

According to Eq. (2) in one year after formation  $f = 1.2 \times 10^{-2}\%$  and in ten years  $f = 0.12\%$ .

It is therefore to be expected that the properties of vacancies can be studied in this way in a reasonable timescale.

Measurements of the electronic properties of electron irradiated samples with  $\sim 10^{-4}\%$  of Frenkel defects[7], taken at 5K show that these can be readily detected, so that the above estimates are not unreasonable. It is possible however that  $^{14}\text{N}_7$  might be retained in the sample and interfere with the measurements of vacancy properties. However the  $^{14}\text{N}_7$  release could be monitored, and the sample could be annealed up to quite high temperatures to promote the release without causing significant vacancy mobility.

Thus, given the availability of  $^{14}\text{C}_6$  in gm quantities, which could be recovered at the end of the experiment, there is a high probability of success in the determination of vacancy properties.

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## On the description of micropore distributions by various mathematical models

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**Key Words** - Micropore distributions, active carbons

Jaroniec and Choma [1] recently compared the micropore distributions based on their adsorption isotherm [2,3] and the distribution used by Dubinin [4]. We feel that their interesting paper calls for some comments, which may lead to a possible generalization. Both approaches are based on an integral transform of the type.

$$\theta(A) = \int_a^b f(x) \cdot g(A;x) dx \quad (1)$$

where  $A = RT \ln(p_0/p)$ , involving a "core" equation  $g(A;x)$  and a suitable distribution  $f(x)$  of the micropore size  $x$ . Dubinin uses a Gaussian, whereas Jaroniec and Choma proposed a Gamma-type distribution, which leads to a simple overall isotherm. It is important to realize that both approaches use the classical Dubinin-Radushkevich (DR) eqn

$$g = \exp [-(A/\beta E_0)^2] \quad (2)$$

as the core and both require a functional relation between the characteristic energy  $E_0$  and a pore dimension, either its width  $L$  or its half-value  $x$ .

(The latter was used in an earlier correlation based on the gyration radius of the pores [5], but for slit-shaped micropores it can be replaced by their actual width  $L$ ). If one postulates a relation of the type

$$E_0 = K/L \quad (3)$$

it follows that

$$g(A;L) = \exp[-(A.L/\beta K)^2] \quad (4)$$

By using suitable distribution functions  $f(L)$ , eqn(1) can be solved within the framework of classical Laplace transforms [6] and overall isotherms  $\theta(A)$  of varying complexity are obtained [2-4]. At this stage, two important points must be discussed.

The first is based on the mathematical property [6] that the integral transform of a Dirac  $\delta$ -function  $f(L)$  reduces  $\theta(A)$  to the core eqn, i.e. to the original DR eqn in the present case. The analysis of adsorption data which follows the DR eqn would therefore lead to an extremely small distribution  $f(L)$ . In other words, the overall equations obtained by Dubinin and by Jaroniec and Choma rest on the earlier hypothesis [7] that carbons

following exactly the DR eqn (2) are homogeneous. However, from extended work with molecular probes of various sizes, it appears now that this is only a first approximation [8-10]. As shown in fig. 1, carbon CEP-18 displays some degree of heterogeneity, whereas the DR plot for the adsorption of  $N_2O$  and  $CH_2Cl_2$  at 298K is linear over an extended range of relative pressures ( $A = 5$  to  $25$  kJ/mol). This means that isotherms based on the DR core (2) are not suitable for the description of adsorption by carbons of low and medium degrees of activation, nor can they reflect their true micropore distributions. On the other hand, the difference should become less important as the degree of heterogeneity increases and strongly activated carbons should be described in a satisfactory way by such equations.

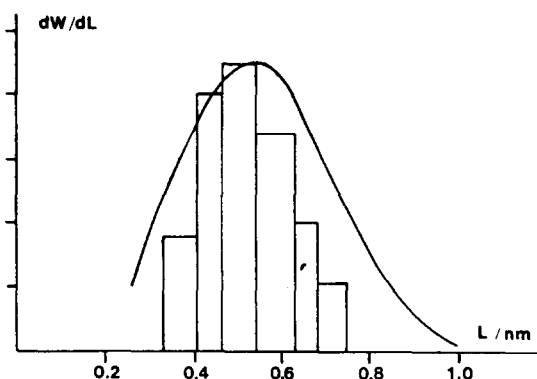


Fig. 1. Experimental and calculated distributions of the micropore widths  $L$  for carbon CEP-18, following exactly the DR eqn. The continuous line corresponds to eqn (9), with  $\nu = 1.25$  and  $a = 6.09 \text{ nm}^{-3}$ , obtained by fitting the  $N_2O$  adsorption isotherm to eqn (8).

On the basis of earlier observations [5], it was shown by Stoeckli et al. [11] that the DR adsorption isotherm of carbon CEP-18 could be generated from the histogram of fig. 1 by the sum

$$W_i(A) = \sum W_{oi} \exp [-(A/\beta E_{oi})^3] \quad (5)$$

with a relation of type (3) between  $E_{oi}$  and  $L_i$ . This approach is based on the fact that molecular sieve carbons tend to follow the Dubinin-Astakhov (DA) eqn with values of  $n$  close to 3 [5,8]. This suggests the use of

$$g(A;L) = \exp \{-(A/\beta K)^3\} \quad (6)$$

as the core eqn in (1) rather than eqn (4),

This principle has also been applied successfully by Wojsz and Rozwadowski [12,13] in their generalization of Stoeckli's earlier model [7], based on a Gaussian distribution of the structural constant  $B$ . Unfortunately, the corresponding adsorption equation  $\theta(A)$  is somewhat difficult to use for data fitting.

A convenient generalization, leading to a relatively simple and acceptable isotherm  $\theta(A)$ , is based on the use of eqn (6) with a Gamma-type distribution, as in Jaroniec and Choma's treatment [3]. With the important proviso (discussed below) that  $E_0 = K/L$ ,  $K$  being a constant, one can use the standard Laplace transform [6]

$$\int_0^\infty x^{\nu-1} \exp[-ax] \cdot \exp[-px] dx = \frac{\Gamma(\nu)}{(a+p)^\nu} \quad (7)$$

where  $x = L^3$  and  $p = (A/\beta K)^3$ . This leads to

$$\theta(A) = \left( \frac{a}{a+(A/\beta K)^3} \right)^\nu \quad (8)$$

and to the normalized distribution of the micropore-sizes

$$f(L) = \frac{3L^{(3\nu-1)} a^\nu \exp[-aL^3]}{\Gamma(\nu)} \quad (9)$$

These eqns are similar to those of Jaroniec et al. but have different powers. (It is also preferable to use exponent  $\nu$  instead of  $n$ , in order to avoid confusion with the DA eqn). Their advantage, illustrated by fig. 2, lies in the fact that they also provide reasonable distributions for carbons following closely the DR eqn. It is obvious, however, that for very heterogeneous carbons, the two approaches should yield similar results. From the mathematical analysis of eqn (9) it also appears that the quantity  $a^{-1/3}$ , expressed in nm, is close to the average pore width  $L$  (but not identical with it).

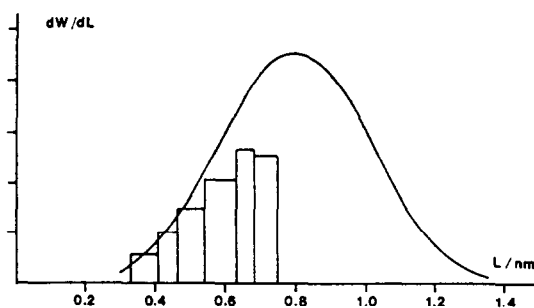


Fig. 2. Molecular sieve data and calculated distribution of the micropore width  $L$  for carbon CEP-59. Same procedures as for carbon CEP-18, leading to  $\nu = 1.85$  and  $a = 2.99 \text{ nm}^{-3}$ .  $N_2O$  adsorption follows the DA eqn with exponent  $n = 1.7$  and CEP-59 is more heterogeneous than carbon CEP-18.

The second important point relates to parameter  $K$  in eqn (3). It is generally assumed - but incorrectly - that this quantity is a constant: whereas the gyration radii  $R_i$  of the micropores are related to  $E_0$  by a constant equal to  $14.8 \pm 0.6 \text{ nm} \cdot \text{kJ/mol}$  [5] this is no longer the case for the actual pore-widths  $L$ , where  $K$  varies between 16 and 35 when  $L$  increases from 0.4 to 2.0 nm [9,14].

The presence of a variable parameter  $K$  has direct implications on the integral transforms (1) or (7). Mathematical modelling suggests, however, that the use of a constant value  $K_0$ , corresponding to  $E_0$  of the DR or DA eqn for the given carbon, should lead to a satisfactory agreement. This is shown in fig. 1 ( $E_0 = 32 \text{ kJ/mol}$ ;  $K_0 = 16.5 \text{ nm} \cdot \text{kJ/mol}$ ) and in fig. 2 ( $E_0 = 25 \text{ kJ/mol}$ ;  $K_0 = 19.5 \text{ nm} \cdot \text{kJ/mol}$ ). It may be the result of internal averaging in the integral,  $L_0 = K_0/E_0$  being close to the maximum of the distribution  $f(L)$ .

On the other hand, the use of a unique constant  $K$  for the whole range of microporosity close to  $24 \text{ nm} \cdot \text{kJ/mol}$ , as assumed by different authors, may cast

doubts on the validity of the resulting micropore distributions. A direct comparison with experimental data for distributions, as shown in fig. 1-2, is therefore essential to assess the validity of the different models. This stresses again the need for independent data on the micropores of strongly activated carbons.

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## BOOK REVIEWS

**Coke - Quality and Production** edited by Roger Loison, Pierre Foch and André Boyer (Butterworths Scientific, Ltd.) Westbury House, Bury Street, Guildford, England, 1989, 555 pp., (£95).

This book originally published by Dunod (Paris) in French as "Le Coke" in 1970, has recently been revised and published in English.

The authors many total years experience with CERCHAR, France, and their comfort with the subject is revealed in the informative and masterful presentation. The translation into English, by D.G. Edwards and G. A. Wade, is excellent and very readable. The text covers the manufacture of coke from coal in an industrially applicable, but academically thorough, manner. The authors have included an extensive bibliography as well as numerous tables, graphs, and figures to illustrate their conclusions. To all concerned with carbon, graphite and coal, this book is an important addition to their reference library.

The chapter titles are: (1) "Coal in general," (2) "Fundamentals of carbonization," (3) "Phenomena of carbonization in a coke oven chamber. Theory of relationship to coke quality," (4) "Coke quality criteria," (5) "Conditions of the industrial and semi-industrial test mentioned in this book," (6) "Formation of coke oven blends," (7) "Production factors," (8) "Wall pressure in coke oven blends," (9) "Production factors," (10) "Heat balances," (11) "Yields of coke and by-products," and (12) "Industrial applications."

Of importance to all are Chapters (2), (3), (4) and (5). Chapter (2), "Fundamentals of carbonization" is presented from the point of view of using coal as the "green" or "feedstock" material. However, the sections dealing with the plastic state of coal and its consequences concerning resolidification and the formation of texture are pertinent to those interested in the formation of any type of graphite or carbon. Because the text deals solely

with coal, new insights into the baking - carbonization process are discussed which will aid in the production of improved graphite produced from the traditional petroleum coke - coal tar pitch formulations.

Chapter (3), "Phenomena of carbonization in a coke oven chamber. Theory of relationship to coke quality," presents an excellent bridge from the laboratory experimentation found in Chapter (2) to the "real world" conditions found in commercial processes. The sections on fissuring and the relation between mechanical properties of coke and coking parameters are extremely useful and well presented for those interested in the transfer of data from the laboratory to the plant.

Chapter (4), "Coke quality criteria," is a well-written section describing the significance of the measured chemical and mechanical properties to the eventual use of the coke. Discussions of the strengths and weaknesses of one test versus another and why one test may be more useful than another in a specific application are especially informative and useful.

Chapter (5), "Conditions of the industrial and semi-industrial tests mentioned in this book," is a superb review of sampling on both an industrial and pilot plant scale to obtain valid and meaningful laboratory data to characterize a given coke.

The balance of the book provides much detail on the coke oven process. If the book has any weakness, it is the lack of information on coal tars and coal tar pitches. This weakness is negated by the thoroughness of the treatment of the manufacture of coke from coal. All who are interested in the broad area of carbon science will find this book a most useful addition to their libraries.

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