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Molecular sieve characteristics of slightly activated anthracite

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Attempts have been made to improve the molecular sieve properties of anthracite by devolatilization and subsequent activation to low burn-offs (B.O.) in oxygen at 427 ± 3°C. Methane diffusion into samples reacted up to 8·0% B.O. was activated. With further increase in B.O. to 9·1%, the effect of temperature on diffusion became negligible. Surface areas of the activated samples available to carbon dioxide at 25°C, nitrogen at −195°C and neopentane at 0°C have been measured. It was observed that at the B.O. where the neopentane area approaches the nitrogen area, the activation energy of methane diffusion is small. This indicates that activation of coal to small B.O. can lead to the production of molecular sieves.

The molecular sieve characteristics of coal have been reviewed by Walker et al[1] and also by Spencer[2]. Anderson and co-workers[3] found sorption of n-butane to be considerably greater than that of isobutane on most coals at 0°C. Mason and Eberly[4] heat-treated an anthracite in hydrogen at 650°C and reported that the adsorption of n-butane was about five times that of isobutane at 0°C. The original anthracite showed no adsorption for isobutane and had about one sixth the capacity for n-butane, compared to the heat-treated product. These results are of little practical importance, as sorption was very slow and capacity much lower compared to the synthetic zeolite molecular sieves.

Metcalfe et al[5] attempted to improve molecular sieve properties of a sample of anthracite by activation. Anthracite seems to be the most suitable material amongst coals because of its high carbon content and its having a significant fraction of its pore volume closed to helium at room temperature[6]. The sorption of n-butane, isobutane and neopentane was studied on raw and activated (34·8% burn-off − B.O.) anthracite. It was shown that the activated anthracite had twice the sorption capacity for n-butane as did the zeolite molecular sieves; though selective adsorption properties of activated anthracite were not as sharp, anthracite activated to a B.O. of 34·8% still retained some molecular sieve properties. Therefore, it was decided to study the molecular sieve behaviour of devolatilized and low B.O. St. Nicholas anthracite to see if these properties could be sharpened.

In this laboratory considerable work has been done on the diffusion of different gases from coals and synthetic zeolites[1]. It has been shown that the activation energy of diffusion for a gas through a porous solid depends on the minimum diameter (e.g. the diameter of the ring formed by lattice oxygen, which acts as the entrance to a wider cavity in crystalline zeolites; the diameter at the constricted region in otherwise wider pores in amorphous porous solids, etc.) of the pore system. When the pore diameter approaches the kinetic diameter of the diffusing molecule, the activation energy of diffusion becomes significant. In the present study the diffusing species chosen was methane. It has a kinetic diameter of 3·8 Å, and so any carbonaceous material showing activated diffusion of methane would have a minimum pore diameter of about 5·6 Å (the kinetic diameter plus twice the π-electron overlap of 0·8 Å over the carbon basal plane). Diffusion of methane into devolatilized anthracite of different B.O. at different temperatures in the pressure range 54 to 94 psia* was measured. Carbon dioxide, nitrogen and neopentane surface areas were determined, to follow the activation process.

EXPERIMENTAL

Devolatilization of anthracite

St. Nicholas anthracite of (42 × 65) mesh Tyler was heated in a current of nitrogen in a tube furnace to a temperature of 950°C. The heating rate was 5°C/min with a soak time of 2 h at 950°C. The sample was cooled in nitrogen to room temperature.

Activation of anthracite

The samples were activated in very thin layers by air at 425−430°C to the desired B.O., after which the sample was heated in nitrogen to a temperature of 950°C, allowing 1 h to remove the oxygen complex on the surface of the sample.

Surface area

Surface areas (perhaps a better expression would be 'monolayer equivalent values') were determined from nitrogen and neopentane adsorption isotherms at −195°C and 0°C respectively using the BET equation. A volumetric all-glass adsorption apparatus was used[7]. Carbon

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* 1 psia = 6·895 kN/m² absolute

dioxide isotherms were determined at 25°C in a pressure sorption apparatus[8]. Carbon dioxide surface areas were also calculated using the BET equation.

Diffusion measurement and computational procedure

The apparatus used was a volumetric sorption apparatus constructed of stainless steel. The description and experimental procedure has been given in detail by Nandi and Walker[8]. In the present work, a Heise pressure gauge was used instead of a transducer. The gauge had a dial diameter of 10 in. with 0·5 psi as minimum divisions and a range up to 250 psi. The apparatus was calibrated by pressurizing it with methane and then bleeding out the gas in stages and noting the amount discharged as a function of the reading of the pressure gauge. To perform a diffusion run, the sample was first degassed at 150°C for 5 h under a vacuum of 10^{-5} torr. A known quantity of gas was taken and then added to the sample chamber. Pressure readings, as a function of time, were followed for 100 min, after which the sample was allowed to come to equilibrium. It was observed that adsorption was practically complete after 24 h; and, consequently, adsorption at that time was taken to be the equilibrium value.

With this experimental procedure, adsorption takes place under constant volume but variable pressure. The solutions of diffusion equations have been discussed by Crank[9]. The most appropriate solution directly applicable to the present experimental condition has been given by Barrer[10]. It has been shown by Barrer that, under the above-mentioned conditions and provided that the diffusion coefficient D is independent of concentration and the adsorption isotherm obeys Henry's law, the fractional completion of the diffusion process for spherical geometry can be expressed by the following equation:

$$Q_t/Q_\infty = (K + 1) \left\{ 1 - \frac{1}{a + \beta} \left[ae^{-a^2\tau} (1 + \mathrm{erf}\ a\tau^{1/2}) - \beta e^{-\beta^2\tau} (1 + \mathrm{erf}\ \beta\tau^{1/2}) \right] \right\} \quad (1)$$

where Q_t and Q_∞ are amounts adsorbed at times $t = t$ and $t = \infty$

$$K = \frac{Q_0 - Q_\infty}{Q_\infty}$$

Q_0 = quantity of gas initially present in gas phase

$\tau = Dt/r_0^2$

a and β are roots of the equation, $x^2 - 3x/K - 3/K = 0$

r_0 = diffusion path length

For small enough values of $(\tau/K)^{1/2}$, that is very small times, equation (1) reduces to

$$Q_t/Q_\infty = \frac{6}{r_0} \left(\frac{Q_0}{Q_0 - Q_\infty} \right) (Dt/\pi)^{1/2} \quad (2)$$

Therefore, from the initial slope of Q_t/Q_∞ versus $t^{1/2}$ plots, the diffusion parameter[1] $D^{1/2}/r_0$ can be calculated.

RESULTS AND DISCUSSION

Correction for ash and correlations of amount of burn-off

The proximate analysis of the anthracite (St. Nicholas) is given in *Table 1*. The weight loss of the devolatilized anthracite upon activation was determined. In correlating the data, the ash yield of the activated anthracite should be taken into account. It was assumed that on devolatilization and activation the mineral matter in the anthracite did not undergo any change nor was it removed. The ash yield of the raw anthracite was 8·5% on a dry basis. Based on the volatile matter value in *Table 1*, the ash in the devolatilized anthracite was calculated to be 8·9%. This value was used as the basis of calculations. The calculated ash percentages are shown in *Table 2* in which the percentages of B.O. on an ash-free basis also are listed. These percentages of B.O., based on an ash-free basis, were used for all correlations unless otherwise indicated.

Table 2 Ash yield from activated anthracite at various stages of burn-off

Sample	Ash (%)	Burn-off %.	
		AWB*	AFB*
Devolatilized	8·9	0	0
Activated	9·5	6·2	6·9
	9·6	7·3	8·0
	9·7	8·2	9·1

* AWB   Actual weight basis
* AFB   Ash-free basis

Effect of pressure on the diffusion parameter and the nature of the adsorption isotherm

To investigate the effect of concentration on the diffusion coefficient, runs at three different initial starting pressures (which are equivalent to different concentrations of methane) with the 6·9% B.O. sample were made at 40°C. One of the typical plots of the experimental results is shown in *Figure 1*. The values of the diffusion parameter shown in *Table 3* indicate clearly that the diffusion parameter is independent of pressure in this pressure range.

Table 1 Proximate analysis of St. Nicholas anthracite (as received basis)

Item	Amount (%)
Moisture	1·2
Volatile matter	4·0
Ash	8·4
Fixed carbon	86·4

Table 3 Effect of pressure on diffusion parameter for methane at 40°C through anthracite activated to 6·9% burn-off

Initial pressure (psia)	$D^{1/2}/r_0\ (s^{-1/2})$
54·1	0·00305
74·8	0·00309
94·0	0·00307

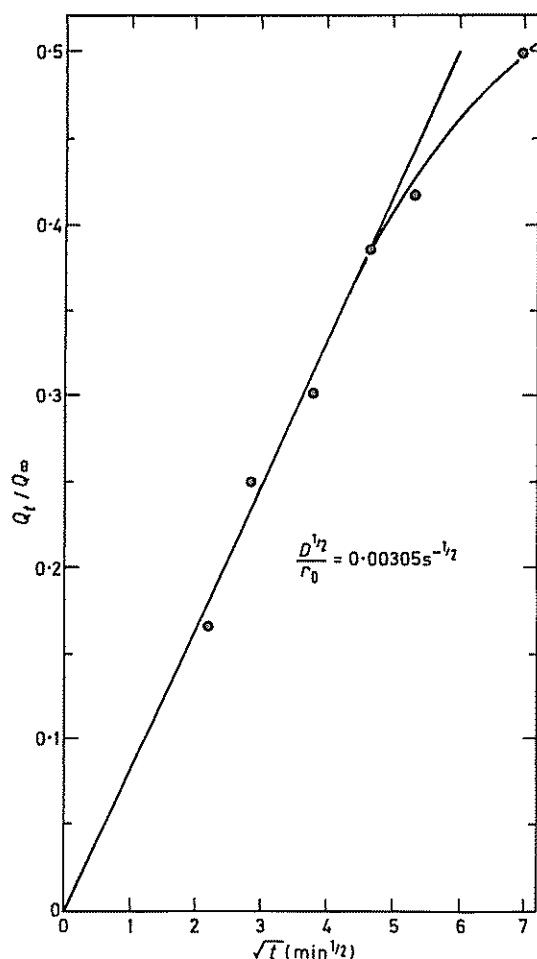$$\frac{D^{1/2}}{r_0} = 0.00305s^{-1/2}$$

Figure 1   Diffusion plot of methane into 6·9% burn-off anthracite at 40°C and at initial pressure of 54·1 psia

Adsorption isotherms of methane on these samples were not determined in the present investigation. Nandi and Walker[8] followed methane isotherms on raw anthracites and found them to be rectilinear over the pressure range used in the present study. It appears, therefore, that for the system investigated the use of equation (2) to calculate $D^{1/2}/r_0$ is valid.

Effect of temperature on diffusion parameter

Diffusion of methane into 6·9, 8·0 and 9·1% B.O. samples of anthracite was studied at 25, 40 and 70°C. Diffusion into the devolatilized sample and those activated up to 6% B.O. was too slow to be accurately measured. A typical plot of the experimental results is shown in *Figure 2*, where diffusion into the 6·9% B.O. sample at 25°C was measured at an initial methane pressure of 75·1 psia. This plot has a positive intercept on the ordinate. It was found that except for the 40 and 70°C diffusion runs with the 6·9% B.O. sample, all the plots had a positive intercept. The magnitude of the intercept decreases with increasing temperature and decreasing B.O. of the anthracite. This is taken to mean that the activated samples have a significant volume of transitional and macropores into which diffusion is very rapid (non-activated, physical). As the B.O. increases, the easily accessible fraction of the pores

increases and with it the intercept. A decrease in the amount of adsorption due to this rapid process is expected with increasing temperature, as the process may be imagined to be purely physical in nature.

To calculate the diffusion parameter for the micropore system, the value of Q_t at $t = 0$ (obtained from experimental plots like *Figure 2* where the intercept on the ordinate provides the value) was subtracted from Q_∞ to give a new Q'_∞, for diffusion into the micropores. New values of Q'_t were also calculated. Plots were then made of Q'_t/Q'_∞ versus $t^{1/2}$, as shown in *Figure 3*. Diffusion parameters calculated from plots like *Figure 3* are summarized in *Table 4*.
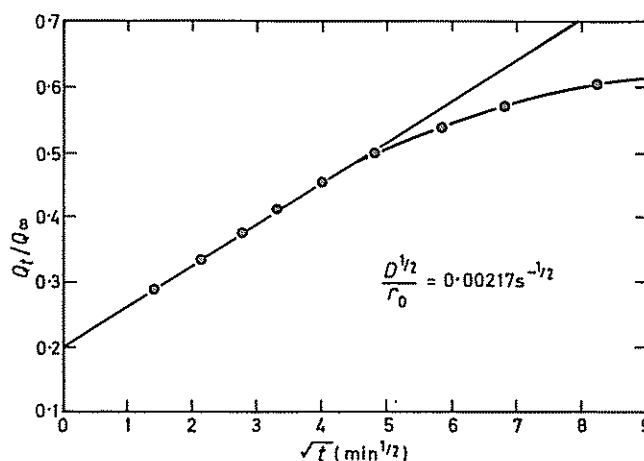

$$\frac{D^{1/2}}{r_0} = 0.00217s^{-1/2}$$

Figure 2   Diffusion plot of methane into 6·9% burn-off anthracite at 25°C and at initial pressure of 75·1 psia

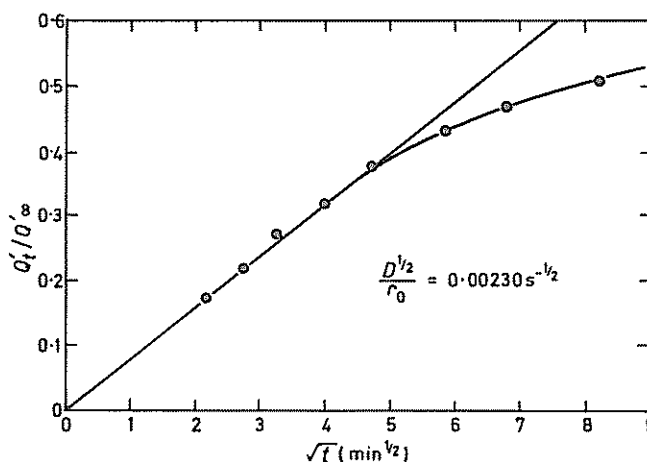$$\frac{D^{1/2}}{r_0} = 0.00230s^{-1/2}$$

Figure 3   Diffusion plot of methane into 6·9% burn-off anthracite at 25°C after correction for methane taken up instantaneously (see Figure 2)

Table 4   The effect of temperature on diffusion parameter for methane through activated anthracite

Burn-off (%)	Temperature (K)	$D^{1/2}/r_0$ s$^{-1/2}$
6·9	298	0·00230
	313	0·00307
	343	0·00463
8·0	298	0·00658
	313	0·00726
	343	0·00894
9·1	298	0·0238
	313	0·0234
	343	0·0236

Arrhenius plots of diffusion parameters are given in *Figure 4*. Assuming that the diffusion path length r_0 is independent of temperature, the activation energy values (E) of D for 6·9, 8·0 and 9·1% B.O. samples were found to be 6·7, 2·8 and 0·0 kcal/mol, respectively. This decrease in activation energy with increasing B.O. can be explained by assuming that increased gasification increases the size of the micropores or constrictions in the pores. The ease of methane diffusion is thereby enhanced until finally diffusion no longer requires that methane pass over an activation energy barrier. Diffusion now passes into the region of Knudsen diffusion where the rate is only weakly dependent on temperature, i.e. proportional to $T^{1/2}$. Such a small temperature effect would be difficult to observe over the limited range of temperature used in this study.
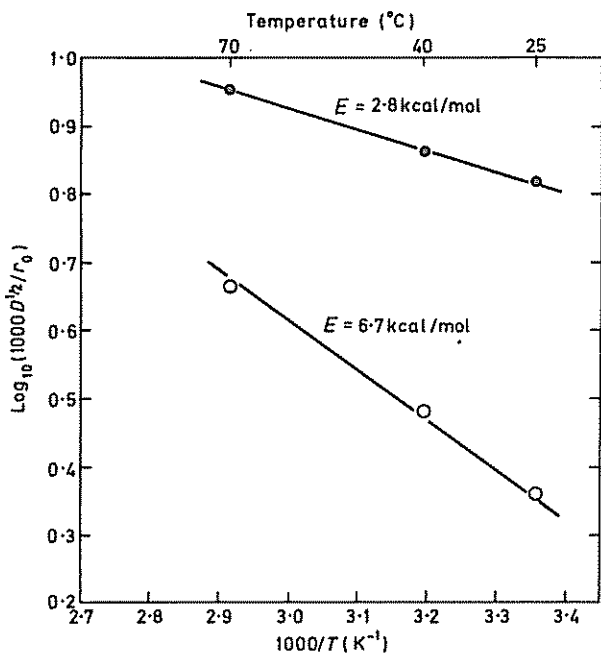
Table 5 Variation of surface area of anthracite with burn-off

Burn-off (%)	Surface area (m²/g)*		
	CO_2	N_2	Neopentane
0	80	<1	0·0
6·9	128	41	0·8
8·0	185	59	5·5
9·1	207	87	87

* Surface area without correction for ash

Table 6 Comparison of surface area changes with activation of anthracite

Burn-off (%)	Final area/initial area		
	CO_2	N_2	Neopentane
6·9	1·0	1·0	1·0
8·0	1·4	1·4	6·6
9·1	1·6	2·1	105

Figure 4 Activation energy plots for the diffusion of methane into anthracites of low burn-off
● 8·0% B.O. anthracite, ○ 6·9% B.O. anthracite

Variation of surface area with burn-off

Surface area data of activated anthracites are summarized in *Table 5*. Nitrogen at low temperature is not accessible to most of the fine pore system of coal, because of the high activation energy involved in the diffusion process[1]. Dubinin[11] has pointed out that the pore system in coal can be divided into three categories: macropores, transitional pores, and very fine or micropores. It has been concluded previously that nitrogen at −195°C adsorbs rapidly in macropores, transitional pores and a small fraction of micropores[12].

Adsorption of neopentane, which is larger than nitrogen (a kinetic diameter of 6·2 Å as compared to 3·7 Å for nitrogen) was measured with the thought that it could more closely approximate the macropore and transitional pore area. Neopentane surface areas, shown in *Table 5*, were significantly smaller than the nitrogen areas for the lower burn-off samples. However, it is noted that the neopentane

area increased more sharply with B.O. than did the nitrogen area. For the sample of B.O. 6·9%, the neopentane area was only 2% of the nitrogen area, while for the 9·1% B.O. sample the areas measured by nitrogen and neopentane were equal. This is a graphic example of the effect of B.O. on the molecular sieve properties of anthracite.

Looking at the area results in another way, the easier the molecule can get into the devolatilized anthracite the less the increase in surface area with increase of B.O. will be. The devolatilized anthracite has a carbon dioxide area of 80·0 m²/g, whereas its nitrogen and neopentane areas are not measurable. The devolatilized sample had a significant carbon dioxide area and its fractional increase with B.O. was small compared to the areas measured by nitrogen or neopentane adsorption. Activation from 6·9 to 9·1% increased the carbon dioxide, nitrogen and neopentane areas 1·6, 2·1 and 105-fold, respectively, as is seen in *Table 6*. These results clearly show that the process of activation involves two definite steps: (1) opening of closed pores and (2) enlargement of already accessible pores. By 6·9% B.O., most of the pores are opened to carbon dioxide and additional activation only enlarges the pores, thereby further increasing the surface area. Clearly, following 6·9 and 8·0% B.O., most of the micropores were still closed to neopentane. Undoubtedly, as B.O. proceeds to higher values, the surface areas as measured by carbon dioxide, nitrogen and neopentane would approach each other more closely. That is, the molecular sieving of these molecules would steadily decrease. It is evident that to produce a suitable molecular sieve material from anthracite the process of activation should be stopped at a stage where the second step of the activation process, that is pore enlargement, has just started.

Further work by S. P. Nandi in this laboratory with this same anthracite indicates that the critical B.O. is dependent on the particle size of the devolatilized sample and also upon the activating gas used. Studies in this area are continuing.

SUMMARY AND CONCLUSIONS

The unsteady-state diffusion of methane into samples of St. Nicholas anthracite activated to low burn-offs has been measured. The computational method developed by Barrer has been used to obtain the diffusion parameter $D^{1/2}/r_0$. It was found that the diffusion of methane, measured in the pressure range 54 to 94 psia and temperature range 25 to 70°C, was independent of pressure.

For anthracite activated to 6·9 and 8·0% B.O., the diffusion of methane was activated. On further activation to 9·1% B.O., the effect of temperature on diffusion was negligible. This is consistent with an increase in average pore size with activation. It was found that, at the particular B.O. at which the neopentane surface area sharply increased, activated diffusion of methane ceased.

ACKNOWLEDGEMENT

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