Microporosity in Carbons.

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Transitional porosity can be characterised by methods of adsorption and mercury porosimetry (use of Kelvin equation). Microporosity is inherently much more difficult to characterise. Methods available rest principally upon gas adsorption phenomena. The difficulties arise in the obtaining and interpretation of adsorption data. It is now well established that microporous materials can exhibit molecular sieve effects and very slow rates of adsorption (due to the temperature dependence of the adsorption process). There is the additional problem of interpretation of the isotherm in terms of a mechanism of micropore filling. To avoid the above experimental difficulties requires the use of the highest adsorption temperatures and the smallest admolecules. In this study, the adsorption of carbon dioxide has been measured in the temperature range 195°-363° K up to pressures of one atmosphere only. The BET equation cannot be used satisfactorily with these isotherms obtained at low relative pressures and recourse is made to the Dubinin theory of pore filling. This theory predicts an equation of the form:

$$\log W = \log W_0 - \frac{BT^2}{2.303\beta} \log^2 p/p_s$$

where W = volume adsorbed at relative pressure p/p_s and temperature T°K. W_0 is the limiting micropore volume and B and β are 'shifting' functions dependent respectively upon the microporosity of the adsorbent and the nature of the admolecule. An analysis has been made of certain conditions of applicability of the Dubinin theory. It can be shown that the obeyance of an isotherm to the Dubinin theory (by a linear plot of $\log W$ against $\log^2 p/p_s$) is not a general phenomenon in the sense that all isotherms can be linearised, but is dependent upon a particular type of distribution of micropore size. There is evidence to suggest that, during carbonisation of organic material, certain structural characteristics are carried through into the subsequent carbon; one of these characteristics promoted is a form of Gaussian distribution of size in microporous structures. The obeyance of an isotherm to the Dubinin theory of pore-filling is dependent upon this Gaussian distribution. The adsorption isotherms of carbon dioxide can be replotted as characteristic curves (plot of W against $RT\ln p/p_s$) from which can be obtained the distribution curve of $\Delta W/\Delta(RT\ln p/p_s)$ with $RT\ln p/p_s$. From the relative positions and shapes of these distribution curves, of values of W_0 and of B, there can be obtained semi-quantitative information of pore development and closure. Carbons examined have been prepared from polyvinylidene chloride, polyfurfurylalcohol, a coking coal and an anthracite. Activation by carbon dioxide of the polymer carbons, some of which contained known catalytic impurity, can alter the initial distribution of pore-size and non-obeyance of the Dubinin theory is observed.