropores of various sizes and of supermicropores, resulting from the burning-out of walls between adjacent micropores. As a consequence, the distribution of the micropore sizes becomes broader, and the DR and DA equations can no longer be linearized in the usual representation. This situation is clearly illustrated in Figs. 1 and 2 of Ref. (5). In this case, the volume of the micropores becomes a function of parameter B , and instead of Eq. [5] a more general expression is used for the adsorption by heterogeneous micropore systems (5),

$$W = \int_0^\infty f(B) \cdot \exp\{-By\} dB. \quad [12]$$

One may postulate, to a good first approximation, that the distribution of the micropore volume W_0 with B is given by the normalized Gaussian of half-width Δ ,

$$\begin{aligned} \frac{dW_0}{dB} &= f(B) \\ &= \frac{W_0^0}{\Delta(2\pi)^{1/2}} \exp\left\{-\frac{(B_0 - B)^2}{2\Delta^2}\right\}, \quad [13] \end{aligned}$$

where W_0^0 denotes the total volume of the micropores. Integral [12] leads to a possible generalization of the D-R Eq. [1], which is valid for the adsorption of various vapors by heterogeneous micropore systems,

$$W = W_0^0 \exp\{-B_0 y\} \exp\{y^2 \Delta^2 / 2\} \times 0.5[1 - \text{erf}(z)], \quad [14]$$

where the quantity

$$z = (y - B_0/\Delta^2)\Delta/2^{1/2}. \quad [15]$$

Equation [14], hereafter called the D-R-S equation, contains three parameters: W_0^0 , B_0 , and Δ .

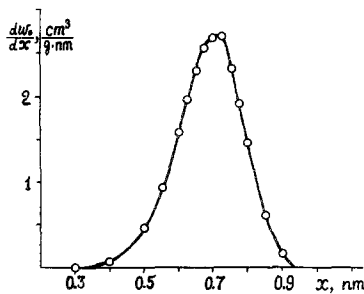


FIG. 1. Differential curve for the distribution of the micropore volume in active carbon F-02, according to the characteristic dimension of the micropores, calculated from Eq. [19].

It is in good agreement with experimental results for the adsorption of simple vapors over a large range of temperature and relative pressures (5, 6, 17).

A broad distribution of micropores may be considered as resulting from the combination of a large number of narrow distributions, for which Eq. [9] individually applies, with the corresponding approximation mentioned earlier.

From Eqs. [4] and [9], it follows that

$$B = Mx^2, \quad [16]$$

where

$$M = (0.01915/k)^2. \quad [17]$$

It is easy to see that the distribution of the micropore volume W with respect to the characteristic dimension x , dW_0/dx , is given by

$$\frac{dW_0}{dx} = \frac{dW_0}{dB} \cdot \frac{dB}{dx} = \frac{dW_0}{dB} \cdot 2Mx. \quad [18]$$

From Eqs. [18] and [13] it follows that

$$\frac{dW_0}{dx} = \frac{2W_0^0 Mx}{\Delta(2\pi)^{1/2}} \times \exp\left\{-\frac{M^2(x_0^2 - x^2)^2}{2\Delta^2}\right\}. \quad [19]$$

A similar relation can also be derived for the distribution of the micropore volume according to the gyration radii, dW/dR_i , in

view of the relation existing between B and R_i (9).

As mentioned earlier, one may use the average value $k = 13.0$ kJ nm/mole for the case of active carbons of industrial origin, without very fine micropores. Figure 1 shows the approximate distribution function [19] computed for the highly activated carbon F-02, having parameters $W_0^0 = 0.64$ cm³/g, $B_0 = 1.03 \cdot 10^{-6}$ K⁻² and $\Delta = 0.29 \cdot 10^{-6}$ K⁻². The distribution function presents a maximum near $x = 0.7$ nm and is tailing off before the limiting region between large micropores and mesopores is reached (this carbon has virtually no mesoporosity). The volume corresponding to $x > 0.8$ nm only represents 0.08 cm³/g, but if one uses the value $k = 12$ kJ nm/mole, this volume practically vanishes.

It should be kept in mind that distribution [19] has a semiquantitative character, owing to the approximation underlying Eq. [9] for the proportionality between x and R_i . As mentioned earlier, R_i is a shape-dependent average dimension of the micropore. A distribution of type [19], expressed in terms of R_i , might also be considered, with the limitation of its exact meaning in terms of a relevant pore dimension such as the width $2d$, for example. In both cases, the exact mathematical form of the distribution plays a role. As mentioned in Ref. (5), the Gaussian distribution [13] was chosen for mathematical convenience, as it leads to a known Laplace transform. Other distributions may also be considered. However, as shown by computer simulations (5), they do not modify significantly the form of the generalized DRS Eq. [14], although their influence may be perceptible for the distributions of W with x or R_i . This means that further experimental data are needed from independent methods for the determination of pore-size distributions, in order to gain a clear picture.

(2) According to TVFM, a broad distribution of micropore sizes can be approximated by the following two-term equation:

$$W = W_{01} \exp\{-(A/\beta E_{01})^2\} + W_{02} \exp\{-(A/\beta E_{02})^2\}, \quad [20]$$

in which parameters W_{01} and E_{01} correspond to micropores, and W_{02} and E_{02} correspond to supermicropores. Consequently, Eq. [20] enables one to differentiate the smaller pores of active carbons, by distinguishing micropores from supermicropores. Table III shows the results obtained by applying Eqs. [14] and [20] to the experimental adsorption data for carbon F-02 (5, 6, 17).

In the case of the D-R-S Eq. [14], one obtains $W_0^0 = 0.64 \text{ cm}^3/\text{g}$, $B_0 = 1.03 \cdot 10^{-6} \text{ K}^{-2}$, and $\Delta = 0.29 \cdot 10^{-6} \text{ K}^{-2}$. The two-term Eq. [20], on the other hand, leads to $W_{01} = 0.178 \text{ cm}^3/\text{g}$, $E_{01} = 25.5 \text{ kJ/mole}$, $W_{02} = 0.462 \text{ cm}^3/\text{g}$, and $E_{02} = 17.7 \text{ kJ/mole}$.

These results correspond, formally, to the adsorption of benzene. As shown by the values of Table III, both equations lead practically to the same results and are in good agreement with the experimental data. Equation [20] appears to be a rational approximation, whose parameters can be derived from a single isotherm and over a large range of relative pressures. Of course, it does not lead to a distribution of the micro-

TABLE III

Average Volumes W of Gases Adsorbed by Active Carbon F-02, According to the Experimental Data (5, 6, 17) for N_2 (78, 249, 273, and 318°K), Xe (226, 273, and 323°K), SF_6 (255, 273, and 316°K), C_6H_6 (273 and 327°K), and $n\text{-C}_4\text{H}_{10}$ (273°K), as Calculated from Eqs. [14] and [20]^a

$y \cdot 10^{-6}$	p/p_s	$W \text{ (cm}^3/\text{g)}$		
		Experiment	From Eq. [14]	From Eq. [20]
8.00	$2.25 \cdot 10^{-10}$	0.0020	0.0024	0.0020
4.00	$1.50 \cdot 10^{-7}$	0.020	0.020	0.023
2.00	$1.30 \cdot 10^{-5}$	0.093	0.097	0.102
1.00	$3.89 \cdot 10^{-4}$	0.244	0.238	0.228
0.50	$3.87 \cdot 10^{-3}$	0.395	0.386	0.391
0.10	$8.30 \cdot 10^{-2}$	0.581	0.577	0.579
0.05	$1.73 \cdot 10^{-1}$	0.610	0.608	0.609

^a The relative pressures p/p_s correspond to the case of benzene at 293°K.

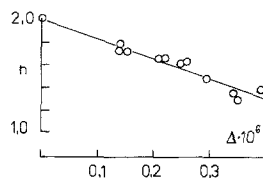


FIG. 2. Relation between parameters n and Δ of Eqs. [2] and [14], given in Table IV.

pore volume, as shown in Fig. 1 for carbon F-02, but as far as the adsorbability is concerned, Eq. [20] is equivalent to Eq. [14].

(3) Following Kadlec (18), Rand (19) showed that in the case of active carbons with a broad micropore distribution, the D-A Eq. [2] can be used with noninteger values of n between 1 and 2. In this case, Eq. [2] contains three parameters, W_0 , E_0 , and n , and a graphical representation of $\ln a$ versus A^n is reasonably linear. It can also be shown that parameter n is directly related to the characteristic variable Δ of the D-R-S Eq. [14]. This is illustrated by Fig. 2, representing the results obtained from the simultaneous fitting of adsorption data (5, 17) to Eqs. [2] (variable n) and [14] (Table IV). Their best fit leads to the linear equation

$$n = 2.00 - 1.78 \cdot 10^6 \Delta \quad [21]$$

which is valid for the range of B_0 , Δ , and n considered here.

As mentioned earlier, the D-R-S Eq. [14] is based on the D-R Eq. [1], where $n = 2$. This value of n has a real meaning for micropores and supermicropores, but noninteger values appear to be the effective ones.

(4) One can also consider a generalization of the D-A Eq. [2], similar to the one leading to the D-R-S Eq. [14], and in which a distribution of the characteristic energy E_0 is considered instead of variable B of Eq. [1]. This approach leads to the same results as Eqs. [14] and [20], as far as the adsorption isotherm is concerned, but it may have interesting repercussions on the distribution of micropore dimensions. A detailed analysis will be described later.

TABLE IV

Comparison of Parameters Obtained for Various Active Carbons (5, 17), by Using Eqs. [2], [14], and [21] (Benzene as the Reference Vapor)

Active carbon	Eq. [14]			<i>n</i>		Difference in (%)
	W_0^3 (cm ³ /g)	$B_0 \cdot 10^6$ K ²	$\Delta \cdot 10^6$ K ²	Eq. [2]	Eq. [21]	
U-02	0.43	0.92	0.21	1.65	1.63	-1
U-03	0.48	1.27	0.39	1.38	1.31	-5
F-02	0.64	1.03	0.29	1.47	1.48	0
F-85	0.75	0.98	0.35	1.28	1.38	7
T	0.40	0.61	0	2.00	2.00	0
Carbosieve	0.51	0.57	0	2.00	2.00	0
AC-400 deashed	0.42	0.61	0.15	1.71	1.73	1
AC-900 deashed	0.41	0.70	0.14	1.70	1.75	3
CAL	0.44	0.99	0.26	1.63	1.53	-7
M1	0.23	0.63	0.14	1.79	1.75	-2
M2	0.29	0.87	0.22	1.66	1.61	-3
M3	0.34	0.96	0.25	1.61	1.56	-3
M4	0.55	1.07	0.34	1.33	1.39	4

OTHER POSSIBLE ALTERNATIVES FOR THE DESCRIPTION OF MICROPOROUS STRUCTURES

The adsorption experiments for benzene and carbon dioxide on molecular sieves MSC-4A and MSC-5A, described above, show that the value $n = 2$ describes well the case of adsorption in micropores having sizes almost identical to the dimensions of the adsorptives. As shown in Table II, the use of $n = 3$ does not lead to further improvement. Graphical representations of Eq. [2] with $n = 2$ and $n = 3$ are found to be of comparable accuracy, but they do not reproduce the experimental data over more than two orders of magnitude in p/p_s . How-

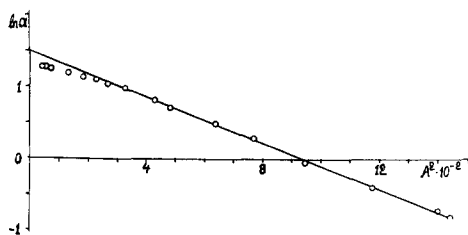


FIG. 3. Adsorption isotherm of benzene on a "Saran" based active carbon, at 362°K, represented in the linearized form of Eq. [2] with $n = 2$.

ever, an interesting exception has been found for an active carbon obtained from the thermal decomposition of granules of polyvinylidene chloride, where the temperature was increased quite slowly. Figure 3 corresponds to the linear representation of Eq. [2], with $n = 2$, for the adsorption of benzene by this carbon at $T = 362^\circ\text{K}$, as reported by Finger and Bülow (20). In the interval $3 \cdot 10^{-6} < p/p_s < 4 \cdot 10^{-3}$, the experimental data yield a straight line corresponding to parameters $a_0 = 4.39$ mmole/g or $W_0 = 0.421$ cm³/g, and $E_0 = 25.0$ kJ/mole ($v^* = 0.0958$ cm³/mole). For the region $4 \cdot 10^{-3} < p/p_s < 0.1$, one observes a characteristic departure from linearity, with a maximum deviation of -14%, in terms of the adsorbed amount a .

According to the authors (20), practically all the experimental data can be fitted to Eq. [2] with $n = 2.5$, $a_0 = 3.73$ mmole/g, or $W_0 = 0.358$ cm³/g, and $E_0 = 27.0$ kJ/mole. In this case, the micropore volume is not increased with respect to the result of Eq. [2] with $n = 2$, as frequently observed.

On Fig. 4, the same experimental data are represented in the form of $\ln a$ versus A^3 , corresponding to Eq. [2] with $n = 3$. It can

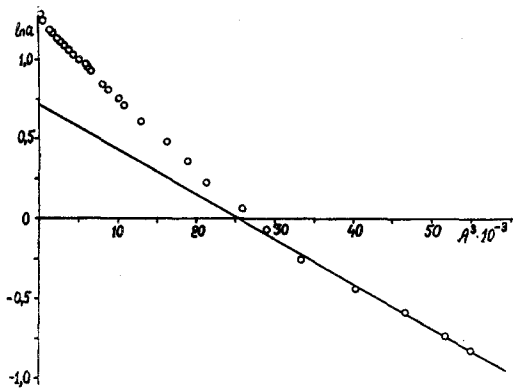


FIG. 4. Same adsorption isotherm as in Fig. 3., in the linearized form of Eq. [2] with $n = 3$.

be seen that only six points, corresponding to the initial region of p/p_s between $3 \cdot 10^{-6}$ and $3 \cdot 10^{-5}$, fall in a straight line. The other points show a deviation from linearity which is similar to the one observed in the case of heterogeneous carbons with $n = 2$. By analogy, one may suggest that the case $n = 3$ corresponds to very fine micropores, with a high characteristic energy E_0 . The larger micropores, corresponding here to normal micropores, may appear during the formation of the carbonaceous material and during its activation. The presence of both types of micropores, fine and normal, is also in agreement with the noninteger value of n between 2 and 3. By extension of Eq. [20], one can also postulate the following two-term expression,

$$W = W_{01} \exp\{-A/\beta E_{01}\}^3 + W_{02} \exp\{-A/\beta E_{02}\}^2. \quad [22]$$

The parameters of Eq. [22] can be calculated from a single isotherm over a large range of relative equilibrium pressures, either by mathematical fitting or by a simple graphical method, as in the case of $n = 2$ (1). In this way, the benzene isotherm for $T = 362^\circ\text{K}$ yields $W_{01} = 0.191 \text{ cm}^3/\text{g}$ ($a_{01} = 2.00 \text{ mmole/g}$) and $E_{01} = 32.86 \text{ kJ/mole}$ for the term with $n = 3$, and $W_{02} = 0.186 \text{ cm}^3/\text{g}$ ($a_{02} = 1.94 \text{ mmole/g}$) and $E_{02} = 18.34 \text{ kJ/mole}$ for the term with $n = 2$. The overall micropore volume $W_0 = 0.377 \text{ cm}^3/\text{g}$.

The physical character of the two-term Eq. [22] deserves further investigation, as well as the fact that the "Saran" based material contains a type of fine micropores which is not present in the molecular-sieve MSC-5A.

It is worthwhile to point out that Eq. [22] can be used to describe accurately all benzene adsorption isotherms in the range of $340\text{--}500^\circ\text{K}$.

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