

COAL AS A MICROPOROUS SOLID

P. L. Walker, Jr.\*

The Pennsylvania State University  
University Park, Pennsylvania, 16802

ABSTRACT

By saying that coal is a microporous solid, we mean that it possesses a significant void volume and area in small pores. A large fraction of these pores exhibit molecular-sieve properties, i.e., they are certainly under 10A in size. Some of the pore volume is even inaccessible to helium at room temperature. A close approximation of the exact size of the pores is difficult since we do not know precisely what arrangement of carbon and other atoms exists in the pore walls. If we can assume that the walls are predominantly basal planes of small graphitic-like crystallites, then we can make a closer estimation of the size of the pores. This is discussed. The use of the BET and Dubinin-Polanyi equations to estimate surface areas (or micropore volumes) of coals is discussed. The amount and nature of the micropore volume in coals can be changed drastically by both thermal treatment and gasification. The latter process is of particular interest, since gasification enlarges the size of very small micropores, thereby converting coal into a commercially acceptable activated carbon material. Some fundamentals of activation and techniques to achieve better activation of coals will be considered.

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Microporosity - Its Measurement, Structure and Utility.

Harry Marsh.

Northern Coke Research Laboratories, School of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, England.

The time is opportune to examine and assess our knowledge of microporosity in coals and immediately related materials. In the United Kingdom we are witnessing the cessation of the British Coal Utilisation Research Association (BCURA) as a Research Association<sup>(1)</sup>, this organisation being responsible for much of our detailed knowledge of the organic and physical chemistry of coals. Such occasions give rise to a response incorporating analysis and appraisal.

Historically, it is interesting to note the parallelism of theories of adsorption with those of coal structure giving now a measurement of microporosity, i.e. a volume parameter, or effective surface area which has been evaluated relatively thoroughly ranging from about 0.04 to 0.12 cm<sup>3</sup> g<sup>-1</sup>, the minimum occurring with the coking coals<sup>(2)</sup>. What is not so definite is the detail of the structure of microporosity and the mechanism(s) of change which occur on heat treatment of coals. This is essentially a multi-variant problem if extremes of fusibility with rank and the composition of coking blends are considered.

This problem of the structure or characterisation of microporosity in coals and carbons is intractable. Classical adsorption theory, in the sense of the BET or Langmuir approach helps little. It is just conceivable that the Dubinin-Radushkevich (D-R) approach and the consequences of its applicability may give some insight into the structure of microporosity. These consequences take one into the realm of statistical distributions and it may be possible to say something of the frequency distribution of micropore size (measured unfortunately not in units of length).

The D-R approach, which is not based upon a theoretical model of adsorption processes, but has a semi-empirical origin, in utilising some of the Polanyi adsorption potential theory, postulates a rectilinear relationship between  $\log V$  ( $V$  is amount adsorbed) and  $(\Delta G)^2$  ( $\Delta G$  is the free energy of adsorption). Whereas it is impossible to anticipate, a priori, how such a relationship is related to an adsorption process it is possible to be more pragmatic and analyse the consequences. These tell us that the frequency distribution of micropore volume filling at specific values of  $\Delta G$  has formulation in the Rayleigh distribution, which is a distribution describing some natural phenomena. This suggests that over the entire micropore volume there is a natural, progressive distribution of size of micropore. The specificity of this Rayleigh distribution is reasonably established. Other distributions which describe natural phenomena, such as Poisson, Gaussian and log-normal distributions, have been used to 'synthesise' D-R graphs, and except in one case (a unique selection of constants in the Poisson distribution) the D-R graphs are all non-linear. Although such a conclusion is not dramatic, it suggests that the size distribution of microporosity is random with formulation which is a step forward in the creation of possible theoretical isotherms which must take such matters into account using summations of atom-atom interactions.

The detailed picture of how micropores of different size are interconnected and of any relationship between the ordered and disordered carbon atoms (not begging the question at this stage) still remains obscure. However, high resolution electron microscopy<sup>(3,4)</sup> is now available and it would be pleasant to have these problems solved to some extent by direct visual inspection.

The successful description of micropore volume hinges upon the realisation that rates of adsorption are temperature dependent — that for coals adsorption temperatures of about 298°K must be used and that the adsorbate molecule must not be too large. The successful description hinges also upon the method of interpretation of the isotherm obtained at 298°K. Again, the use of Dubinin-Radushkevich theory appears sensible, but it has its critics. One way to obviate the problems of interpretation of gas phase adsorption at 298°K is to attempt adsorption from solution at 298°K. Immediately one meets the difficulty of assessing the extent of adsorption of solvent as opposed to solute (adsorbate). Results will be presented which illustrate (for microporous carbons) that a worthwhile procedure must incorporate analysis at low relative concentrations,  $C/C_s$ , (equivalent to  $p/p_0$ ) and that one of the simplest of suitable adsorbates is p-nitrophenol. Iodine is still under investigation. Adsorption of nonane at 298°K<sup>(5)</sup> appears to give reliable micropore volumes for cokes or carbons (coals perhaps not). In this latter technique, nonane is adsorbed on outgassed carbons at 298°K for 24 hours, followed by desorption at 298°K for a further 24 hours. Appreciable quantities of nonane are retained under these conditions, the nonane molecule evidently entering the microporosity and being retained there by reason of multiple adsorption sites per molecule. With ultra-microporosity molecular sieve action is apparent. The micropore volumes are evaluated from volume of nonane adsorbed and compared with micropore volumes obtained from CO<sub>2</sub> isotherms using the D-R approach and from N<sub>2</sub> isotherms (77°K) made prior and subsequent to adsorption of nonane. The agreement between these three methods is good but obviously limited by our lack of precise knowledge of densities of adsorbed phases.

An interesting question, for non-graphitic, non-graphitising carbons, (not carbon blacks) is the exact mechanism of development of microporosity by chemical activation (gasification with H<sub>2</sub>O or CO<sub>2</sub>). A review of available evidence leaves much to be desired in terms of the theory of preferential gasification of 'disordered' as opposed to 'ordered' carbon atoms. Other factors such as impurity content, chemical surface heterogeneity, etc., may be more important.

A considerable investment has been put into the analysis of microporosity in coals. What are the areas of applicability of this knowledge? Safety in mines is relevant where maximum methane content and rates of diffusion of methane out of microporosity are important. Spontaneous combustion must not be overlooked. There are the uses of coal as an adsorbate, but for coal itself probably what is more important are the changes occurring on carbonisation (particularly during the plastic stage) to produce the metallurgical coke etc., or the precursor for active carbons and for carbons used as catalysts or catalyst supports. Control of these changes may possibly influence coke quality — there is yet to be acquired an understanding of the improvements in coke resulting from the preheating of coals prior to carbonisation. Is there an unexplored field of "catalytic carbonisation" in which a scientific attempt is made to influence the chemistry of carbonisation with amelioration of product? Mechanisms of burning of pulverised fuels (rates of internal combustion) are clearly relevant. Is further investment of effort worthwhile into the extraction of organic materials from coal, or will it not be more economical to use coal as a source of carbon for synthesis of organic molecules?

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## MOISTURE SORPTION ON COALS

O. P. Mahajan

Materials Science Department  
Pennsylvania State University  
University Park, Pennsylvania 16802

A considerable amount of work has been reported in the literature on moisture sorption on coals, carbon blacks, charcoals and graphitized carbon blacks. However, the results and interpretation of the data even for the same type of adsorbents have often been at variance with one another.

In the present study, moisture sorption isotherms have been determined at 0 and 20°C on a series of 200x325 mesh coals, varying in rank from anthracite to high volatile bituminous coals. Moisture sorption was followed gravimetrically using a helical quartz spring having a sensitivity of  $2 \times 10^{-5}$  g.

Both the isotherm shape and the extent of adsorption depend on the coal rank. Bituminous coals adsorb significantly more water at low relative vapor pressures than anthracites. Further, sorption on bituminous coals is characterized by Type II isotherms, while anthracite gives a Type III isotherm.

It has been reported that moisture sorption is influenced by the volatile matter content of the carbon. Our results show that for a given coal rank, the moisture sorption capacity does not vary necessarily in the same order as the volatile matter content. This could be due either to the influence of the amount or type of impurities or to the role of specific functional groups present on the carbon surface on moisture sorption.

A pronounced hysteresis has been observed in the case of bituminous coals. Anderson et al (1) have reported that in the case of coals, hysteresis loops usually do not close until the relative pressure is reduced to zero. However, in our work, sorption-desorption isotherms do not meet even at zero relative vapor pressure; a certain amount of water cannot be desorbed even on outgassing the system to a constant weight at 20°C. The irreversibly adsorbed water is presumably chemisorbed on impurities, or held tightly within the micropores, or, as suggested by Puri (2), held at the surface by a mechanism involving hydrogen bonding to certain oxygenated functional groups.

Conventional capillary condensation cannot explain hysteresis in the case of pores of molecular dimensions. An attempt has been made to explain the hysteresis in terms of swelling and shrinkage effects during adsorption and desorption (3,4), a "cluster" model (5), and the independent domain theory (6).

BET plots give sensible straight lines, even for the anthracite which gives a Type III isotherm. The uncertainty regarding the assignment of a definite value for the molecular area of water when adsorbed on a carbon surface has been discussed. The BET surface areas calculated from the moisture sorption isotherms are much less than those calculated from CO<sub>2</sub> adsorption isotherms obtained at 25°C. In this respect, these results differ from those of Anderson et al (7) who have reported that the surface areas of coals from CO<sub>2</sub> isotherms are of the same magnitude as those calculated from water and methanol isotherms.

The discrepancy in our water and CO<sub>2</sub> surface areas is explicable in terms of the difference in the nature of adsorptive forces involved in the sorption of water on carbons and those envisaged for the BET model. Since a carbon surface is essentially hydrophobic, the role of dispersive forces involved in moisture sorption is negligible. It appears reasonable that sorption of water on coals involves adsorption at the 'primary' specific oxygen sites. Because of the strong intermolecular forces in water, the adsorbed water could act as 'secondary' sites for the adsorption of additional water, thus leading to 'cluster' formation, the growth of the clusters increasing with increasing surface coverage. At a certain stage, the clusters could merge to cover the coal surface with a unimolecular layer of adsorbed water, leading ultimately to the filling of the entire micropore volume.

The isosteric heats of adsorption calculated from the 0 and 20°C isotherms show that the net heat of adsorption over the entire pressure range is zero, i.e.,  $E_1 = E_2$ . This would imply that the value of the constant C in the BET equation is unity. This is in direct conflict with the values of C obtained from the BET plots, where the values vary from 5 for anthracite to 25 for the bituminous coals. For  $C=1$ , the BET equation predicts that the isotherm should be of Type III. However, the correlation of the isotherm shape with the relative values of  $E_1$  and  $E_2$  is based on certain faulty assumptions (8). If C is assumed  $\approx 1$ , the BET equation predicts that the amount adsorbed at a relative vapor pressure of 0.5 should correspond to monolayer capacity. This approach has recently been used successfully by Walker and Janov (9) to estimate the 'active' surface area of Graphon samples and the values agree remarkably well with those obtained from oxygen chemisorption. In the present work, arguments have been presented to emphasize that in the case of coals this approach can hardly be used to estimate the fraction of the surface which is hydrophilic in character.

Thermodynamic considerations show that when the net heat of adsorption is zero, a decrease in free energy and hence spontaneous adsorption can occur only if the process of adsorption is accompanied by an increase in entropy. Calculations show that the entropy of adsorption has a positive value over the entire relative pressure range, the value decreasing in magnitude with progressive increase in the extent of adsorption.

The BET surface areas calculated from the moisture sorption isotherms have been compared with those obtained by Harvey's method (10), and the significance of the results have been discussed in the light of the work of Puri and Sharma (11).

Brunauer and coworkers (12) have suggested recently that the t curves obtained from water vapor adsorption can be used for pore structure analysis. The feasibility of using this approach for the pore structure analysis of coals is discussed.

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ACTIVATED DIFFUSION OF METHANE IN COAL

S. P. Nandi

Materials Science Department  
Pennsylvania State University  
University Park, Pennsylvania 16802

Unsteady state diffusion of methane in powdered coal has been measured by two experimental approaches. In the first, methane diffused out of a sample previously equilibrated with methane at about 1.5 atmospheres to a space maintained at a constant pressure of one atmosphere. Unsteady state diffusion is relatively insensitive to particle shape and so coal particles could be treated as spheres of equivalent volume as that of the actual particles. The well known (1) solution of Fick's Law for a concentration independent  $D$ , under the boundary conditions imposed by the experimental technique, has been used to determine the micropore diffusion parameter ( $D^{1/2}/r_0$ ). In the second method, the rate of sorption of methane into degassed samples was measured. The pressure change during the measurements was in the range of eight to two atmospheres. It has been shown by Barrer (2) that if the diffusion coefficient is concentration independent and if the isotherm obeys Henry's Law, then for a constant volume but variable pressure system, the solution of Fick's Law for very small times reduces to the following equation:

$$\frac{Q_t}{Q_\infty} = \frac{Q_0}{(Q_0 - Q_\infty)} \frac{6}{r_0} \sqrt{Dt/\pi}$$

where  $Q_0$  = quantity of gas initially in the gas phase  
 $Q_t$  and  $Q_\infty$  = adsorption at  $t = t$  and  $t = \infty$   
 $D$  = diffusion coefficient.

The above expression differs from the solution of Fick's Law in the constant pressure case only by the factor  $Q_0/(Q_0 - Q_\infty)$ . The micropore diffusion parameter was obtained in this case from the initial slope of  $Q_t/Q_\infty$  vs  $\sqrt{t}$  plots. Satisfactory agreement was obtained between the values of the micropore diffusion parameter obtained by the two methods.

Twelve samples of (100x150) mesh coals of volatile matter ranging from 4 to 40% (d.a.f.) and three sizes, (42x65), (65x100) and (100x150), of two anthracites were used in this study. Adsorption isotherms of methane up to a pressure of 15 atmospheres in the temperature range 25 to 75°C were measured on an anthracite and two bituminous coals. The isotherms for the two bituminous coals are linear with pressure, but for the anthracite there is a slight bending towards the pressure axis. However, over a smaller pressure range the isotherms approximate Henry's Law behavior. In agreement with earlier findings, (3) anthracite adsorbs more methane compared to the bituminous coals under the same experimental conditions. For the (100x150) mesh samples, diffusion was measured over the temperature range 50 to 150°C; and for the (42x65) and (65x100) mesh sizes, the temperature range was 120 to 300°C. It was found that methane diffusion was activated for all samples. The activation energy of diffusion was obtained from the slope of  $\ln(D^{1/2}/r_0)$  vs  $1/T$  plots. It was found that in cases where the temperature range of measurement was more than 100°C the slope becomes greater at higher temperatures.

Two distinct physical models (4) might be applicable in the methane-coal system. In the first, the gas held by the solid can be considered to be in an occluded state (one phase). In the second, the gas might be in two phases:

1) as relatively free molecules in the open porosity, 2) as relatively non-mobile molecules present on the internal surface of the solid. In both cases the same differential equation results, but the diffusion coefficient  $\bar{D}$  of the second model is related to  $D$  for the first model by the relation

$$\bar{D} = D/(\epsilon + KC_g)$$

where  $\epsilon$  = open porosity

$K$  = equilibrium constant of adsorption

$C_g$  = adsorption at saturation

It can be shown that for the first model the slope of the Arrhenius plot should be constant and for the second model at low temperatures, where the quantity of adsorbed gas is high, the porosity term would be negligible and the heat of adsorption would be added to the true activation energy. At higher temperatures, the contribution of heat of adsorption would diminish. Therefore, as the temperature is increased, the slope of the Arrhenius plot should become smaller in magnitude for the second model. The results obtained tend to show that the first model is still generally applicable, but at higher temperatures pores of smaller diameter start contributing significantly. It might be added, however, that in the case of (100x150) mesh samples relatively good straight line plots were obtained in the temperature range 50 to 150°C.

For the twelve samples, the values of activation energy vary from 3.5 kcal/mole for an anthracite of 4.2% V.M. to 5.2 kcal/mole for an anthracite of 9.0% V.M. The activation energy does not change significantly in the bituminous range, with a value of about 7.0 kcal/mole being obtained for the six samples studied. These results are in disagreement with those of the argon-coal system, (5) where a maximum in activation energy appears in the range of good coking coals. A probable explanation could be found by considering the following. The activation energy is related to the interaction energy of the gas-solid system. The interaction energy is a strong function of the geometry (pore diameter) of the solid as well as its chemical nature. Making a gross simplification, one can imagine that on the pore surface of a high rank coal, like anthracite, the predominant atomic species would be carbon. As the rank becomes lower the carbon atoms are being substituted by oxygen groups on the surface. Therefore, the change in chemical nature of the surface atoms may mask the effect of pore geometry to some extent. This change is likely to alter methane diffusion more than that of argon as the methane molecule is more polarizable. (6) Other complicating factors are the size distribution in the micropores and the presence of different petrographic constituents in bituminous coals.

Diffusion parameters obtained from three sieve sizes of the two anthracites tend to give higher activation energies for the larger particles. Evaluation of the diffusion coefficient ( $D$ ) from the experimental diffusion parameter ( $D^{1/2}/r_0$ ) poses problems because of the difficulty in estimating the diffusion path length ( $r_0$ ). As the diffusion path length should be temperature independent, the value of activation energy should not be affected. Different approaches for the estimation of  $r_0$  are indicated.

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