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A Generalization of the Dubinin–Radushkevich Equation for the Filling of Heterogeneous Micropore Systems

Physical adsorption of gases by microporous solids such as active carbons and zeolites is described by the theory of Dubinin (1, 2). In the earlier formulation of the theory (1), the adsorption isotherm is given by the Dubinin–Radushkevich (D–R) equation

$$W = W_0 \exp[-B(T/\beta)^2 \log^2 (P_0/P)], \qquad [1]$$

where W represents the volume of liquid-like adsorbate present in the micropores at temperature T and relative pressure P/P_0, and W_0 is the total micropore volume. The affinity coefficient β depends only on the adsorptive and B, the structural constant, characterizes the solid. There also exists a modification of Eq. [1], due to Nikolaev and Dubinin (3), for adsorption at $T > T_c$.

In the formulation of 1971, Dubinin and Astakhov (2) introduced the more general expression

$$W = W_0 \exp[-(A/E)^n] \quad (n = 2 \text{ to } 6) \qquad [2]$$

where $A = RT \ln (P_0/P)$ is the thermodynamical potential, and E is the characteristic energy depending on the system. The presence of the variable exponent n modifies the earlier formulation of the theory of micropore filling as expressed by the D–R equation (1).

Equation [1] can be applied with variable success, as revealed by the extent of the linear part of a log W vs $\log^2 (P_0/P)$ plot. The recent study of adsorption over a large range of temperature by Stoeckli and Houriet (4) leads to the conclusion that B is not constant, but decreases for large values of the quantity $y = (T/\beta)^2 \log^2 (P_0/P)$. Recent experiments carried out in this laboratory with mixtures of known active carbons also show that in its present form the D–R equation is unable to account for a certain degree of heterogeneity in the material under investigation. The values of B derived from the log–log² plot of nitrogen adsorption at 78°K, for example, are only average values which do not reflect the intrinsic heterogeneity of the mixture. It is therefore obvious that a more general expression is needed in order to account for the observations described above.

If we postulate that the D–R equation [1] has a general validity, but only applies to homogeneous systems of micropores, adsorption by heterogeneous micropore systems should be described by a sum of contributions of the type

$$W = \sum_j W_{0j} \exp[-B_j(T/\beta)^2 \log^2 (P_0/P)]. \qquad [3]$$

Such a sum, with only two terms, was used by Izotova and Dubinin in 1965 (5), and it led to the discovery of two quite distinct systems of micropores in certain active carbons (later confirmed by X ray studies).

For mathematical convenience, the sum [3] may be replaced by the integral

$$W(y) = \int_0^\infty f(B) \exp[-B \cdot y]dB, \qquad [4]$$

where $f(B)$ is the distribution function of the micropore volume with respect to B.

The general expression [4] is an integral transform of the Laplace type, with the D–R equation as the core equation. Various functions with known Laplace transforms (6) can be used for $f(B)$ in order to obtain analytical expressions for the isotherm $W(y)$. As a first approximation, one can use the (normalized) Gaussian

$$f(B) = (W_0/\Delta(2\pi)^{\frac{1}{2}}) \exp[-(B - B_0)^2/2\Delta^2], \qquad [5]$$

where B_0 represents the maximum and Δ is the half-width of the distribution. The transform [4] leads to the corresponding adsorption isotherm

$$W(y) = W_0 \exp[-B_0 y] \cdot \exp[y^2\Delta^2/2] \cdot [1 - \operatorname{erf}(x)]/2, \qquad [6]$$

where $x = (y - B_0/\Delta^2)\Delta/(2)^{\frac{1}{2}}$, and $\operatorname{erf}(x) = -\operatorname{erf}(-x)$ is the tabulated (7) error function.

One can see that the D–R equation [1] is the limiting case of [6], when the distribution tends to a Dirac delta function.

In order to assess the possibilities of the more general adsorption isotherm [6], model isotherms were computed for typical values of B_0, ranging from $0.5 \cdot 10^{-6}$ to $1.0 \cdot 10^{-6}$, and for increasing values of Δ, starting at $0.05 \cdot 10^{-6}$. It is found that the deviations between the D–R equation and Eq. [6] become increasingly important for values of y greater than 1.5–$2.0 \cdot 10^6$ approximately, depending on Δ. When the same value of B_0 is used, it is found that Eq. [6] predicts larger amounts adsorbed than the D–R equation. The difference between the two can be as high as one order of magnitude when $y \sim 7 \cdot 10^6$.

The derivative of the logarithmic form of Eq. [6] is

$$\partial \ln W(y)/\partial y = -B(y) = -B_0 + y\Delta^2 \qquad [7]$$

to a very good approximation.

For values of y smaller than $1.5\cdot10^6$ approximately, $B(y)$ is practically equal to B_0. This corresponds to the linear part of the usual log–log² plot, when adsorption is measured near or below the normal boiling point temperature of the adsorptive (N_2 at 78°K, for example). For adsorption at higher temperatures, within the same pressure range, higher values of y are obtained (5 to $7\cdot10^6$) and $B(y)$ decreases, as observed (3).

Results obtained for various gases (N_2, Xe, SF_6, N_2O, C_6H_6) between 78 and 450°K were analyzed by curve fitting to Eq. [6] and by using the simpler relation [7]. With the exception of local deviations caused by restricted entry into certain pores (C_6H_6 below 50–100°C, for example), all gases lead to similar values for Δ for a given solid. For three types of active carbons, consistent values of Δ were found, ranging from $0.05\cdot10^{-6}$ (polymer based material with molecular-sieve properties) to $0.30\cdot10^{-6}$ (overactivated coconut shells with $W = 0.65$ cm³/g).

With respect to the Dubinin–Astakhov expression [2], the present general equation, [4] or [6], has the following characteristics:

1. It is based on the original D–R equation, and it therefore preserves its general validity, as postulated earlier (1). Equation [2], on the other hand, implies variable distributions for the so-called adsorption potential A, which makes a physical interpretation more difficult.

2. Through the distribution function $f(B)$, the new isotherm has a direct physical meaning, since Δ is a measure of the heterogeneity of the micropore system (B is related to the size of the micropores). A given microporous solid can therefore be described more accurately by the three physical quantities, W_0, B, and Δ, instead of only two.

A systematic investigation of Eqs. [4] and [6] is now being carried out on mixtures of zeolites and of active carbons. The results will be published in due course, with an extended discussion of the present approach.

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