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Activated diffusion of methane in coal

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Two techniques have been used to study the diffusion of methane in American coals of rank varying from low volatile matter anthracite to high volatile content bituminous. Diffusion of methane out of coal at sub-atmospheric pressures has been studied using a constant pressure apparatus. Diffusion of methane into coal at elevated pressures has been studied using a constant volume apparatus. Diffusion in the micropore system is activated, the activation energy varying from 3.5 kcal/mol* for low volatile matter anthracite to about 7.0 kcal/mol for bituminous coals. This suggests that the average size of the accessible micropores in the anthracites is larger than that in the bituminous coals.

THE PRESENCE of methane in coal seams is one of the hazards of coal mining operations. The amount of methane entering the mine from the coal seam depends on geological, physical and mining factors. The kinetics and equilibrium of sorption of methane and their dependence on temperature and pressure are properties of the coal present in the seam. That portion of the coal which is not fractured has a structure of ultrafine pores of molecular dimensions. Penetration into these pores is diffusion controlled.

Unsteady state diffusion data obtained by various workers¹⁻⁶ have shown that diffusion of methane in coal is activated. The activation energy of diffusion is a rough guide to the minimum diameter of the micropore system⁷.

Peters and Juntgen⁵ have reported diffusion data of methane and its higher homologues up to isobutane in coals. The values of activation energy for methane diffusion for four coals of volatile matter contents (VM) 8.2, 14.8, 26.8 and 38.0% were 6.4, 9.7, 17.5 and 9.1 kcal/mol* respectively. The rather high value of 17.5 kcal/mole for the 26.8% VM coal tends to show that the average micropore size in this coal would be very small. The activation energy values of ethane diffusion from four other coal samples, however, do not show any significant change with rank. The values reported for coals with 10.0, 19.0, 29.0 and 39.5% VM were 8.0, 9.0, 8.6 and 7.5 kcal/mol, respectively. The ethane diffusion data were obtained by a slightly different experimental technique, but the rather constant value of activation energy is in conflict with the methane diffusion data.

All published results report diffusion coefficients at pressures near or below one atmosphere. It was thought worthwhile to study unsteady state diffusion of methane from coals of different rank over an extended temperature and pressure range.

* Units of activation energy: 1 kcal/mol = 4.187 kJ/mol.

EXPERIMENTAL

Coals used

Twelve samples of (100 × 150) mesh coal and three sieve sizes of two anthracites were used in this study. The standard volatile matter yields of the coals are given in *Table 3*.

Diffusion measurement

Two experimental approaches have been used: (1) A constant pressure apparatus measuring diffusion out of the coal particles; and (2) a constant volume but variable pressure apparatus measuring diffusion into the particles.

Constant pressure apparatus

The apparatus, experimental procedure, and the computational procedures used to calculate the diffusion parameter $D^{1/2}/r_0$ (where D is the diffusion coefficient and r_0 is the diffusion path length) have been described in detail previously^{8,9}. A differential experimental system was used to avoid errors caused by small temperature fluctuations. In principle, the procedure consisted of charging the sample with methane to an absolute pressure of about 1.6 atm (an equilibrium time of about 24 h was allowed) and then measuring the unsteady state release of the gas after suddenly reducing the pressure outside the particles back to atmospheric. Prior to being charged with methane, the coal samples were degassed for 24 h at temperatures ranging from 350°C for the anthracites, to 150°C for the lowest rank coal. The temperatures of degassing were in every case higher than the temperature of diffusion measurements.

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 particle. The solution of Fick's Law¹⁰ for spherical geometry for a concentration independent D , where external gas pressure is constant, is given by the following equation:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{r_0^2}\right) \quad (1)$$

where Q_t and Q_∞ are volumes at time $t = t$ and $t = \infty$. The above equation was used in conjunction with experimental Q_t versus $t^{1/2}$ curves to calculate the micropore diffusion parameter $D^{1/2}/r_0$ by a procedure described by Nelson and Walker⁹. For very small values of t , equation (1) reduces to

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

Constant volume apparatus

The apparatus used is shown in *Figure 1*. Constructed of stainless steel, it had three valves V_1 , V_2 , and V_3 (Aminco high pressure) connected by means of capillary tubing through the intermediary of an Aminco super pressure cross C. A Satham Instrument transducer T, connected to the cross at the remaining end, measured the pressure inside the system.

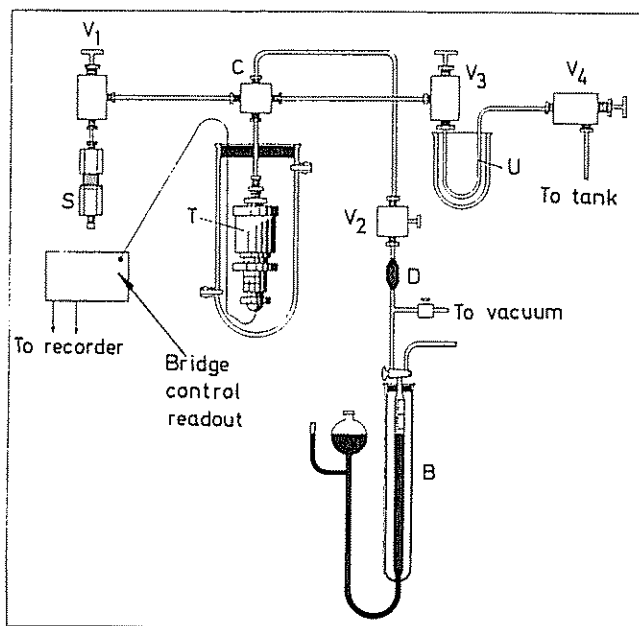


Figure 1 Diagrammatic view of pressure adsorption apparatus

The sample (2–3 g of powder) was held in tube S of about 5 cm³ capacity connected to valve V_1 . A condensing coil U was connected to valve V_3 , the other end of the coil being closed by a fourth valve V_4 . The apparatus could be evacuated through valve V_2 to a residual pressure of 10^{-5} mmHg using a mercury diffusion pump and a high vacuum pump.

The stainless steel section of the apparatus was connected to a Pyrex glass burette B and vacuum line through an Apiezon wax seal at D. Through a T-piece and a three-way high vacuum stopcock after D, the adsorption system could be connected either to the vacuum pumps or to atmosphere. Chemically pure methane (Matheson Co.) was bled into the condensing coil directly from a tank through valve V_4 . After thoroughly purging the system, the condensing coil was cooled with liquid nitrogen to freeze a suitable quantity of methane in the coil. The desired pressure of purified methane was generated in the adsorption apparatus by evaporating an appropriate quantity of gas from coil U.

The pressure of methane was measured by the transducer. The output of the transducer was measured on a Statham instrument bridge control readout instrument coupled to a recorder. Since the transducer has a temperature coefficient, it was enclosed in a water jacket maintained at a constant temperature. The transducer was calibrated using propane vapour as a standard. The transducer output was found to be linear with pressure, but it showed a slight hysteresis. A correction was applied by noting the residual reading of the transducer under vacuum after each equilibrium point. This corrected reading was used for calibration.

To avoid uncertainty about the compressibility factor of methane at higher pressures and also any uncertainty in the determination of free space in a metal apparatus having different temperature regions, the following procedure was adopted for the calibration of the sorption system. A suitable known volume of metal block was placed in the sample tube S. At first the space between valves V_1 , V_2 and V_3 was calibrated by pressurizing this space to the desired pressure, bleeding out the gas in stages to the burette B, and noting the volume discharged as a function of pressure. Then, the entire adsorption system including the sample tube (with the metal block inside) was calibrated by the same procedure at each temperature that would be used in subsequent diffusion experiments. Care was taken to keep the sample tube S immersed up to a fixed level in the constant temperature bath during calibration, as well as during sorption runs. During sorption runs, the same volume of coal (calculated from its helium density) as that of the metal block used during calibration was taken so that the calibration could be used directly.

To make a run, the sample was first degassed for about 24 h. A known quantity of methane was taken in the space between V_1 , V_2 , and V_3 and added to the sample maintained at a desired temperature by opening valve V_1 . The transducer reading was followed as a function of time for about 100 min and then the sample was allowed to come to equilibrium with methane. It was observed that there was very little change in uptake after 24 h for all the samples studied. Adsorption at 24 h was taken to be equal to the equilibrium value, Q_∞ , for the pressure prevailing. Isotherms were measured in the usual way, allowing 2 h for each point up to a pressure of about 15 atm. It was determined that during a period of 100 min, hysteresis in the transducer reading introduced a maximum variation of ± 34 mmHg in the pressure reading. A correction was introduced where appropriate.

It has been shown by Barrer¹¹ 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 fractional completion of the diffusion process is given by the following equation:

$$\frac{Q_t}{Q_\infty} = (K + 1) \left\{ 1 - \frac{1}{\alpha + \beta} [\alpha e^{-\alpha^2 \tau} (1 + \operatorname{erf} \alpha \tau^{1/2}) - \beta e^{-\beta^2 \tau} (1 + \operatorname{erf} \beta \tau^{1/2})] \right\} \quad (3)$$

where Q_t and Q_∞ equal adsorption at time $t = t$ and $t = \infty$

$$K = (Q_t - Q_\infty)/Q_\infty$$

$$\tau = Dt/r_0^2$$

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

For small enough values of $(\tau/K)^{1/2}$, i.e. for very small times, equation (3) can be written in the following simple form:

$$\frac{Q_t}{Q_\infty} = \frac{6}{r_0} \left(\frac{Q_0}{Q_0 - Q_\infty} \right) (Dt/\pi)^{1/2} \quad (4)$$

where Q_0 equals the quantity of gas initially present in the gas phase. Therefore, from the initial slope of the Q_t/Q_∞ versus $t^{1/2}$ plot, the diffusion parameter can be obtained. It is clear that the initial slope in this case differs from the constant pressure case by the factor $Q_0/(Q_0 - Q_\infty)$. (See equation 2).

RESULTS AND DISCUSSION

Diffusion under constant pressure

Effect of temperature on diffusion parameter. For the (100 × 150) mesh samples, diffusion was measured over the temperature range 50–150°C; and for the (42 × 65) and (65 × 100) mesh sizes, the temperature range was 120–300°C. It was observed that methane diffusion was activated for all the samples. The activation energy of diffusion was obtained from the slope of $\log(D^{1/2}/r_0)$ versus $1/T$ plots. It was found that in cases where the temperature range of measurement was more than 100°C the slope became greater at higher temperature. This effect was not observed when diffusion of argon was studied from a number of coals⁵ by the same procedure. Since methane has a larger diameter than argon, its rate of diffusion was slower and consequently measurements could be followed over a more extended temperature range. A typical Arrhenius plot is shown in *Figure 2*.

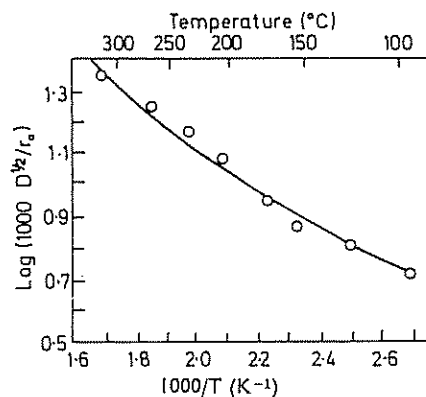


Figure 2 Activation energy plot of methane diffusion from St Nicholas (65 × 100) (Data by constant pressure apparatus)

Two distinct and extreme physical models¹² might be applicable to the diffusional process 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 which it does not behave as a free gas following ideal gas laws. In the second, the gas taken up by the solid might be considered to be present in two phases: (1) as relatively free molecules occupying the open porosity of the solid and (2) as relatively non-mobile molecules adsorbed in a layer on the internal walls of the solid. Diffusion will then occur via the 'free' gas molecules, which again will meet the potential-energy barriers of restrictions. In both cases the same differential equation results, but the diffusion coefficient D of the second model is related to D for the first model by the relation¹³

$$\tilde{D} = D/(\epsilon + KC_s) \quad (5)$$

where ϵ = open porosity

K = equilibrium constant of adsorption = $K_0 \exp(-q/RT)$

C_s = adsorption at saturation

q = heat of adsorption

It can be shown, by using the methods of absolute rate theory, that for the first model

$$D = D_0 \exp(-E/RT) \quad (6)$$

where D_0 has a significance similar to the pre-exponential term of the rate expression for a reaction rate constant and E is the activation energy. By the same methods, it can be shown that¹³

$$\tilde{D} = \frac{D_0 \exp(-E/RT)}{\epsilon + C_s K_0 \exp(-q/RT)} \quad (7)$$

It is clear that a plot of $\ln \tilde{D}$ versus $1/T$ will not be linear over a wide temperature range. This gives one method of distinguishing between the first and second model. At low temperatures, where the quantity of gas or vapor adsorbed is high, the porosity term would be negligible, giving

$$\tilde{D} = (D_0/C_s K_0) \exp[-(E+q)/RT] \quad (8)$$

At higher temperatures,

$$\tilde{D} = (D_0/\epsilon) \exp[-E/RT] \quad (9)$$

As the temperature is increased, the slope of the Arrhenius plot should decrease. The plot shown in *Figure 2* has a curvature in the reverse direction, as could be expected if the second model was applicable. Therefore, the first model is considered to apply. The upward curvature can be explained by assuming a pore size distribution in the micropores. At higher temperatures narrower micropores, with higher potential barriers, become important; and the overall activation energy increases. It might be added, however, that in the case of (100 × 150) mesh samples relatively good straight line Arrhenius plots were obtained in the temperature range 50–150°C.

Peters and Juntgen⁵ and Kayser and Peters⁶ have analysed their diffusion data by assuming the two-phase model for the diffusion process in the methane-coal system. The temperature coefficient of D or D/d^2 (where d is the particle diameter) has been reported as an apparent activation energy. The above authors have used equation (8) to calculate the true activation energy. It might be noted that the Arrhenius plots in figure 1 of reference 5 do not show any decrease of slope at higher temperature as could be expected. The experimental activation energy values reported are much higher compared to those obtained in the present work. Even the 'true' activation energy for one sample of coal was high. On the other hand, the activation energy values of ethane diffusion reported in the same paper⁵ tend to agree with the present findings.

Effect of particle size on diffusion parameter. Diffusion parameters were obtained for (42 × 65), (65 × 100), and (100 × 150) mesh sizes of St Nicholas and Loree anthracites. The results are summarized in Table 1.

Table 1 Diffusion parameters of methane in anthracites of different particle sizes (from constant pressure apparatus)

Coal	Size Tyler mesh	$D_0^{1/2}/r_0$ ($s^{-1/2}$)	Activation energy (kcal/mol)	Temperature range (°C)
St Nicholas	42 × 65	0.188	5.4	140-227
St Nicholas	65 × 100	0.154	5.0	100-200
St Nicholas	100 × 150	0.209	4.4	100-200
Loree	42 × 65	0.279	4.8	100-227
Loree	65 × 100	0.352	4.8	90-190
Loree	100 × 150	0.314	3.9	60-140

The activation energy and the pre-exponential term have been obtained using equation (6). The activation energy tends to increase with an increase of particle size. This is in agreement with the diffusion data on nitrogen and argon from the same anthracites obtained earlier¹⁴. The higher temperature range of diffusion measurement for the larger particle size may be a factor contributing to the increase of activation energy. There is also the possibility of altering the physical assembly of the particles due to the grinding process.

To calculate a numerical value for the diffusion coefficient D , an estimate of the diffusion path length is necessary. A coal particle can be assumed to consist of macro, transition and micro pores. As diffusion has been found to be activated, the process should be almost entirely dependant on the micropores (that is where the diameter is comparable to the size of the methane molecule). The macropores and transition pores divide the particle into smaller units, and it is the size of these smaller units consisting of the micropores alone that controls the activated diffusion process. Therefore, the average particle size should not be used for the diffusion path length. The problem then is to obtain a reliable estimate of the size of these sub-units. These units may be

assumed to be spherical. For a sphere, the radius is equal to $3V/A$ where V is the volume and A is the surface area. For a collection of spheres the same relation should hold and an average radius could be obtained from specific volume and area data. Ideally, the sum of the geometric, macropore, and transition pore area is the required quantity A . To obtain the correct specific volume V , a fluid has to be used that does not penetrate the micropore system.

Published data¹⁵ on surface area of coals indicate that nitrogen at -195°C does not penetrate the micropore system significantly. Thus the BET area calculated from nitrogen adsorption (equilibration time of 30 min for each adsorption point) has been used to estimate r_0 . In an attempt to, perhaps, get a better estimate of A , BET areas calculated from neopentane adsorption at 0°C were also used in some cases.

The determination of specific volume with a fluid like nitrogen or methane is not possible because of adsorption. Helium, at room temperature, does penetrate the micropore system, but it has been concluded that helium displacement gives the best value of V in the calculation of r_0 . This means that since V is underestimated (from helium displacement) and A is overestimated (from nitrogen adsorption), the value of r_0 will be somewhat too small. This in turn means that the values of D will be somewhat too small.

Results for the two anthracites of variable average particle size are given in Table 2. It is seen that the specific volumes of the anthracites (as measured by helium) do not vary significantly with particle size. On the other hand, there is a marked increase in the specific surface areas with decreasing particle size when either nitrogen or neopentane is used as the adsorbate. The increase in area is much more marked than could be attributed just to an increase in the geometric area of the particle with decrease in size. It is suggested that with the fine grinding of anthracite in the size ranges examined, a more extensive system of macro-cracks is produced, which permeates the particle and opens up area behind closed pores that were previously inaccessible to nitrogen and neopentane but not to helium. As previously reported¹⁶, neopentane areas of anthracites are significantly smaller than nitrogen areas. However, in the case of bituminous coals, the neopentane areas are larger¹⁶, possibly because of some imbibition by the coal. It is because of this possibility that A was not estimated for the bituminous coals using neopentane.

As a result of the essential constancy of V and the increase in A with decreasing particle size, r_0 decreases with decreasing particle size. However, D does not show a marked change with particle size (using A from nitrogen adsorption) except for the 100×150 mesh Loree anthracite. D does show a continuous decrease in value with decreasing particle size for the St Nicholas anthracite when neopentane surface area values are used. As described above, undoubtedly there is some decrease in r_0 with decreasing particle size, but this fact means that the extent by which A is overestimated also increases with decreasing particle size. That is, some diffusion of nitrogen and neopentane into the micropore system occurs during the 30 min equilibration time and the amount obviously will increase with a decrease in r_0 . Thus it is felt that the value of D is more correct, the larger the particle size. Further, for anthracite, the value of D using the neopentane area is thought to be the

Table 2 Estimate of diffusion coefficients for three sieve sizes of two anthracites (from constant pressure apparatus)

Coal	Sieve size Tyler	Specific volume (cm ³ /g)	10 ⁻⁴ × Specific surface area (cm ² /g)		10 ⁴ × Diffusion path length (cm)		10 ¹¹ × Diffusion coefficient at 110°C (cm ² /s)	
			Nitrogen	Neopentane	r ₀ (N ₂)	r ₀ (Neopentane)	From r ₀ (N ₂)	From r ₀ (Neopentane)
St Nicholas	42 × 65	0.588	8.0	1.0	0.220	1.76	1.74	111
St Nicholas	65 × 100	0.598	12.5	1.3	0.143	1.38	0.63	59
St Nicholas	100 × 150	0.610	22.6	3.7	0.081	0.49	1.00	36
Loree	42 × 65	0.581	11.8	-	0.147	-	3.27	-
Loree	65 × 100	0.591	15.3	-	0.116	-	3.15	-
Loree	100 × 150	0.606	56.0	-	0.033	-	0.69	-

more correct, since neopentane has penetrated into a smaller percentage of the micropore area during the measurement of A .

Variation of diffusion parameter with rank. Diffusion data have been obtained for twelve samples of coal of (100 × 150) mesh over a range of temperatures. The data presented in *Table 3* were obtained in the temperature range 50–150°C, where the activation energy plots are fairly linear. Activation energies vary from 3.5 kcal/mol for an anthracite of 4.2% VM to 5.2 kcal/mol for an anthracite of 9.0% VM. The activation energy does not change significantly in the bituminous range, with a value of about 7.0 kcal/mol being obtained for the six samples studied. These results are in disagreement with those of the argon-coal system⁷, where a maximum in activation energy appears at a volatile matter content of about 28%, or in the range of good coking coals.

Table 3 Diffusion parameters of methane from (100 × 150) mesh coals (from constant pressure apparatus) in the temperature range 50–150°C

Coal	VM (% d.a.f.)	$D_0^{1/2}/r_0$ ($s^{-1/2}$)	Activation energy (kcal/mol)
Jeddo	4.2	0.090	3.5
St. Nicholas	4.5	0.172	4.1
Loree	5.4	0.315	3.9
Dorrance	5.8	0.402	4.2
Powderly	7.2	0.471	5.2
Treverton	9.0	0.370	5.2
912	19.7	1.87	7.3
Upper Freeport	33.0	1.52	7.0
956	35.9	2.21	7.4
Pittsburgh	39.5	1.63	7.6
885	39.7	1.26	7.0
888	40.5	1.12	6.5

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 minimum diameter of the pore system 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 decreases, carbon atoms are being substituted for by oxygen and other functional groups on the surface. Therefore, the change in the 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 polarizable¹⁷. Other complicating factors are the size distribution in the micropores and the presence of different petrographic constituents in bituminous coals.

Diffusion under variable pressure

Adsorption isotherms. Adsorption isotherms of methane for three samples of coal at 24°C, 47°C, and 72°C are presented in *Figures 3-5*. Equilibration time for each adsorption point was at least 120 min. Isotherms, shown in *Figures 4 and 5* for the two bituminous coals, are linear; but for the St Nicholas anthracite, there is a slight curvature towards the pressure axis. However, over a smaller pressure range the isotherms approximate to Henry's Law behaviour, thus fulfilling a requirement for the derivation of equation (3).

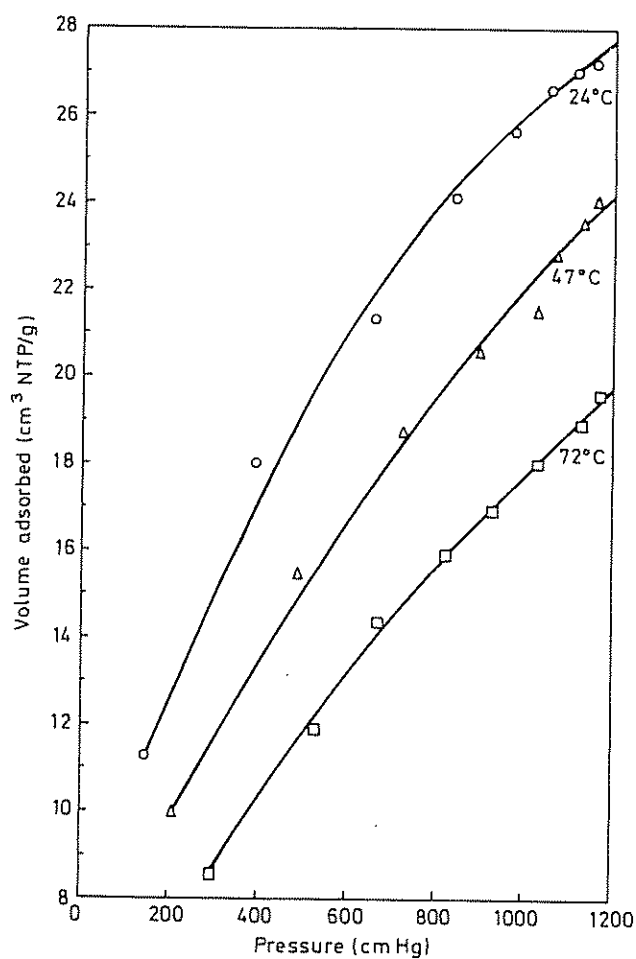


Figure 3 Adsorption isotherms of methane in St Nicholas (100 x 150)

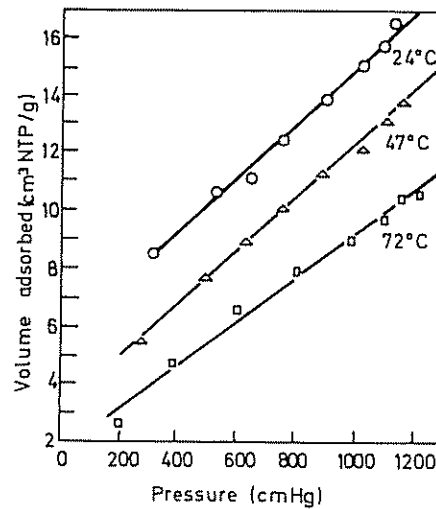


Figure 4 Adsorption isotherms of methane in 912 (100 × 150)

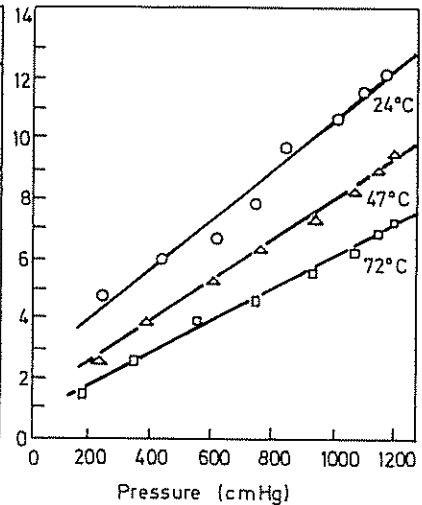


Figure 5 Adsorption isotherms of methane in 888 (100 × 150)

It is seen from *Figures 3-5* that the adsorption of methane, over the pressure range studied, is greater for the anthracite than for the bituminous coals. This is in agreement with earlier findings¹⁸.

Diffusion data Diffusion data were obtained on two sieve sizes of St Nicholas and two bituminous coals at three temperatures in the pressure range of 2-8 atm. The concentration dependence of the micropore diffusion parameter in this pressure range was not determined in this work. However, Patel¹⁹ working with slightly activated, heat treated St Nicholas anthracite has shown that the micropore diffusion parameter is pressure independent in the range 3.6-6.4 atm. The rate of sorption of methane at 24°C as a function of fractional completion of sorption is plotted against $t^{1/2}$ in *Figures 6* and *7*. The initial slope of these and similar plots was taken to be equal to $6/\pi^{1/2} [Q_0/Q_0 - Q_\infty](D^{1/2}/r_0)$, assuming the applicability of equation (4) to the system. An estimate of r_0 was obtained from nitrogen areas and helium densities. The results are given in *Table 4*. When compared with the values in *Table 2*, it is seen that the D 's for the two sieve sizes of the St Nicholas anthracite are in reasonable agreement. For the (42 × 65) mesh samples, the value of D at 100°C, obtained by the variable pressure method, is 0.55×10^{-14} cm²/s, whereas the value obtained by the constant pressure method is 1.74×10^{-14} cm²/s. This agreement indirectly shows that D is concentration independent and that the use of equation (4) to calculate the diffusion parameter is justified.

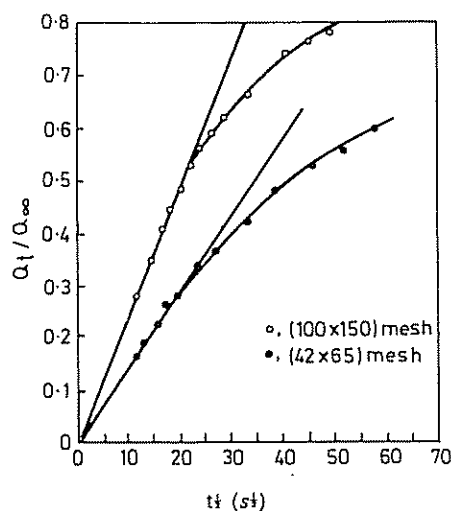


Figure 6 Rate of sorption of methane in St Nicholas anthracite at 24°C

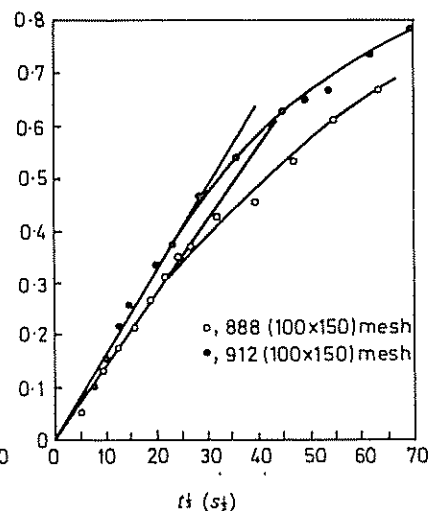


Figure 7 Rate of sorption of methane in selected bituminous coals at 24°C

Table 4 An estimate of diffusion for different coals (from constant volume apparatus)

Coal	Sieve Size Tyler	Specific Volume (cm ³ /g)	10 ⁻⁴ × Specific area by nitrogen (cm ² /g)	10 ⁴ r ₀ (cm)	10 ¹⁴ × Diffusion coefficient (cm ² /s) (at 72°C)
St Nicholas	42 × 65	0.588	8.0	0.220	0.28
St Nicholas	100 × 150	0.610	22.6	0.081	0.08
912	100 × 150	0.719	2.4	0.898	23.5
888	100 × 150	0.746	4.8	0.461	8.2

Even though diffusion coefficients are given in Table 4, it is suggested that they be viewed with caution. That is, the D 's for the bituminous samples are listed as being significantly higher than that for the anthracite. At least one factor which makes them higher is the low values obtained for their specific surface area relative to the anthracite. It is important to remember that these areas are taken to represent the sum of only the macro and transition pore areas. These values may be correct or they may be high because of the nitrogen penetrating some fraction of the micropore area as well. It is possible that the contribution of the micropore areas to the total nitrogen areas in the case of the anthracite is significantly higher than that for the bituminous coals.

The diffusion data obtained by the constant pressure apparatus are summarized in Table 5. When compared with the results in Table 3, it is seen that there is satisfactory agreement. The results in Table 5 have been obtained from the initial slope of the experimental curve; whereas to obtain the results in Table 3, the entire experimental curve has been utilized. Consequently, the data in Table 3 are felt to be more reliable.

Table 5 Diffusion parameters of methane in coals (from constant volume apparatus) in the temperature range 24–72°C

Coal	Size Tyler Mesh	VM (% d.a.f.)	Pressure range (atm)	$D_0^{1/2}/r_0$ ($s^{-1/2}$)	Activation energy (kcal/mol)
St Nicholas	42 × 65	4.5	2.0–7.8	0.086	4.9
St Nicholas	100 × 150	4.5	1.8–7.8	0.156	5.2
912	100 × 150	19.7	2.0–6.5	0.436	6.0
888	100 × 150	40.5	2.0–5.0	0.646	6.5

CONCLUSIONS

By measuring diffusion parameters by two experimental approaches which in principle measure 'diffusion out of' and 'diffusion into' a coal particle, it has been demonstrated that the two phenomenon operate by the same mechanism. That is, the interaction of methane with coal in the temperature range 25–300°C is primarily physical.

Values of the diffusion parameter $D^{1/2}/r_0$ can be accurately measured and show that the diffusion of methane into the micropores of coals is activated. The activation energy for diffusion is less for the anthracites than for the bituminous coals studied, suggesting that the latter have a smaller average micropore size.

The diffusion coefficient is more difficult to obtain, however, because of uncertainty in the value of r_0 , the average diffusion distance. It is certain that r_0 is less than the particle radius; and thus D for methane at room temperature is less than about 10^{-9} cm²/s. Depending upon the correct value for r_0 , D may be as small as 10^{-16} cm²/s for some coals.

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REFERENCES

- Joy, A. S., Conference on Science in the Use of Coal, Sheffield, 1958, p A-67
- Zweitering, P., Overeem, J. F., and Van Krevelen, D. W. *Fuel. Lond.* 1956, **35**, 66
- Schilling, H., Juntgen, H. and Peters, W., 6th International Conference on Coal Science, Munster, W. Germany, 1965
- Hofer, L. J. E., Bayer, J. and Anderson, R. B., *US Bureau of Mines, Report of Investigations*, 1966, p 6750
- Peters, W and Juntgen, H. *Chemie-Ingenieur-Technik* 1968, **40**, 1039
- Kayser, H. G. and Peters, U., 7th International Coal Science Conference, Prague, 1968, Paper No 8, Section 1
- Nandi, S. P. and Walker, P. L. Jr., 'Coal Science', American Chemical Society, Washington, D.C. 1966, p 379

- 8 Nandi, S. P. and Walker, Jr., P. L. *Fuel Lond.* 1964, 43, 385
- 9 Nelson, E. T. and Walker, Jr., P. L. *J. appl. Chem.* 1961, 11, 358
- 10 Crank, J., 'The Mathematics of Diffusion', The Clarendon Press, Oxford, 1956, p 85
- 11 Barrer, R. M. *Trans. Faraday Soc.* 1949, 45, 358
- 12 Walker, Jr., P. L., Austin, L. G. and Nandi, S. P. 'Chemistry and Physics of Carbon' Vol 2, Marcel Dekker New York, 1966, p 289
- 13 Walker, Jr., P. L. Austin, L. G. and Nandi, S. P. *Fuel Lond.* 1966, 45, 173
- 14 Nandi, S. P., Ph.D. Thesis, Pennsylvania State University, 1964
- 15 Walker, Jr., P. L. and Kini, K. A. *Fuel, Lond.* 1965, 44, 453
- 16 Walker, Jr., P. L. Cariaso, O. and Patel., R.L. *Fuel Lond.* 1968, 47, 322
- 17 Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., 'Molecular Theory of Gases and Liquids' John Wiley and Sons, New York, 1964, p 942
- 18 Nandi, S. P., Kini, K. A. and Lahiri, A. *J. Sci. Ind. Res. (India)* 1959, 18B, 511
- 19 Patel, R. L., M. S. Thesis, Pennsylvania State University, 1968