

A Generalization of the Dubinin–Radushkevich Equation for the Filling of Heterogeneous Micropore Systems in Strongly Activated Carbons

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A generalization of the Dubinin–Radushkevich equation, recently proposed by Stoeckli as an alternative to the Dubinin–Astakhov equation, is discussed theoretically and is tested with new experimental data. The extended equation applies to the filling of heterogeneous micropore systems in strongly activated carbons. It is based on the assumption that the original D–R equation only applies to relatively homogeneous systems of micropores, if adsorption is considered over a large range of temperature and pressure. This is suggested by adsorption experiments on carbons with marked molecular-sieve properties. Heterogeneity is dealt with by introducing weighted contributions from the various systems, all following the D–R equation, but with different structural parameters. A Gaussian distribution of the micropore volumes with respect to constant B leads to a satisfactory general isotherm, with an extended range of applicability. This isotherm is also compared with the generalization of Dubinin and Astakhov.

INTRODUCTION

Adsorption by microporous solids in general, and by active carbons in particular, is described by the theory of volume filling of micropores (TVFM), elaborated in successive stages by Dubinin and his co-workers (1–3). The fundamental relations are the Dubinin–Radushkevich and the Dubinin–Astakhov equations [1] and [2]. The latter reflects the present formulation of the theory, and it includes the D–R isotherm as a special case. The D–R and D–A equations have been discussed by Marsh and Rand (4) and by Rand (5).

For temperatures smaller than T_c , the D–R equation is

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(p_0/p)], \quad [1]$$

where W represents the volume of the liquid-like adsorbate present in the micropores at temperature T and at relative pressure p/p_0 , and W_0 is the total volume of the micropores. B and β are two specific constants, depending, respectively, on the nature of the solid and on the adsorptive. The equation of Dubinin and Astakhov (3), on the other hand, is

$$W = W_0 \exp[-(A/E)^n], \quad [2]$$

where $A = RT \ln(p_0/p)$ and E is a characteristic free energy, depending on the adsorbate–adsorbent system under investigation. E contains implicitly the quantities B and β of Eq. [1]. The new variable, with respect to Eq. [1], is the exponent n . In the case of adsorption by carbonaceous materials, n is usually smaller than 2 and it decreases with increasing degree of activa-

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tion. Typical values for strongly activated carbons are found in the range 1.20 to 1.80 (5). In the case of zeolites, on the other hand, n can vary from 3 to 6 (2).

Different authors (4–8) have pointed out that the original D–R equation has a variable range of validity, which seems to depend on the degree of burn-off. It now appears clear that, under similar experimental conditions, carbons with molecular-sieve properties follow much closer the D–R equation than carbons with high degrees of burn-off. The deviation from linearity in a $\log W$ vs $\log^2 (p_0/p)$ plot increases with activation and corresponds to type *B* in the classification of Rand (5). At an earlier stage, Izotova and Dubinin (9) showed that the absence of linearity could be explained in terms of a sum of two equations, corresponding to the contributions of two different types of micropores, in agreement with X-ray measurements (10).

Adsorption experiments carried out in this laboratory with a number of simple molecules adsorbed by strongly activated carbons, suggest that the D–A Equation [2] cannot linearize satisfactorily the entire set of data, if a large range of temperature and pressure is considered. Moreover, no clear correlation can be found between the variation in the degree of activation and the variable n . Similar conclusions are also reached from the data published by Mahajan *et al.* (7), where the departure from linearity in the D–R plot already begins near $\log^2 (p_0/p) = 10$ for the adsorption of CO_2 . At the same time, the work of different authors (4, 5, 7) and our own investigations show that under similar experimental conditions, the less activated carbons and carbons with molecular-sieve properties follow much closer the D–R equation [1].

It has been pointed out by Dubinin (2), that the validity of TVFM, and implicitly of Eq. [2], is limited to degrees of micropore filling higher than 0.15 approximately. This limit is suggested by the condition that the

entropy of adsorption should be negative. This has also been discussed by Dovaston *et al.* (11), who point out that the condition that $\Delta S < 0$ is consistent with the postulates of the potential theory, but not generally valid. In practice it is also found that our experimental data can be fitted to the D–A equation as far as $\theta = 0.01$ and less. The limitations of TVFM, suggested by theoretical considerations should therefore not be an absolute obstacle to new attempts for the description of adsorption by activated carbons, as in the present case.

Since the D–A Eq. [2] cannot describe the entire range of experimental data in the case of strongly activated carbons, alternative descriptions are needed. One such possibility, recently proposed by Stoeckli (12), is developed below. It is based on the assumption that adsorption by heterogeneous carbons can be represented by a sum of contributions of the D–R type for the various classes of micropores. It is therefore a refinement of the earlier approach of Izotova and Dubinin (9), and it is still based on the general principles of the theory (1).

EXPERIMENTAL RESULTS

The experimental procedure has already been described elsewhere (6). Further data, used in the present work, has been collected for different active carbons, including two carbons of polymer origin, which display molecular-sieve properties. One of them (Carbosieve, from Supelco Inc., USA) is available commercially and is used in GSC separations. All measurements were carried out with spring balances and transducer gauges covering a pressure range from 10^{-4} to 10^3 mm Hg. In the present work, we considered only temperatures smaller than critical, for the various gases used as adsorbates.

Since microporous carbons may also contain meso- and macropores, their external surface area must also be deter-

mined in order to correct the initial adsorption data, if needed. This area can be assessed either by using the method of Dubinin and Kadlec (13), based on the t -plot, or by using the method of Gregg and Langford (14). In the latter technique, used here, one compares the adsorption of nitrogen at 77 K before and after preadsorption of n -nonane at room temperature. If one assumes total accessibility of the micropores to nonane, the second nitrogen isotherm corresponds virtually to the adsorption on the external surface (meso- and macropores). This method has also been used by Marsh and Campbell (15), but no details are given by the other authors (4-5, 7, 8) for their active carbons. In the case of Mahajan *et al.* (7), it appears that the external surface area of the molecular-sieve carbons CMS-A and -B is only 20 m²/g, against total equivalent surface areas of 860 to 950 m²/g. The former value corresponds to the uptake of n -butane, which is practically excluded from the micropore system. The correction to the total isotherm is therefore small, and it may be concluded that the extended linearity of the D-R plot observed for the adsorption of CO₂ at 25°C is real and specific. In the case of our samples of series U and F (Table I), the method of Gregg and Langford (14) shows unambiguously that the external surface is small. It does not exceed 5% of the equivalent micropore area. This feature must be ascribed to the origin and to the specific conditions of activation of our samples, since the external surface area is more important in the examples described by Dubinin and Kadlec (13) and by Marsh and Campbell (15).

After correcting for the external surface, if needed, the volume W of the adsorbate in the micropores has to be calculated from the amount adsorbed, usually expressed in moles per gram. According to Dubinin and Nikolaev (2, 16), the molar volume of the adsorbate in the pores can be obtained from a linear interpolation of

TABLE I
Comparison of Results for Various Active Carbons

Carbon	Origin	Eq. [7]			Eq. [2] n
		$W_0/$ cm ³ g ⁻¹	$B_0/$ 10 ⁻⁶	$\Delta/$ 10 ⁻⁶	
U-02	Mineral	0.43	0.92	0.21	1.65
F-02	Vegetable	0.64	1.03	0.29	1.47
F-85	Vegetable	0.75	0.98	0.35	1.28
T	Polymer	0.40	0.61	—	2.0
Carbosieve	Polymer	0.51	0.57	—	2.0
AC-400 (7)	Mineral	0.42	0.73	0.21	1.18
AC-900 (7)	Mineral	0.43	0.72	0.28	1.22
AC-400 (7) de-ashed	Mineral	0.42	0.61	0.15	1.71
AC-900 (7) de-ashed	Mineral	0.41	0.70	0.14	1.70

the densities between T_c and a relatively low temperature such as the triple point or the normal boiling point. It is also assumed that at T_c , the limiting value of the molar volume is Van der Waal's constant b . This arbitrary choice for the volume of the adsorbate has to be compared with the values derived from the orthobaric densities of the pure liquid, which increase more rapidly as the temperature approaches T_c . In this case, the limiting value is V_c , which is 2 to 3 times larger than b . It is reasonable to assume that in a micropore the adsorbate may exist with a density higher than in the liquid state, at higher temperatures, as confirmed by the work of Dubinin (1-2). However, deviations from the exact relationship postulated by Nikolaev and Dubinin (16) cannot be ruled out a priori.

Figure 1 shows the results for the adsorption of N₂O by a strongly activated carbon of vegetable origin (F-85), at 243 and 293 K. The heterogeneous character of this material is suggested by the strong curvature in the plot of $\ln W$ versus the quantity $y = (T/\beta)^2 \log^2(p_0/p)$. If one uses the molar volumes of the pure liquid, two distinct curves are obtained. It is found that they are parallel within experimental error, and the results for the higher temperature overlap completely with the curve for the lower

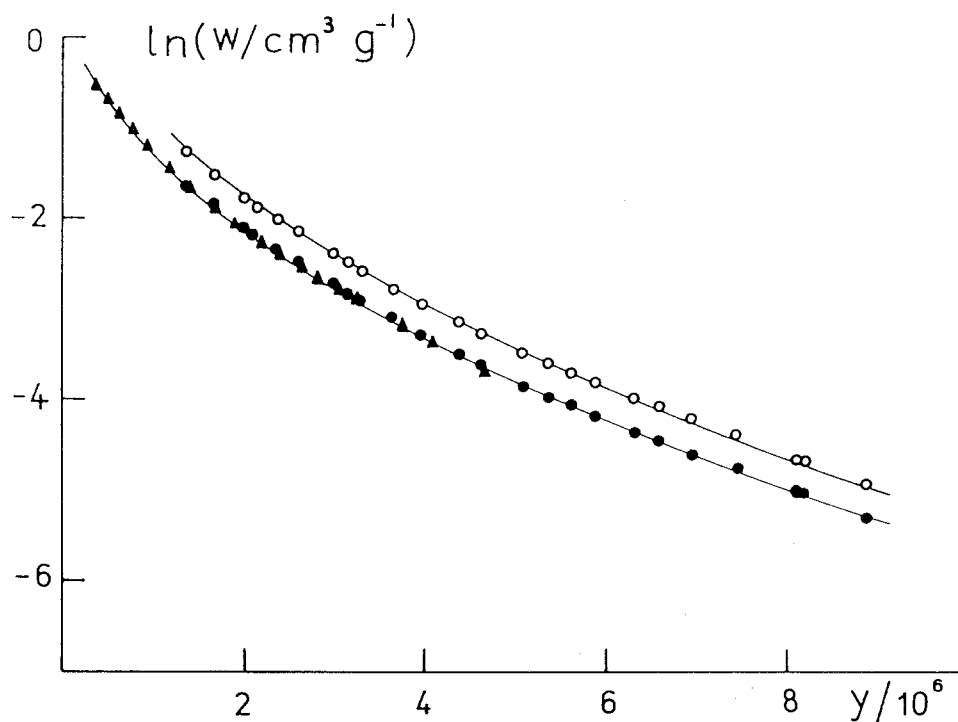


FIG. 1. The adsorption of N_2O by carbon F-85 at 243 K (\blacktriangle) and 293 K, using either the orthobaric density of the pure liquid (\circ) or a slightly modified value from the Dubinin-Nikolaev interpolation method (\bullet). The quantity $y = (T/\beta)^2 \log^2(p_0/p)$.

temperature if one uses a molar volume which is slightly different from the value obtained by the interpolation method of Dubinin and Nikolaev. For other systems and temperatures, it is also found that the best fits to the low temperature results occur for values of the molar volume which are usually 10 to 15% higher than the predictions from the interpolation method. In some cases, they can also be smaller. This suggests that the density of the adsorbed state may be influenced by the geometry of the micropores, especially at higher temperatures. This problem has not been met by the other authors (4-5, 7, 8), who studied adsorption at one temperature only, for a given system.

As illustrated by the examples of Figs. 2 and 3, a single characteristic curve is obtained for each solid, when $\ln W$ is plotted against the quantity $y = (T/\beta)^2 \log^2(p_0/p)$,

for various simple gases adsorbed at different temperatures. The only adjustable parameter, as discussed above, is the volume of the adsorbates at relatively high temperatures. The distinctive feature, in the case of strongly activated carbons, is the characteristic curvature in the logarithmic plot. This property is directly related to the parameters of the generalized D-R equation discussed in the following section. Figure 3 shows the adsorption of various simple gases by a typical molecular-sieve carbon, with pores in the region of 6-7 Å. The experimental conditions are the same as in the case of carbon F-02, but there is no deviation from the classical D-R equation [1]. Similar examples are also given by Marsh and Rand (4, 5) and by Mahajan *et al.* (7), and it may be concluded that the linearity of the plot in the case of molecular-sieves is a specific property.

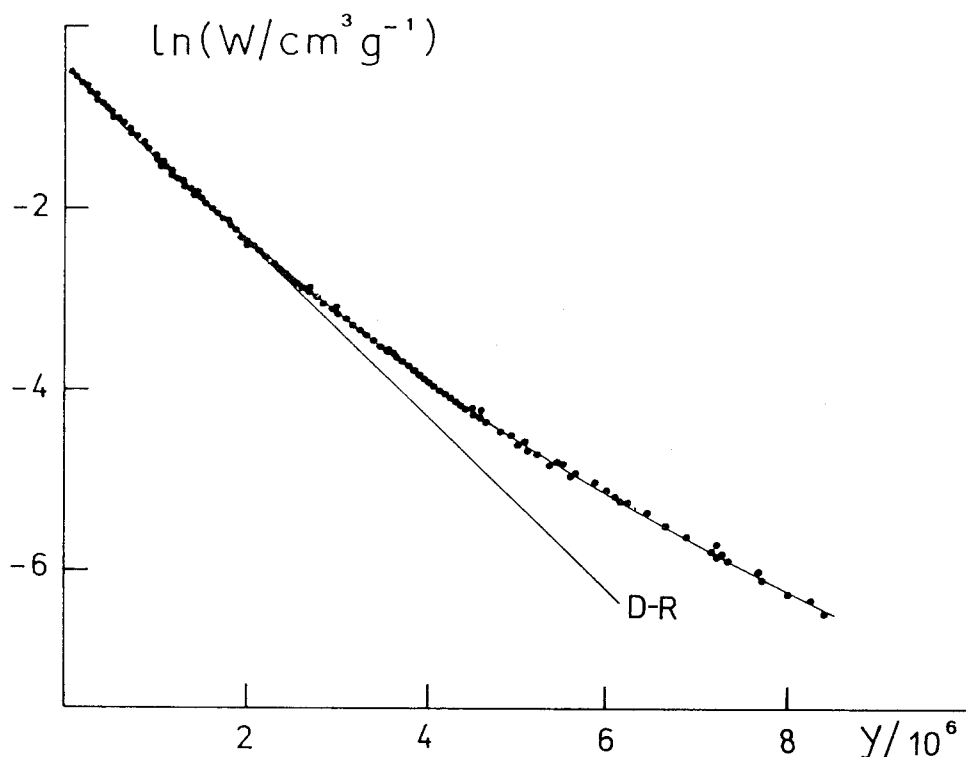


FIG. 2. The adsorption of N_2 (77 K), Xe (226, 273, and 293 K), N_2O (273 and 293 K), SF_6 (255, 273 and 318 K), C_6H_6 (273 and 323 K) and *n*-butane (273 K) by carbon F-02. For the sake of clarity, not all points are shown in the region $y < 4 \times 10^6$.

THE EXTENDED EQUATION

If we postulate that Eq. [1] applies strictly to homogeneous systems of micropores, adsorption by a heterogeneous collection of micropores should be expressed in the form of a sum of contributions,

$$W = \sum W_{0j} \exp[-B_j(T/\beta)^2 \log^2(p_0/p)], \quad [3]$$

where W_{0j} and B_j correspond to a given class of micropores. If one excepts discrete and widely different contributions, as in the assumption of Izotova and Dubinin (9), one may postulate, for mathematical convenience, a continuous distribution $f(B)$ for the volumes W_{0j} . The sum is then replaced by the integral

$$W = \int_0^{\infty} f(B) \exp[-B \cdot y] dB. \quad [4]$$

The variable $y = (T/\beta)^2 \log^2(p_0/p)$ already contains the adsorptive-dependent shifting factor β (affinity coefficient), and therefore simplifies the overall graphical representation. The total volume of the micropores in the solid is given by the normalization condition

$$W_0 = \int_0^{\infty} f(B) dB. \quad [5]$$

From a mathematical point of view, the general expression [4] is an integral of the Laplace type, with the D-R equation [1] as the core equation. Various functions can be used for $f(B)$, the simplest being the normalized Gaussian,

$$f(B) = [W_0/\Delta(2\pi)^{1/2}] \times \exp[-(B - B_0)^2/2\Delta^2]. \quad [6]$$

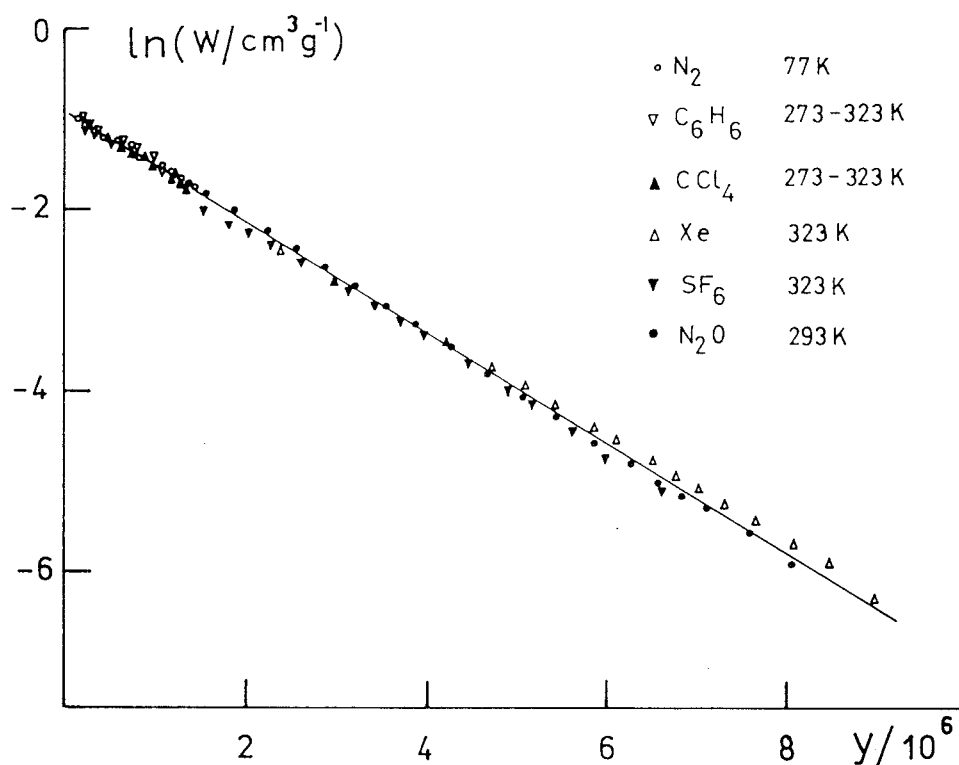


FIG. 3. The adsorption of various simple gases by the polymer-based carbon T. This solid shows molecular-sieve properties and has pores in the range of 6-7 Å.

With [6], the integral transform [3] leads to the Gaussian-based general equation for the filling of micropores

$$W(y) = W_0 \exp[-B_0 \cdot y] \times \exp[y^2 \Delta^2 / 2] \cdot [1 - \operatorname{erf}(x)] / 2, \quad [7]$$

where $x = (y - B_0 / \Delta^2) \Delta / (2)^{1/2}$, and $\operatorname{erf}(x)$ is the tabulated error function (17).

Tables of Laplace transforms (18), and direct computations of the type described below, show that the three-parameter Gaussian [6] is a very good approximation for various distributions. This distribution is also sufficient at present, in view of the experimental errors, to describe heterogeneity in terms of a spread around an average value B_0 of the structural parameter B .

Like the Dubinin-Astakhov equation [2], the proposed expression [7] contains three

parameters. However, since B is known to be related to average pore dimensions (2, 6, 9, 10), it follows that a clear physical meaning can be ascribed to Eq. [7]. In the case of the D-A equation, on the other hand, the exact physical meaning of the variable exponent n is not evident, although it varies with the degree of activation and the volume of the micropores (see Table I).

The experimental data for adsorption by various carbons investigated in our laboratories and elsewhere (7), were fitted to Eq. [7] by means of an appropriate computer subroutine due to Lang and Müller (19). The results are given in Table I, with the corresponding values of parameter n for the best fit to the D-A equation [2]. It is also found that Eq. [7] provides a better fit for the experimental data of strongly activated carbons, than Eq. [2], where systematic deviations appear when $y > 4-5 \times 10^6$.

This is also in agreement with the finding that a mutual approximation for Eqs. [2] and [7] is only possible over a limited range of values of y (approximately 4×10^6). This implies, indirectly, that there exists a slight difference between the underlying physical models. However, it must be kept in mind that the discrepancies occur for $y > 4-5 \times 10^6$, which corresponds to a low degree of micropore filling and where TVFM does not necessarily apply (2).

The analysis of Eq. [7] also shows that the curvature in the logarithmic plot depends on Δ and increases with it. Let us consider the tangent to the curve at a point of coordinates $\ln W$ and y . According to Eq. [7], the slope is

$$d \ln W(y)/dy = -B_0 + y\Delta^2 \\ -\Delta(2/\pi)^{1/2} \exp[-x^2]/\operatorname{erfc}(X) = -B(y), \quad [8]$$

and the corresponding intercept on the $\ln W$ axis, $W_0(y)$ is given by

$$\ln W_0(y) = \ln W(y) + y \cdot B(y). \quad [9]$$

The quantities $B(y)$ and $W_0(y)$ are only apparent D-R parameters in the case of heterogeneous carbons, and they correspond to a narrow range of data. They would, for example, be obtained from classical D-R plots of $\ln W$ vs $\log^2(p_0/p)$ with adsorption data at one temperature only and for relative pressures covering approximately two orders of magnitude.

If the curvature of the generalized representation is pronounced, as in Figs. 1 and 2, a change in temperature will lead to new values of W_0 and B for the same system. This is precisely the feature which has been observed earlier (6), when the adsorption of simple gases by strongly activated carbons was measured over a large range of temperatures. By combining Eqs. [7], [8], and [9], it can be shown that the apparent distribution of the D-R parameter $W_0(y)$ vs $B(y)$ found earlier (6) is directly related to $f(B)$ of Eq. [4]. This shows clearly that it is preferable to consider $\ln W$ as a function of

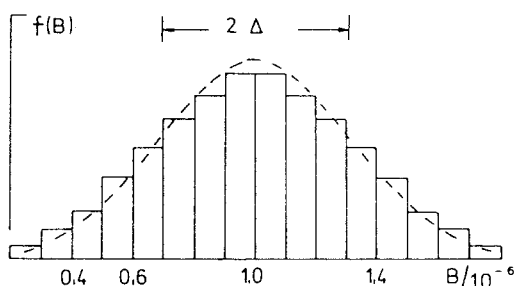


FIG. 4. Gaussian distribution function $f(B)$ with $B_0 = 1.0 \times 10^{-6}$ and a spread $\Delta = 0.30 \times 10^{-6}$. It corresponds closely to the case of carbon F-02. The segments were used in the computer simulations described in the text.

y , rather than of $\log^2(p_0/p)$ alone. It is also found that the heterogeneity of the material will be mostly unnoticed, if adsorption is limited to conditions corresponding to small values of y , such as the normal boiling point of the adsorptive (N_2 at 78 K or benzene near room temperature, for example). This type of experiment is limited to values of $y < 2-3 \times 10^6$, where the curvature is not obvious.

The generalized Eq. [7] has also been tested by computer simulations, and compared with the D-A equation [2]. The main reason was to assess the validity of Eq. [7] with respect to various approximations for $f(B)$, since transforms are not very sensitive to modifications in the function to be transformed. The simulations were started by generating isotherms of type [7], in which typical values of B_0 and Δ were used (1.0×10^{-6} and 0.15 to 0.30×10^{-6} , respectively). The total micropore volume was $W_0 = 0.60$ and $\beta = 1$. The calculations, carried out in the range of $y \leq 10^7$, formally corresponded to the adsorption of benzene by a strongly activated carbon, over a large range of temperature and pressure. In a second step, similar isotherms were calculated by using finite sums of type [3], based on discrete contributions from the original Gaussian distributions $f(B)$. Figure 4 shows the case of the Gaussian with $\Delta = 0.30 \times 10^{-6}$, divided into 16 steps. The compari-

son of the two types of isotherms shows that there is no significant difference between them, so that Eq. [7] could in fact also represent discrete contributions of different micropore systems.

The effect of truncation in the discrete sums [3] was also investigated, by fitting the new isotherms to the analytical expression [7]. Physically, this corresponds to the approximation of the truncated distribution to a new Gaussian distribution. The results of the various tests can be summarized as follows:

a. Truncation from the left (suppression of the smaller values of B in Fig. 4) reduces W_0 and Δ , as expected, and shifts B_0 towards higher values.

b. Truncation from the right has the same effect on W_0 and Δ as before, but B_0 is shifted towards smaller values.

c. In both cases, there is a good agreement between the isotherms calculated from the truncated sums, and their best fit to a Gaussian approximation through Eq. [7].

The last point reflects a certain lack of sensitivity in the Laplace transform, and fully justifies the use of a Gaussian curve to approximate the true distribution $f(B)$, which may be nonsymmetrical. A further limitation in the calculation of the real distribution $f(B)$ is the experimental error in the real adsorption data, which further reduces the sensitivity of the method.

Observation (a) has interesting implications, and it corresponds to the case of restricted adsorption of certain molecules with respect to others. In the case of static adsorption, molecular-sieve effects will produce changes in the apparent distribution function $f(B)$, since the accessibility of the pore system changes. This effect has clearly been observed in this laboratory, in the case of microporous Cr_2O_3 . The adsorption of nitrogen at 77 K ($W_0 = 4.5 \times 10^{-3} \text{ cm}^3/\text{g}$, $B = 1.8 \times 10^{-6}$) and of neopentane at 273 K ($W_0 = 1.3 \times 10^{-3} \text{ cm}^3/\text{g}$, $B = 2.6 \times 10^{-6}$) indicate the presence of a range of microporosity, of which only the upper part is ac-

cessible to the larger molecules of neopentane.

A similar shift is also observed in the case of adsorption isotherms derived from dynamic GSC measurements (20), when compared with the results from static measurements. For strongly activated carbons, the differences between the static and dynamic values of W_0 and B for the D-R equation [1] can be as high as 20%.

Finally, the various adsorption isotherms generated by computer were compared with the D-A equation [2]. It was found that the mutual approximation was limited to a range of $y < 4-5 \times 10^6$. The best agreement was found for the case of isotherms generated either from rectangular distributions $f(B)$, or from two spaced contributions of the Dirac delta type. The latter is evidently a double-pore system, poorly approximated by a Gaussian, and closer to the case of zeolites. However, it must be stressed, that the differences between Eq. [7] and the D-A equation [2] only become significant at small degrees of micropore filling.

CONCLUSIONS

The present work shows that in the case of adsorption by strongly activated and heterogeneous carbons, deviations from the classical Dubinin-Radushkevich equation [1] can be described in a satisfactory way by the alternative generalization proposed by Stoeckli (12). Like the equation of Dubinin and Astakhov [2], the new expression [7] has three parameters, to which a clear physical meaning can be ascribed.

REFERENCES

1. Dubinin, M. M., *J. Colloid Interface Sci.* **23**, 487 (1967); "Chemistry and Physics of Carbon" (E. D. Walker, Jr., Ed.), Vol. 2, pp. 51-120. Dekker, New York, 1966.
2. Dubinin, M. M., "Progress in Membrane and Surface Science" (D. A. Cadenhead, Ed.), Vol. 9, pp. 1-70. Academic Press, New York, 1975.

3. Dubinin, M. M., and Astakhov, V. A., *Izv. Akad. Nauk SSSR Ser. Khim.* **1971**, 5.
4. Marsh, H., and Rand, B., *J. Colloid Interface Sci.* **33**, 101 (1970).
5. Rand, B., *J. Colloid Interface Sci.* **56**, 337 (1976).
6. Stoeckli, H. F., and Houriet, J. P., *Carbon* **14**, 253 (1976).
7. Mahajan, O. P., Morishita, M., and Walker, P. L., Jr., *Carbon* **8**, 167 (1970).
8. Tsunoda, R., *Bull. Chem. Soc. Japan* **50**, 2058 (1977).
9. Izotova, T. I., and Dubinin, M. M., *Zh. Fiz. Khim.* **39**, 2796 (1965).
10. Dubinin, M. M., and Plavnik, G. M., *Carbon* **6**, 183 (1968).
11. Dovaston, N. G., McEnaney, B., and Weedon, C. J., *Carbon* **10**, 277 (1972).
12. Stoeckli, H. F., *J. Colloid Interface Sci.* **59**, 184 (1977).
13. Dubinin, M. M., and Kadlec, O., *Carbon* **13**, 263 (1975).
14. Gregg, J. S., and Langford, J. F., *Trans. Faraday Soc.* **65**, 1394 (1969).
15. Marsh, H., and Campbell, H. G., *Carbon* **9**, 489 (1971).
16. Nikolaev, K. M., and Dubinin, M. M., *Izv. Akad. Nauk SSSR. Ser. Khim.* **1958**, 1165.
17. Abramowitz, M., and Stegun, I. A., "Handbook of Mathematical Functions." Dover, New York, 1965.
18. Magnus, W., Oberhettinger, F., and Soni, R. P., "Formulas and Theorems for the Special Functions of Mathematical Physics." Springer Verlag, Heidelberg, 1966.
19. Lang, J., and Müller, R., *Computer Phys. Commun.* **2**, 79 (1971).
20. Kiselev, A. V., and Yashin, Y. Y., "La Chromatographie Gaz-Solide", Masson, Paris, 1969.