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# Activated diffusion of methane from coals at elevated pressures

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Diffusion of methane from three coals ranging in rank from anthracite to HVA bituminous has been studied at initial methane pressures up to about 2.76 MPa (400 psi). Unsteady-state diffusion conditions existed, the methane pressure within the coal particle decreasing with time while the methane pressure outside the particles remained at atmospheric. The diffusion parameter  $D^{1/2}/r_0$  increased with increasing methane concentration at high values of methane sorption. Diffusion was activated but the exact magnitude of the activation energy is uncertain owing to the suspected contribution of the heat of sorption to the temperature coefficient.  $D^{1/2}/r_0$  increased with decreasing particle size of coal studied, but  $r_0$  is clearly less than the particle radius.

Methane is present in coal measures, and methane pressures as high as 3.55 MPa have been encountered in some U.S. coal seams<sup>1</sup>. The amount of methane released from a coal seam depends on the nature of the coal, as well as on the geological and mining conditions. It has been suggested by Cervik<sup>2</sup> that most of the methane released into U.S. mines comes from within the intact coal bed. *In situ* methane permeability measurements on three coal beds indicate that the nature of the coal has a more important effect than overburden pressure on permeability<sup>3</sup>. Laboratory data on the sorption characteristics of methane by different coals are expected to provide the inputs to the different mathematical models for the estimation of methane release from coal seams. Information provided by such models is not only important in contributing to a better understanding of the undesirable release of methane during mining operations but also to a better evaluation of the possibility of using degasification of coal beds as a commercial source of pipeline gas.

Various laboratory studies on the adsorption and desorption of methane by powdered coals have been performed<sup>4-7</sup>. High-pressure methane sorption data on some U.S. coals have been recently reported by workers of the USBM<sup>1,8,9</sup>. Nandi and Walker<sup>10</sup> studied the desorption of methane from a number of American coals at sub-atmospheric pressure. Methane diffusion was activated for all the coals studied. A survey of the literature indicates that experimental data on the rate of methane desorption are limited; and, therefore, the present investigation was undertaken to study the methane desorption characteristics of some American coals at elevated pressure.

## EXPERIMENTAL

Rates of desorption have been measured at three temperatures (0, 25 and 50°C) with three coals in the pressure range 1.14–2.52 MPa. In addition, the effect of particle size on diffusion has been followed on one coal. Analytical data on the coals studied are shown in Table 1. PSOC-177, 135, and 171 can be classified as anthracite, medium-volatile bituminous, and HVA bituminous respectively.

### Apparatus and experimental procedure

A volumetric adsorption apparatus shown in Figure 1 was used. The material of construction above the broken line was stainless steel and that below was made of Pyrex glass. The apparatus was similar to that used earlier<sup>10</sup>, except that a precision pressure gauge (Heise Bourdon Tube Co., Newton, Conn., Model C-61364) graduated to 6.9 kPa (1 psi) was used in place of the transducer. A spacer (aluminium) of known volume was placed in the sample container and the apparatus was calibrated with methane in the pressure-temperature range used in subsequent experiments<sup>10</sup>. *w* g of powdered coal having the same volume as that of the spacer were used in all experiments. The coal samples were degassed at 130°C for 12 h under vacuum prior to an adsorption run. For the 40 X 70 mesh (U.S.) samples an equilibrium time of 24 h was allowed for adsorption; for larger particle sizes the time was 48 h. It was noted that there was only a slight increase in adsorption at longer times.

Table 1 Analytical data on coals

PSOC sample	Ultimate analysis (wt % daf)					Physical properties (dry basis)				
	C	H	N	S	O	N <sub>2</sub> area (77 K) (m <sup>2</sup> /g)	CO <sub>2</sub> area (298 K) (m <sup>2</sup> /g)	Helium density (g/cm <sup>3</sup> )	Mercury density (g/cm <sup>3</sup> )	Total open pore volume (cm <sup>3</sup> /g)
177	93.5	2.7	0.25	0.70	2.9	2.9	456	1.65	1.41	0.103
135	88.4	4.9	0.25	0.65	5.8	<1.0	214	1.36	1.29	0.042
171	82.3	5.7	1.4	3.3	7.3	<1.0	185	1.32	1.27	0.030

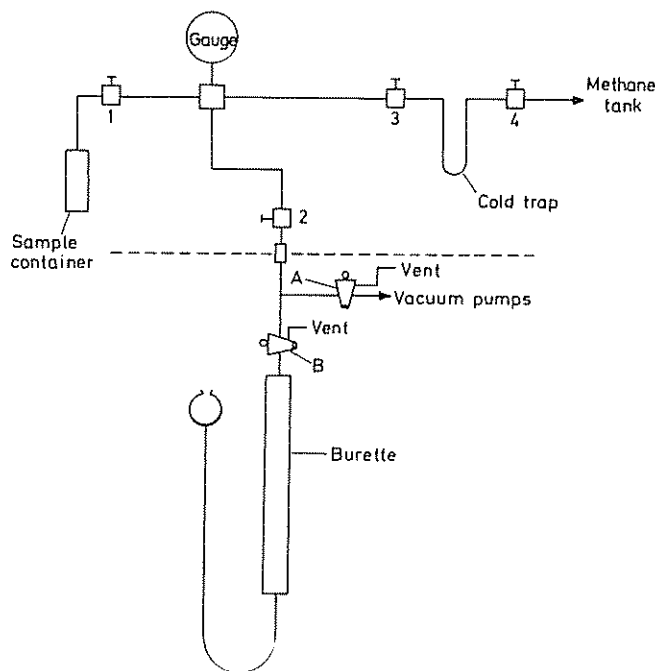


Figure 1 Volumetric adsorption-desorption apparatus

The following procedure was used for desorption measurements. The mercury level in the burette was first brought to a certain mark and the burette was connected to atmosphere by opening stopcocks B and A suitably. After adsorption equilibrium was achieved on a sample, pressure-valve 2 was opened very quickly and methane was allowed to escape through stopcock A. At the same time a timer was started. When the pressure in the system was atmospheric (as indicated by the gauge), stopcock A was closed and the desorbed gas was collected in the burette. It took a maximum of 45 s for the pressure in the system to decrease to atmospheric at the highest equilibrium pressure used in the experiments. Desorption was followed for about 180 min, keeping the pressure in the system constant at atmospheric by changing the mercury level. The amount of methane desorbed at the completion of a run was taken to be the difference of the adsorption values at the equilibrium pressure and that at 1 atm. This value is denoted as  $V_{\infty}$ .

Table 2 Data for a typical methane desorption run (sample PSOC-177)

Time (min)	$\sqrt{\text{Time}}$ ( $\text{min}^{1/2}$ )	Burette reading ( $\text{cm}^3$ )	$wV_t$ ( $\text{cm}^3$ )	$w(V_t - V_0)$ ( $\text{cm}^3$ )	$(V_t - V_0)$ ( $\text{cm}^3/\text{g}$ )	$(V_t - V_0)/V_{\infty}$
2.03	1.42	5.0	4.4	8.3	1.5	0.08
2.84	1.68	6.6	5.9	9.8	1.8	0.10
3.66	1.91	8.1	7.2	11.1	2.1	0.11
4.77	2.18	10.1	9.0	12.9	2.4	0.13
8.48	2.91	15.3	13.6	17.5	3.3	0.18
13.87	3.72	20.8	18.6	22.5	4.2	0.23
20.00	4.47	25.8	23.0	26.9	5.1	0.28
26.86	5.18	30.6	27.3	31.2	5.9	0.32
37.17	6.09	35.7	31.9	35.8	6.7	0.37
49.68	7.05	41.0	36.6	40.5	7.6	0.42
66.94	8.18	46.6	41.7	45.6	8.6	0.47
90.50	9.51	52.4	46.9	50.8	9.5	0.53
121.9	11.04	58.1	52.0	55.9	10.5	0.58
136.9	11.70	60.3	53.9	57.8	10.9	0.60

### Computation of the diffusion parameter

The volume of methane collected in the burette as a function of time of desorption is shown in Table 2 for a 40 × 70 mesh fraction (5.3 g) of PSOC-177. In this run, the initial pressure was 0.78 MPa, the temperature was 25°C, and the barometric pressure was 0.098 MPa.  $V_{\infty}$ , that is the difference in volume of methane adsorbed at 0.78 and 0.098 MPa, was 18.0  $\text{cm}^3$  STP/g. Values of  $V_t$  (at STP) were plotted against  $\sqrt{t}$  as shown in Figure 2 and the value of  $V_0$  was obtained by extrapolation to the ordinate. For this particular run,  $V_0 = -3.90 \text{ cm}^3/\text{g}$ . Using this  $V_0$  value, values of  $(V_t - V_0)/V_{\infty}$  were calculated and are shown in the last column of Table 2. From the initial slope of  $(V_t - V_0)/V_{\infty}$  versus  $\sqrt{t}$  plots, the diffusion parameter  $D^{1/2}/r_0$  was calculated by using the diffusion equation for spherical particles:

$$\frac{(V_t - V_0)}{V_{\infty}} = \frac{6}{\sqrt{\pi}} (Dt/r_0^2)^{1/2} \quad (1)$$

It is to be noted that no assumption about the nature of the methane isotherm is required in the derivation of equation (1).

## RESULTS AND DISCUSSION

### Isotherms

Isotherms for methane adsorption on the three coals are presented in Figure 3. As observed earlier in the case of methane adsorption up to atmospheric pressure<sup>6</sup> and at 101.3 MPa (1000 atm) pressure<sup>4</sup>, adsorption was highest for the anthracite sample. The isotherms bend towards the pressure axis. Deviation from rectilinearity starts at a much lower pressure for the anthracite than for the HVA sample. A Langmuir plot of the methane isotherm for the anthracite is a straight line from which the monolayer volume is estimated as 41.1  $\text{cm}^3$  STP/g. Taking a value of 1.6  $\text{nm}^2$  for the area occupied by a methane molecule on the surface at 25°C<sup>11,12</sup>, a surface area of 178  $\text{m}^2/\text{g}$  is calculated for the anthracite. This is to be compared with the carbon dioxide surface area of 456  $\text{m}^2/\text{g}$  (also measured as 25°C) and is indicative of the molecular sieve nature of the coal<sup>13</sup>.

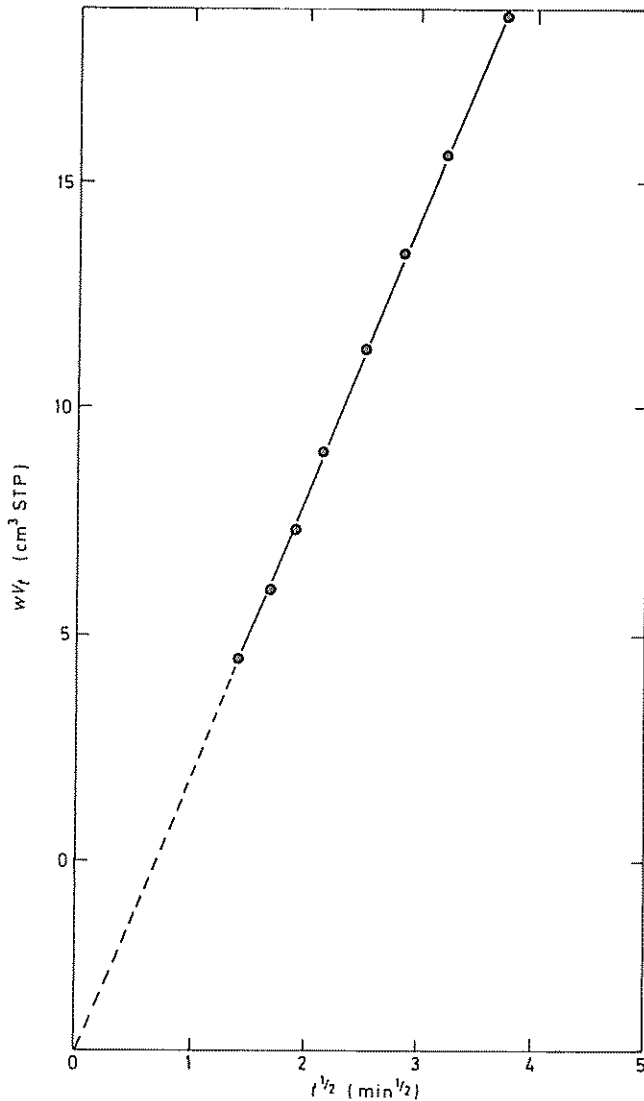


Figure 2 Desorption of methane from PSOC-177 versus time at 25°C

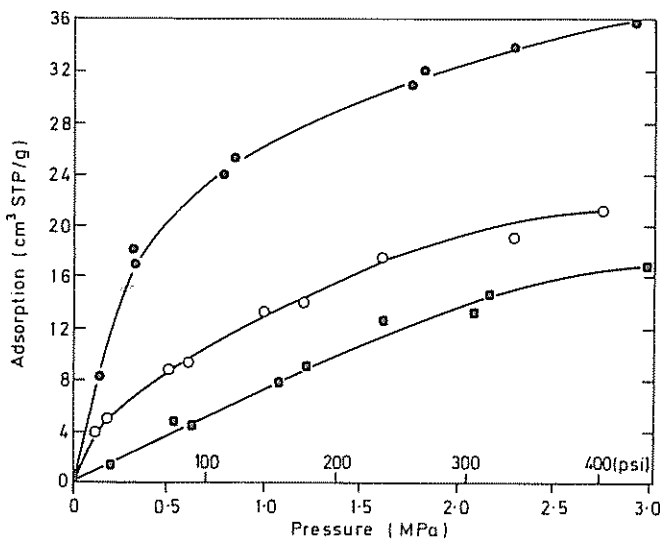


Figure 3 Adsorption isotherms of methane on coals at 25°C  
 ● PSOC-177, ○ PSOC-135, ■ PSOC-171

That is, the minimum kinetic diameters of carbon dioxide and methane are estimated as 0.33 and 0.38 nm respectively.

Methane adsorption was still rising, for each sample, at the highest pressure studied, that is about 2.9 MPa. Volumes of methane sorbed at this pressure are about one-half of those sorbed on coals of similar rank at 101.3 MPa as reported by Moffat and Weale<sup>4</sup>.

#### Rates of desorption

*Effect of pressure on diffusion.* Desorption data for 40 × 70 mesh samples of the three coals at 25°C are shown in Figures 4–6. From Figure 4 it is seen that slopes of plots of  $(V_t - V_0)/V_\infty$  versus  $\sqrt{t}$  increase with an increase in initial desorption pressure (or the pressure differential) for the anthracite sample. The same relation holds for the medium-volatile coal, as seen in Figure 5, but the effect is not as marked. For results on the HVA sample, shown in Figure 6, the same plot is obtained, independent of the pressure range employed. Values of  $D^{1/2}/r_0$  calculated from these plots are shown in Table 3.

On examination of the data it is found that there is a better correlation between the variation of  $D^{1/2}/r_0$  and average concentration of methane (during a desorption run), than with average pressure. In Figure 7 the diffusion parameter at 25°C is plotted against the average concentration of methane in coals PSOC-177 and PSOC-135 during the diffusion runs. It is seen that the concentration-dependence of  $D$  is quite marked for the anthracite sample. It is also apparent that the concentration-dependence is brought about by the amount of methane sorbed. The HVA sample, having a lower sorption capacity, does not show this behaviour. Concentration-dependent  $D$  values have been reported for methane, water or ammonia diffusion through the intercrystalline channels of certain zeolites<sup>14,15</sup> and also in cases of sorption in media where swelling occurs<sup>15</sup>. Some swelling of coal, as a result of methane sorption, has been reported by Moffat and Weale<sup>4</sup> and by Ettinger<sup>5</sup>. However, with our results swelling does not appear to be the main explanation since the effect of methane concentration on the diffusion parameter appears to be more marked on the higher rank (and less swelling<sup>4</sup>) coal. To be certain of this conclusion, values for the diffusion parameter would have to be available over similar ranges of methane concentrations for all the coals.

*Effect of temperature on diffusion.* Values of the diffusion parameter at different temperatures are shown in Table 3. For the HVA sample the diffusion parameter at 0°C tends to increase slightly with average concentration of methane in the sample. When the diffusion coefficient is concentration-dependent there is not a unique temperature coefficient for the diffusion parameter. The diffusion parameter of PSOC-177 for the three temperatures is plotted against the average concentration of methane in Figure 8. Values of  $D^{1/2}/r_0$  at 15 cm<sup>3</sup> STP/g are used to obtain an Arrhenius plot shown in Figure 9. Clearly diffusion is activated with a value of 35 kJ/mol for the temperature coefficient of the diffusion parameter. For sample PSOC-135 a similar approach yields a temperature coefficient of 32.1 kJ/mol for  $D^{1/2}/r_0$  at 6 cm<sup>3</sup> STP/g. Experimental data for PSOC-171 yields a temperature coefficient of 26.3 kJ/mol which is essentially independent of methane concentration over the range studied.

It has been suggested in an earlier publication<sup>10</sup> that if the gas taken up by the solid can be considered to be

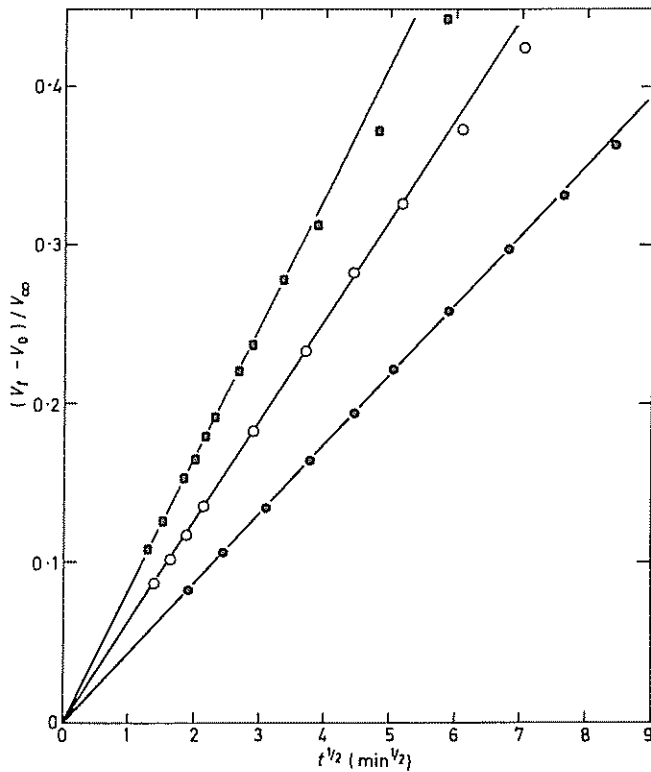


Figure 4 Desorption-rate plots for PSOC-177 at 25°C for different initial methane pressures:  
● 0.32 MPa, ○ 0.78 MPa, ■ 1.75 MPa

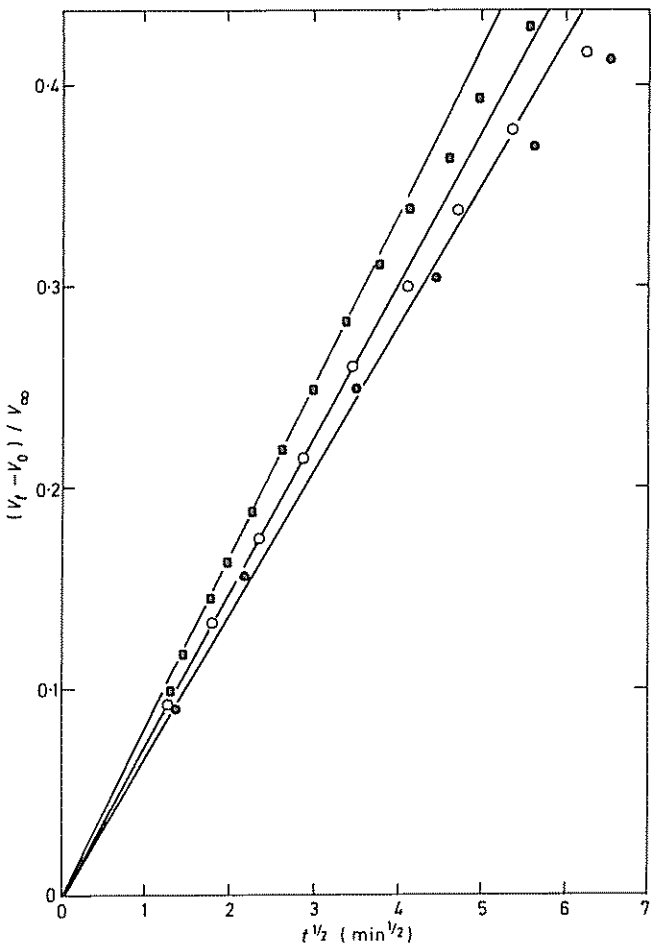


Figure 5 Desorption-rate plots for PSOC-135 at 25°C for different initial methane pressures:  
● 0.49 MPa, ○ 1.00 MPa, ■ 2.00 MPa

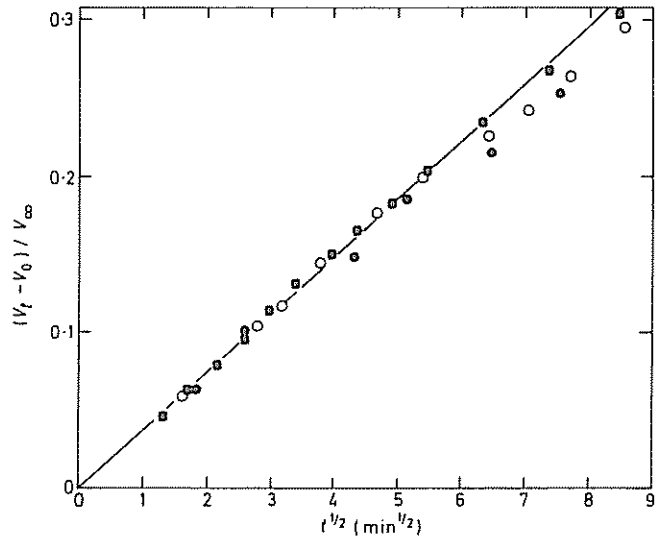


Figure 6 Desorption-rate plot for PSOC-171 at 25°C for different initial methane pressures:  
● 0.56 MPa, ○ 1.06 MPa, ■ 2.09 MPa

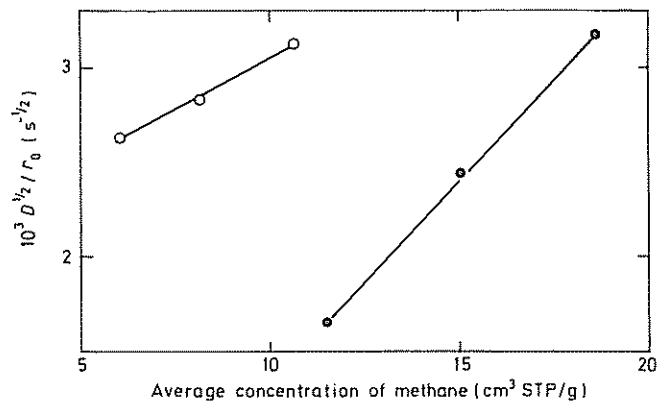


Figure 7 Diffusion parameter at 25°C versus average methane concentration. Desorption runs for 40 X 70 mesh samples of  
● PSOC-177 and ○ PSOC-135

present in two phases ((1) as relatively free gas molecules occupying open porosity and (2) as relatively non-mobile molecules in the matrix), the experimentally determined diffusion coefficient ( $D_{expt}$ ) can be expressed by the following equation:

$$D_{expt} = \frac{D_0 \exp(-E/RT)}{\epsilon + C_s K_0 \exp(q/RT)} \quad (2)$$

where  $\epsilon$  = open porosity,  $K$  = equilibrium constant of adsorption or absorption =  $K_0 \exp(q/RT)$ ,  $C_s$  = adsorption at saturation,  $q$  = heat of adsorption,  $D_0$  = pre-exponential term in the expression  $D = D_0 \exp(-E/RT)$ , and  $E$  = activation energy.

Under conditions where the quantity of gas adsorbed is high the equation reduces to:

$$D_{expt} = (D_0/C_s K_0) \exp[-(E + q)/RT] \quad (3)$$

Thus in the present study if the above condition prevailed the apparent activation energy ( $E + q$ ) would be about

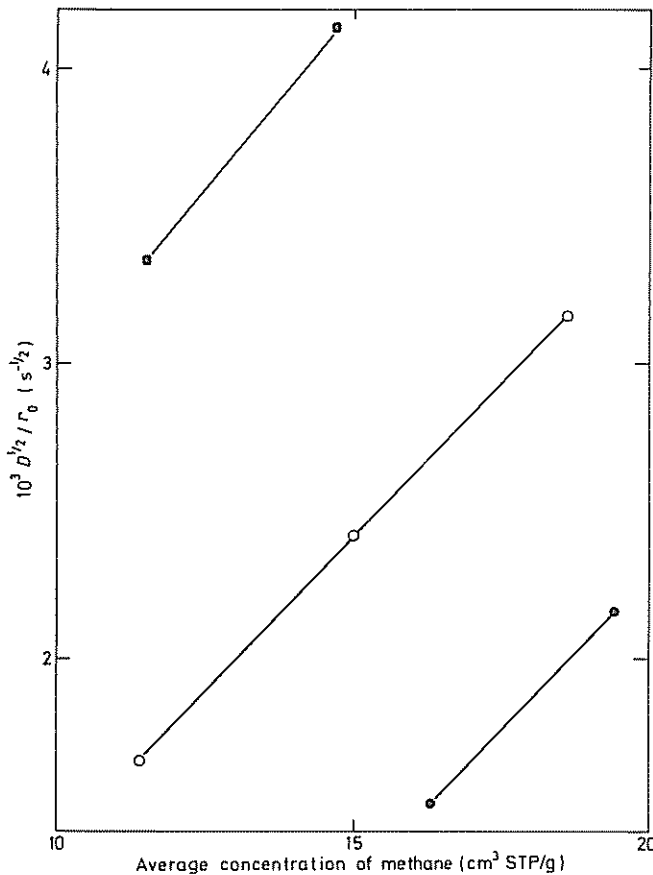


Figure 8 Diffusion parameter versus average methane concentration. Desorption runs for 40 X 70 mesh samples of PSOC-177 at ● 0°C, ○ 25°C, ■ 50°C

20 kJ/mol greater than the true activation energy, since  $q$  is reported to be about 21 kJ/mol<sup>11</sup>.

Under conditions where adsorption is low equation (2) reduces to:

$$D_{\text{expt}} = (D_0/\epsilon) \exp[-E/RT] \quad (4)$$

Under intermediate situations the temperature coefficient of  $D$  will be the sum of a part of heat of interaction, plus the true activation energy of the diffusion process. For the anthracite sample it appears that a significant portion of the heat of interaction is included in the experimentally obtained temperature coefficient. This contention is supported by the fact that anthracites have smaller activation energies than bituminous coals<sup>16</sup> for argon diffusion (at sub-atmospheric pressure).

*Effect of particle size on diffusion.* Values of  $D^{1/2}/r_0$  for different particle sizes of PSOC-135 are also presented in Table 3. Comparing values obtained at about the same pressure differential, it is seen that the diffusion parameter increases with decreasing particle size, as expected. If the average particle radius is substituted for  $r_0$ , values of  $D$  can be calculated. Calculated diffusion coefficients are seen to decrease sharply with decreasing average particle size. Clearly  $r_0$  is smaller than the particle radius, as previously discussed<sup>10</sup>, but it is not independent of particle size; this can be because additional macropores (cracks) are possibly produced by grinding, the greater the extent of grinding the greater being the density of macropores introduced.

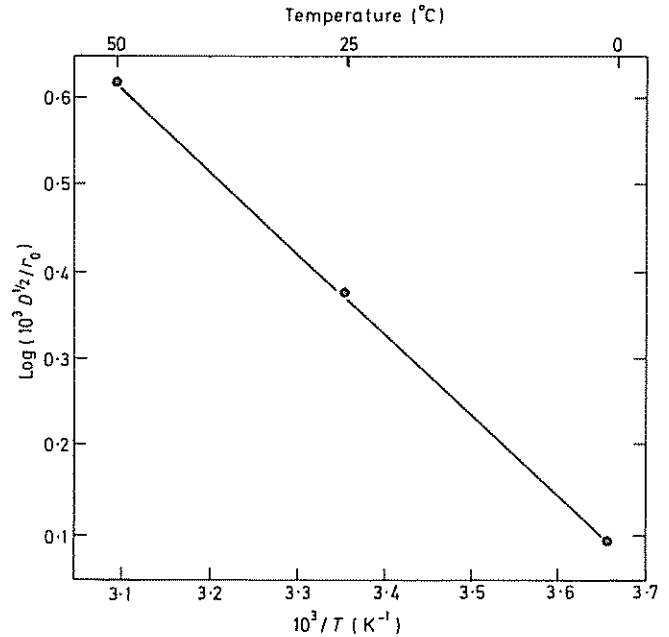


Figure 9 Arrhenius plot of the diffusion parameter. 40 X 70 mesh PSOC-177 at average concentration 15 cm<sup>3</sup> STP/g

## ACKNOWLEDGEMENTS

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Table 3 Diffusion parameters for methane desorption from selected coals

PSOC sample	Sieve size (U.S. mesh)	Average diameter $\times 10^2$ (cm)	Initial pressure (MPa)	Average conc. of methane in coal* (cm <sup>3</sup> /g)	$10^3 D^{1/2}/r_0$ (s <sup>-1/2</sup> )	$10^{10} D^\dagger$ (cm <sup>2</sup> /s)
Temperature 0°C						
177	40 X 70	3.15	0.715	16.3 ✓	1.51	—
177	40 X 70	3.15	1.69	19.3	2.17	—
135	40 X 70	3.15	0.46	7.3	1.52	—
135	40 X 70	3.15	0.93	9.7	1.75	—
171	40 X 70	3.15	0.52	3.9	0.82	—
171	40 X 70	3.15	1.03	6.3	0.88	—
Temperature 25°C						
177	40 X 70	3.15	0.315	11.5	1.66	6.8
177	40 X 70	3.15	0.78	15.0	2.46	14.5
177	40 X 70	3.15	1.76	18.6	3.17	24.9
135	4 X 5	43.3	1.89	8.4 ✓	1.46 ✓	990 ✓
135	4 X 5	43.3	2.66	9.9	1.75	1420 } }
135	14 X 24	9.34	1.79	9.1 ✓	1.81 ✓	71.0 ✓ } }
135	14 X 24	9.34	2.51	11.0	2.09	95.0 } }
135	40 X 70	3.15	0.49	6.0	2.65	17.3 } }
135	40 X 70	3.15	1.00	8.1 ✓	2.82 ✓	19.7 } }
135	40 X 70	3.15	2.00	10.6	3.13	24.2 } }
171	40 X 70	3.15	0.555	2.7	1.43	5.1
171	40 X 70	3.15	1.07	4.1	1.43	5.1
171	40 X 70	3.15	2.08	6.9	1.43	5.1
Temperature 50°C						
177	40 X 70	3.15	0.83	11.5	3.38	—
177	40 X 70	3.15	1.82	14.7	4.12	—
135	40 X 70	3.15	0.53	4.1	3.74	—
135	40 X 70	3.15	1.04	5.7	4.13	—
171	40 X 70	3.15	0.56	2.3	1.98	—
171	40 X 70	3.15	1.08	3.4	1.98	—

1 MPa = 145 psi

\* Average concentration of methane = (adsorption at  $p_0$  + adsorption at 1 atm)/2

† Assuming  $r_0$  = average particle radius

