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Chapter 5

Methane Diffusion in Coals and Chars

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I. INTRODUCTION

As discussed in Chapter 4, coals contain significant amounts of porosity, ranging in size from large cracks of micrometer dimensions to apertures which are even closed to helium at room temperature. Basically, the fine porosity in coal presents an aperture–cavity type system, produced by the more or less poor packing (alignment) of the aromatic and hydroaromatic building blocks. The extent of alignment is determined by such factors as (i) the amount and nature (chemical form) of the cross-linking between the building blocks, (ii) the extent of van der Waals attraction between aromatic regions, and (iii) the extent of hydrogen bonding between acidic and basic groups present at the edges of and within the structure of the building blocks.

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Total open pore volumes in coals vary considerably in amount—from about 0.03 to 0.25 cm^3/g (Gan *et al.*, 1972). These volumes show no apparent trend with coal rank. The amount of open pore volume filled with methane depends on the organic precursor(s) from which the particular coal is derived, the nature and duration of the coalification process, and the methane pressure in the coal seam among other variables. Considering the latter variable, Ruppel *et al.* (1974), who studied methane uptake on coals at 30°C, found that uptake versus pressure could be approximated by a Langmuir isotherm, with additional uptake becoming rather small at pressures above about 50 atm. Methane uptake varied from about 12 to 20 cm^3 (STP)/g of coal at 50 atm—or between about 400 and 600 ft^3 of methane per ton of coal. If the methane in the coal is assumed to be in a liquid state, it is estimated that these volumes of methane gas could be held in 0.02–0.03 cm^3 pore volume per gram of coal. Since it is common for methane in bituminous coal seams to exist at pressures between 25 and 50 atm, it is obvious why considerable quantities of methane do exist in these coals.

Understanding methane diffusion in coals and coal products is of importance for a number of reasons. First, it leads to a better understanding of the phenomenon of methane release from coal during underground mining and during deliberate recovery of methane through drilling into coal seams. Second, knowledge of diffusion coefficients and their temperature coefficients imparts further clarification to the nature of porosity in and structure of coal. Third, during the thermal processing of coal, volatiles are released, usually including substantial amounts of methane. As coals are thermally converted to cokes and chars, their total pore volume and pore size distribution change. Measurements of diffusion coefficients on the cokes and chars produced at different temperatures, at different heating rates, and in different gaseous environments assist in understanding the character of porosity changes and, hence, the coking and charring processes. Fourth, if gasification of coal chars is being conducted in steam or hydrogen leading to the production of methane, diffusion information is necessary if one is to mathematically model the process (Walker *et al.*, 1959).

II. THEORY OF MOLECULAR FLOW IN COAL AND COAL PRODUCTS

Flow in coal is studied on either ground material or solid disks. Information obtained by these two techniques can be complementary. If one wishes to use only one technique, the choice of which to use depends on what information is being sought. When ground material is used, one follows the unsteady state diffusion of molecules either into or out of the coal. For small particles, since diffusion (or flow) in the larger pores is very rapid, the process that is experimentally followed over a period of time is diffusion in the smallest pores. Thus, studies on ground material allow the measurement of diffusion parameters (but not diffusion coefficients as we will see) for molecules moving through at least some of the micropore system of coal. When solid disks of coal are used, flow across the disk can be measured under steady state conditions. Total flow rate is contributed to by Poiseuille flow in the larger macropores and cracks, Knudsen diffusion in the intermediate-sized pores, and activated diffusion in the finer micropores.

A. Unsteady State Diffusion from Ground Material

Where the diffusion coefficient (D) is independent of concentration (C) and measurements are made at isothermal conditions, the equation of continuity for spherically symmetrical flow leads directly to Fick's second law in the form

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 D \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} \tag{1}$$

where r is the radius and t is time. Although similar solutions are available for several nonspherical models, numerous previous investigations have shown the unsteady state diffusion process to be remarkably insensitive to particle shape. Consequently, the radius of an equivalent sphere (r_0) may be used for most particles of irregular shape.

If at the beginning of an experiment, the pressure outside the particles is quickly reduced to some value and held at that value during the diffusion run by increasing the volume of the collector into which the molecules slowly coming out of the micropores of the coal diffuse, Barrer and Brook (1953) show that Eq. (1) has the following solution under conditions far removed from equilibrium:

$$\frac{V_t - V_0}{V_e - V_0} = \frac{2A}{V} \left(\frac{Dt}{\pi} \right)^{1/2} \tag{2}$$

where V_0, V_t, V_e represent volumes of gas in the collector at times $t = 0$, $t = t$, and t at the end of the run where the pressure inside and outside of the coal particles is equal. Assuming a spherical particle and substituting for its volume V and area A, Eq. (2) simplifies to

$$\frac{V_t - V_0}{V_e - V_0} = \frac{6}{\pi^{1/2}} \left(\frac{Dt}{r_0^2} \right)^{1/2} \tag{3}$$

A plot of $(V_t - V_0)/(V_e - V_0)$ versus $t^{1/2}$ should give a straight line from which the diffusion parameter $D^{1/2}/r_0$ can be calculated. As will be seen later, r_0 is less than the particle radius for coals, and its exact value is unknown in all cases. Therefore, the diffusion coefficient D cannot be determined with any certainty using the unsteady state technique.

Even though the use of Eq. (3) implies that diffusion data need only be taken over a short period of time at the beginning of a run (i.e., far removed from equilibrium), it is necessary to have a value for V_e in order to calculate the diffusion parameter. Therefore, one is either faced with waiting a long time for the completion of a run or estimating V_e from other measurements, such as helium and mercury densities. The first approach is inconvenient and the second approach is more or less in error. In this light, Nelson and Walker (1961) suggested that the use of the complete solutions to Eq. (1) has, on balance, considerable merit—apparently much more than most workers in the field have appreciated. These solutions, which are well known (Crank, 1956), are

$$\frac{V_t - V_0}{V_e - V_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{1}{n^2} \exp\left(- \frac{D n^2 \pi^2 t}{r_0^2} \right) \right] \tag{4}$$

$$\frac{V_t - V_0}{V_e - V_0} = 6 \left(\frac{Dt}{r_0^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} \operatorname{erf} \frac{n r_0}{\sqrt{Dt}} \right\} \Bigg] - \frac{3Dt}{r_0^2} \tag{5}$$

The series of Eq. (4) converges well for large values of $D^{1/2}t^{1/2}/r_0$, whereas the same solution expressed in the form of Eq. (5) possesses the advantage of converging rapidly for small values of $D^{1/2}t^{1/2}/r_0$.

Nelson and Walker (1961) have outlined computational procedures to solve for the diffusion parameter using Eqs. (4) and (5). For larger or moderate values of $D^{1/2}t^{1/2}/r_0$, since three unknowns are involved in Eq. (4), three equations are required which may be obtained from three points on an experimental curve. A typical plot is given in Fig. 1. Assuming these three points to be $(V_1, t_1^{1/2})$, $(V_2, t_2^{1/2})$, and $(V_3, t_3^{1/2})$, the problem is to solve the following three equations simultaneously for the required unknowns:

$$(V_1 - V_0) = (V_e - V_0) f_1 \tag{6}$$

$$(V_2 - V_0) = (V_e - V_0) f_2 \tag{7}$$

$$(V_3 - V_0) = (V_e - V_0) f_3 \tag{8}$$

where f_i is used to denote the function

$$f_i = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{D n^2 \pi^2 t_i}{r_0^2} \right) \tag{9}$$

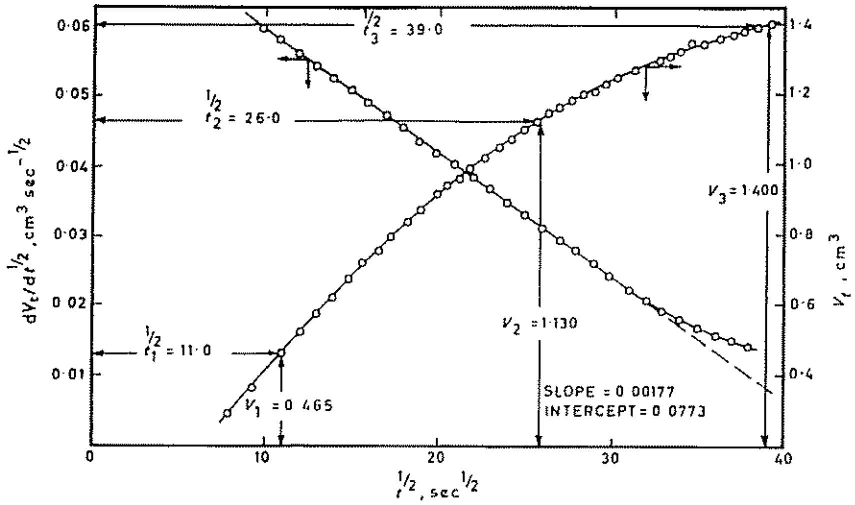

Fig. 1 Plot of experimental data for unsteady state diffusion of gas out of particles. (From Nelson and Walker, 1961.)

Eliminating V_0 and V_e from Eqs. (6), (7), and (8) leads to the equation

$$(f_1V_3 + f_2V_1 + f_3V_2)/(f_1V_2 + f_2V_3 + f_3V_1) = 1 \tag{10}$$

which must be solved for $D^{1/2}/r_0$ by a method of successive approximations. The procedure adopted by Nelson and Walker was to assume values of $D^{1/2}/r_0$ successively and to converge on the required value of $D^{1/2}/r_0$ systematically. The appropriate values of V_e and V_0 were then obtained by backsubstitution. Although a computer was used to perform this reiterative procedure, a satisfactory value of $D^{1/2}/r_0$ can be arrived at by hand calculation after three or four trials. The computer program utilized the complete solution as given by Eq. (4); whereas for hand computation, successive values of f_i were obtained from Fig. 2, which gives Eq. (4) in graphical form.

Nelson and Walker (1961) also considered the case in which the experimental results produced a plot having insufficient curvature to permit application of the method just described. A plot of $dV_t/dt^{1/2}$ versus $t^{1/2}$ can be prepared by measuring release rates at several-minute intervals. The results can be compared with the theoretical requirements of Eq. (5). By differentiating Eq. (5) with respect to $t^{1/2}$, the following relationship is obtained:

$$\frac{dV_t}{dt^{1/2}} = \frac{6D^{1/2}}{r_0}(V_e - V_0)H\left(\frac{D^{1/2}t^{1/2}}{r_0}\right) \tag{11}$$

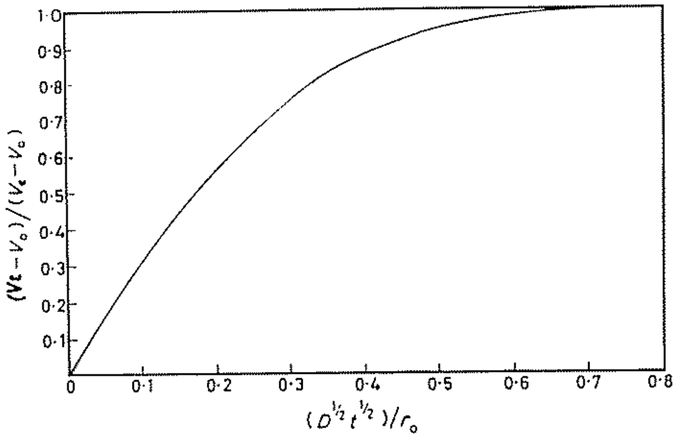

Fig. 2 Solution to Eq. (4). (From Nelson and Walker, 1961.)

$$H\left(\frac{D^{1/2}t^{1/2}}{r_0}\right) = \pi^{-1/2} - \frac{D^{1/2}t^{1/2}}{r_0} + \sum_{1}^{\infty} \frac{2}{\sqrt{\pi}} \exp\left[-\left(\frac{nr_0}{D^{1/2}t^{1/2}}\right)^2\right] \qquad (12)$$

Nelson and Walker (1961) show that terms behind the summation sign in Eq. (12) are insignificant up to 87% completion of the diffusion process. Consequently, for small values of $D^{1/2}t^{1/2}/r_0$, it follows that both $D^{1/2}/r_0$ and $V_e - V_0$ may be obtained from a plot of $dV_t/dt^{1/2}$ versus $t^{1/2}$ by noting S and I, the slope and intercept, respectively, which are related to the required unknowns as follows:

$$D^{1/2}/r_0 = -S/I\pi^{1/2} \qquad (13)$$

$$V_e - V_0 = I\pi^{1/2}/(6D^{1/2}/r_0) \qquad (14)$$

As an example of the use of this technique, reference may be made to Fig. 1 in which a plot of $dV_t/dt^{1/2}$ versus $t^{1/2}$ was prepared by numerical differentiation from the corresponding set of cumulative volume observations. From the slope and intercept of this plot, Eqs. (13) and (14) were used by Nelson and Walker to obtain $D^{1/2}/r_0 = 0.0129\ \text{sec}^{-1/2}$ and $V_e - V_0 = 1.77\ \text{cm}^3$. These values agreed well with the values they obtained by the computational procedure previously described for large values of $D^{1/2}t^{1/2}/r_0$.

B. Unsteady State Diffusion into Ground Material

If unsteady state diffusion into ground material is conducted under conditions in which the pressure outside the particles is held constant during the run, then solutions which have previously been discussed for unsteady state diffusion out of particles, i.e., Eqs. (2), (4), and (5), are operative.

Diffusion of methane into the porous coal or coal product can also be studied under conditions of constant volume but variable external pressure. Barrer (1949) has shown that under these conditions, provided that D is independent of C and the adsorption isotherm obeys Henry's law, the fractional completion of the diffusion process for spherical geometry can be expressed as follows:

$$V_t/V_e = (\zeta + 1)\left\{1 - \frac{1}{\alpha + \beta}\left[\alpha e^{-\alpha^2\tau}(1 + \operatorname{erf} \alpha\tau^{1/2}) - \beta e^{-\beta^2\tau}(1 + \operatorname{erf} \beta\tau^{1/2})\right]\right\} \qquad (15)$$

where V_t and V_e are volumes adsorbed at times $t = t$ and $t = \infty$ expressed at some standard condition; $\zeta = (V_0 - V_e)/V_e$; V_0 is the volume of gas initially present in the gas phase expressed at some standard condition; $\tau = Dt/r_0^2$; α and β are roots of the equation $x^2 - 3x/\zeta - 3/\zeta = 0$; and r_0 is the diffusion path length.

For small enough values of $\tau^{1/2}/\zeta$, i.e., for short times far from equilibrium, Eq. (15) reduces to

$$\frac{V_t}{V_e} = \frac{6}{\pi^{1/2}}\left(\frac{V_0}{V_0 - V_e}\right)\left(\frac{Dt}{r_0^2}\right)^{1/2} \qquad (16)$$

for spherical particles. Therefore, from the initial slope of V_t/V_e versus $t^{1/2}$ plots, the diffusion parameter $D^{1/2}/r_0$ can be calculated.

C. Flow through Solid Disks

At steady state, if flow is by Knudsen diffusion in the gas phase of the porous medium (i.e., where the mean free path of the diffusing species is greater than the diameter of the pore), the rate of flow is given by (Barrer and Barrie, 1952)

$$G = DA\epsilon\, \Delta P/L \qquad (17)$$

where G is the rate of flow (ergs/sec), A the disk area (cm^2), ϵ the fractional open porosity in the disk, ΔP the pressure differential across the disk (dyn/cm^2), L disk thickness (cm), and $D\epsilon$ the Knudsen permeability, K_k (cm^2/sec). For reference, the mean free path of the methane molecule at room temperature and atmospheric pressure is about 500 Å. The mean free path is directly proportional to absolute temperature and inversely proportional to pressure.

It is possible that the diameter of some pores (or cracks) is much larger than the mean free path of the methane molecule. In this case laminar, or Poiseuille, flow can swamp the Knudsen flow, and Eq. (17) will no longer hold. Instead, the rate of flow is given by (Barrer and Grove, 1951)

$$G = K_p A \bar{P}\ \Delta P/L \tag{18}$$

where K_p is the Poiseuille permeability constant (cm^3 sec/g) and $\bar{P}$ is the mean pressure in the disk (dyn/cm^2). All other symbols are as given in Eq. (17). A plot of flow rate versus ΔP under steady state conditions, achieved by varying the inlet pressure to the disk and holding the outlet pressure constant, permits a determination to be made as to whether Poiseuille flow is contributing to total flow. That is, if Poiseuille flow is absent, the G versus ΔP plot will be linear. Thimons and Kissell (1973) demonstrate the principle of this approach.

Theoretically, K_k is expected to be inversely proportional to the square root of the gas molecular weight. As is discussed later, deviations from this proportionality are found when flow through disks of coal is studied, even though G versus ΔP plots are linear. Such deviations can be brought about by contributions from surface flow of adsorbed gas molecules and activated diffusion in pores of molecular dimensions.

Invariably flow through a disk of coal does not immediately reach a steady state condition. There will be a lag time. This is expected for a solid that contains blind pores and a broad distribution of pore sizes. The larger pores will, for the most part, determine the steady state flux through the material. On the other hand, the fine pores and blind pores will delay the establishment of steady state flow until they receive their quota of molecules (Barrer and Strachan, 1955; Barrer and Gabor, 1959). As shown by Thimons and Kissell (1973), lag time can be determined from a plot of pressure buildup as a result of flow out of the disk versus time, where ΔP changes little. Extrapolation of the straight line portion of the plot, i.e., where steady state conditions have been achieved, to the abscissa gives the lag time.

III. EXPERIMENTAL METHODS TO MEASURE MOLECULAR FLOW IN COAL AND COAL PRODUCTS

A. Unsteady State Diffusion in Ground Material

1. *Measurements Close to Atmospheric Pressure*

At temperatures above approximately 300°C, difficulties are encountered in measuring rates of unsteady state flow. The total volume of gas which can be loaded into the open pore structure of a given sample is small when thermal conditions are unfavorable to adsorption. Further, the problem of temperature control frequently cannot be conveniently overcome by the use of a thermostatically controlled bath. For a system which includes a furnace operating at a high temperature, some other means of avoiding errors due to temperature fluctuations must be sought. To overcome these difficulties, a differential experimental system was selected by Nelson and Walker (1961), as shown in Fig. 3. In principle, the procedure consisted of charging the sample under investigation up to some pressure in excess of atmospheric and then measuring the unsteady state release of gas after sudden reduction of the pressure back to atmospheric.

With the exception of the volumeter, which had a capacity of 1.5 cm^3, the main section of the apparatus was constructed as symmetrically as possible. Two quartz sample tubes were used, each connected to the remainder of the apparatus by ball-and-socket joints sealed with high vacuum wax. Each sample tube contained equal weights (~20 g) of identical samples.

The micromanometer employed was of the type described previously

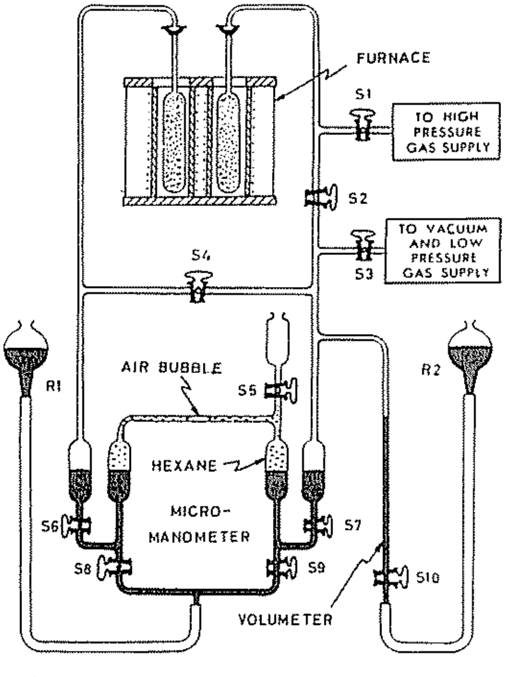

Fig. 3 Apparatus for measuring unsteady state diffusion of gases in coals and chars close to atmospheric pressure. (From Nelson and Walker, 1961.)

(Nelson, 1956). The measurement is based on the movement of a bubble of air trapped in a small-bore capillary tube connecting two U-tube reservoirs containing a low boiling, intermediate fluid, and mercury. Since the reference pressure side of the manometer was exposed to the same unsteady temperatures as the measuring side, it was possible to detect very small rates of gas outflow, even in the presence of furnace temperature and room temperature fluctuations.

After the quartz tubes had been filled with samples and sealed to the apparatus, with taps S6 and S7 closed, the system was evacuated to remove adsorbed species from the pores of the sample.† Following outgassing, the sample tube on the right side of Fig. 3 was then exposed to the desired gas at a known pressure somewhat in excess of atmospheric (up to about 1.5 atm) through S1. The remainder of the apparatus was exposed to the same gas at atmospheric pressure through tap S3. Adequate time was then allowed for the system to attain substantially complete equilibrium.

At the start of each run, the pressure was reduced quickly to atmospheric in the right-hand tube. Then taps S3 and S4 were closed; S6, S7, and S10 were opened; and the reservoir R2 was lowered to displace the air bubble in the micromanometer from its equilibrium position. The time and volumeter readings were then noted when the bubble regained its equilibrium position, as determined by the crosswires of a cathetometer through which the position of the bubble was observed. This process was repeated throughout the run. Nelson (1960) reported that diffusion parameters on duplicate runs, measured up to 300°C, agreed within ±1%.

For unsteady state diffusion of methane into particles under constant inlet pressure, two experimental approaches can be conveniently used to measure uptake as a function of time. In one, increase in sample weight can be measured continually, using a microbalance. In the

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† For molecular sieve materials such as coals and chars, the outgassing conditions selected have a profound effect on the subsequent diffusion rates which are measured. This is so because even a monolayer of adsorbed species markedly changes the effective size of pores when they are of molecular dimensions. All coals contain some chemisorbed oxygen and water which is hydrogen bonded to functional groups on the coal. Selection of an outgassing temperature greater than about 150°C is considered unwise since it can lead to some dissociation of functional groups on the coal, particularly carboxyl groups. However, outgassing at temperatures below 150°C is expected to remove neither all the chemisorbed oxygen (as CO and CO_2) nor water. Thus the outgassing temperature (and time) selected will have an effect on diffusion results. It is of utmost importance that this fact be appreciated when attempting to relate diffusion results to particular applications. Normally, outgassing of coals prior to a diffusion measurement is conducted at 130–150°C for 12–24 hr. Outgassing of chars can be conducted at a temperature close to that which they have previously seen without producing any change in their basic pore structure.

other, the volume of gas diffusing into the particles can be measured using an apparatus similar to that described in Fig. 3.

2. *Measurements at Elevated Pressures*

Nandi and Walker (1970, 1975) describe apparatus which they used to measure methane flow in coals and chars at elevated pressures. Figure 4 shows a schematic of the apparatus. The material of construction above the dashed line was stainless steel and that below was made of Pyrex glass. It had three valves V_1, V_2, and V_3 (Aminco high pressure) connected by capillary tubing through the intermediary of an Aminco super pressure cross. A precision pressure gauge (Heise Bourdon Tube Company Model C-61364) graduated to 1 psi was connected to the remaining end of the cross.

The sample (about 2–3 g of powder) was held in the sample container of about 5 cm^3 capacity connected to valve V_1. A cold trap was connected to valve V_3, the other end of the trap being closed by a fourth valve V_4. The apparatus could be evacuated through valve V_2 to a residual pressure of 10^{-5} torr, using a mercury diffusion pump backed by a high vacuum mechanical pump.

The stainless steel section of the apparatus was connected to a Pyrex

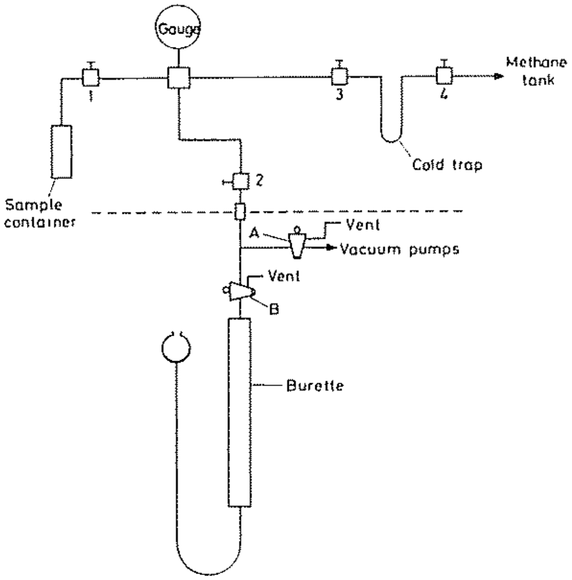

Fig. 4 Apparatus for measuring unsteady state diffusion of gases in coals and chars at elevated pressures. [From Nandi and Walker, *Fuel* 54, 81 (1975) by permission of the publishers, IPC Business Press, Ltd.]

glass burette and vacuum line through an Apiezon wax seal. Through a T-piece and a three-way high vacuum stopcock (A), the adsorption system could be connected either to the vacuum pumps or to atmosphere. Methane was bled into the cold trap directly from a tank through valve V_4. After thoroughly purging the system, the cold trap was cooled with liquid nitrogen to freeze a suitable quantity of methane in the coil. The desired pressure of methane was generated in the adsorption apparatus by evaporating an appropriate quantity of gas from the cold trap.

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 container. 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, and noting the volume discharged as a function of pressure. Then, the entire adsorption system including the sample container (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 container immersed up to a fixed level in the constant-temperature bath during calibration, as well as during diffusion runs. During diffusion 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.

Before starting a run to measure the diffusion of methane out of the ground sample, it was outgassed at 130–150°C. Methane was then adsorbed onto the sample at the desired pressure until no further adsorption was detectable. Adsorption times at room temperature between 24 and 48 hr were found sufficient, the time depending on the particle size studied. The following procedure was used for a diffusion run. The mercury level in the burette was first brought to a certain mark and the burette was connected to the atmosphere by opening stopcocks B and A suitably. After adsorption equilibrium was achieved, valve V_2 was opened very quickly and methane was allowed to escape through stopcock A. Simultaneously, 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 sec for the pressure in the system to decrease to atmospheric at the highest equilibrium pressure used, i.e., about 425 psi. While desorption of methane was followed, the pressure in the system was kept constant at atmospheric by changing the mercury level in the burette. 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 1 atm. This value was denoted as V_e. The value of V_0 was determined by extrapolating the linear V_t versus $t^{1/2}$ plot to $t = 0$.

The same apparatus was used to study the diffusion of methane into ground coals and chars (Patel *et al.*, 1972). Diffusion took place under conditions of constant volume but variable pressure in the apparatus. Following outgassing of the sample, valve V_1 was closed and a known pressure of gas was taken into the volume between valves V_1, V_2, and V_3. Valve V_1 was quickly opened and the timer started. Pressure readings were followed as a function of time. The relation between the volume of gas at standard conditions and pressure was known from previous calibrations so that V_t versus t data were obtained.

Using the elevated pressure apparatus, diffusion parameters on duplicate runs, measured up to 70°C, agreed within ±2%.

B. Flow through Solid Disks

Thimons and Kissell (1973) describe the apparatus and procedure used to measure methane flow through disks of coal. Lumps of coal taken from the mine were cored without any further treatment, and the cores were sliced into disks averaging 3.6 mm in thickness and 5.8 mm in diameter. The disks were polished and examined under an optical microscope. Those with evident fractures were discarded. Samples without visible fractures were mounted in a stainless steel disk which had a hole in the center just large enough to accommodate the sample. A thermoepoxy adhesive was found to provide the best bond.

Figure 5 is a schematic diagram of the apparatus used by Thimons and Kissell to measure permeability. Five identical units were constructed because testing a single sample could take several months. The testing sequence was as follows. The steel disk containing the sample was mounted in the system and the entire system was evacuated at room temperature for 1 week. After a week, valves 1 and 2 were closed. The part of the system to the left of the sample remained evacuated, while dry methane at the desired pressure was introduced on the right side to create a pressure differential across the sample. The gas flow rate across the sample was obtained by measuring the pressure buildup on the left side, as indicated by a thermocouple vacuum gauge. The pressure on the left side was kept below 0.05 torr by periodically opening valve 1 and reevacuating. The pressure on the left side of the system was thus so low that this side was assumed to be a vacuum with respect to the right side of the system when the pressure differential across the

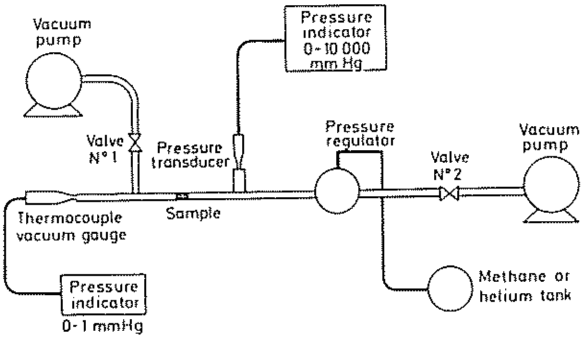

Fig. 5 Apparatus for measuring flow of gases through disks of coal. (From Thimons and Kissell, 1973.)

sample was calculated. The flow of gas across the sample was recorded until it became steady.

After this, the gas pressure was boosted by increments and measurements were taken until a new level of steady flow was reached. This was repeated until the pressure differential was about 3 atm. Frequently, an entire sequence was repeated, beginning with the evacuation, to test sample reproducibility, which Thimons and Kissell found was within 10% for measurements conducted at room temperature.

IV. SELECTED EXPERIMENTAL RESULTS

A. Unsteady State Diffusion in Ground Coals and Chars

1. *Deviation from Ideal Diffusion Behavior*

There are a number of reasons why unsteady state diffusion in coals and chars deviates from the ideal process considered in Section II. Some of the reasons are inherent in the process of molecular diffusion in all porous solids; other reasons are directly related to the nature of ground coals and chars. These reasons should be considered briefly, and future workers are advised to keep them in mind when conducting experiments on unsteady state diffusion of molecules in coals and chars.

a. Nonisothermal Conditions When molecules diffuse into a solid, physical adsorption occurs, the extent depending on the surface area of the solid, the adsorbate, its temperature, and its pressure. Adsorption is an exothermic process, heat is generated, and the temperature rises. When molecules diffuse out of a solid, desorption occurs. This is an endothermic process, heat is consumed, and the temperature decreases.

The amount of temperature change depends on the thermal conductivity of the solid and the transfer coefficient for convective heat transfer to or from the particle surface. Eagan *et al.* (1971) consider temperature effects during diffusion of nitrogen and propane into zeolites. They estimate that transient temperatures within the solid can rise as much as 50°C above the temperature of the surroundings. They conclude that when the temperature maximum occurs early in the process, no pronounced effect on the shape of the rate curve (i.e., fractional approach to equilibrium versus $t^{1/2}$) occurs; the unwary experimenter may conclude that his data were obtained isothermally. In fact, the diffusion parameter calculated from the early part of the rate curve for nitrogen diffusing into the zeolite was shown to be about 50% too high. Eagan and Anderson (1975) suggest that calculations should be made on the rate curve generated later in the process, when the rate of diffusion (and sorption) has decreased, and hence the magnitude of the temperature transients is less. This suggests that the use of Eq. (4), applicable to moderate or extensive completion of the unsteady state diffusion process, is desirable.

The authors are not aware that consideration has been given by workers to the possibility that nonisothermal conditions may have affected their calculated diffusion parameters for flow of methane in coal. In principle, one way to check the magnitude of this effect would be to compare diffusion parameters determined from experiments measuring unsteady state flow of methane both into and out of ground samples.

b. Dependence of Diffusion Parameter on Concentration A number of workers have reported diffusion coefficients that increase with increasing concentration of the diffusing species. The Fick's second law solution, i.e., Eq. (1), was derived for the case of D independent of C. The dependence of D on C is usually found to coincide with an adsorption isotherm that is not linear. Another factor that may contribute to the concentration dependence of diffusivity is change of volume of the solid with increasing uptake of the adsorbate. This latter factor could be important in the case of coal, since organics are known to be imbibed into the solid (Franklin, 1949). This point is considered again presently.

c. Variation of Pore Size and Particle Size The unsteady state diffusion equations presented in Section II have been solved for an ideal collection of particles, i.e., particles of one size having pores or apertures–cavities of a fixed size. Coals and chars satisfy neither of these requirements. A ground material always has a particle size distribution, regardless of the narrowness of cut between sieve sizes taken for study. Further, as is discussed shortly, grinding of coal appears to introduce macropores (cracks) into the particles; the concentration of cracks increases as the severity of grinding increases. Hence, the possibility of determining a particle size distribution and making allowance for this distribution when calculating diffusion coefficients, as was done by Eagan and Anderson (1975) for single-crystal particles of zeolite, does not exist for coals and chars.

Coals and chars do not have single-pore, aperture, or cavity sizes through which molecular diffusion occurs. Gan *et al.* (1972) showed that many coals have trimodal distributions of pore sizes, and called them macropores, transitional pores, and micropores. In unsteady state diffusion, it may be found that equilibrium is reached rapidly in the macropores and transitional pores and that one is then measuring, as a function of time, approach to equilibrium in the micropores. Even in this case, an average effect is being measured, since there is a distribution in aperture size and distance between apertures in this aperture–cavity system. Indeed, there are cases in which sequential unsteady state diffusion from more than one pore system has been observed for coal. It is best seen by plotting $dV_t/dt^{1/2}$ versus $t^{1/2}$ and observing two linear regions in the plots. At short times, diffusion in the larger pore system dominates; at longer times, diffusion in the smaller pore system dominates. Unsteady state diffusion in two pore systems has been observed by Anderson *et al.* (1965) for methane in a medium volatile bituminous coal and by Nelson (1960) for ethane and propane in an anthracite.

2. *Methane Diffusion in Coals*

Considering the purpose of this chapter, this section is not meant to be an exhaustive review of studies on methane diffusion in coals. Rather, some studies have been selected which assist in pointing out certain principles.

Zwietering *et al.* (1956) studied sorption of methane into an anthracite. Over the temperature range 134–157 K and a constant methane pressure of 267 torr, diffusion was found to be activated, with an activation energy of 3.9 kcal/mole. Instead of estimating the value of r_0 from the area and volume of a spherical particle, i.e., using Eq. (3), these authors assumed the area was that calculated from nitrogen adsorption at 77 K and the volume was that given from helium and mercury density measurements. Using Eq. (2), they calculated a D at 293 K of 1×10^{-12} cm^2/sec.

Joy (1958) made unsteady state diffusion measurements of methane into ground anthracite (72–85 mesh BSS) at temperatures between 195 and 303 K and pressures up to about 400 torr. He used the same high rank coal as studied by Zwietering *et al.* (1956). From isotherm data, the heat of adsorption of methane was calculated to be 4.8 kcal/mole. From the initial slope of V_t/V_e versus $t^{1/2}$ plots, diffusion coefficients were calculated, assuming r_0 to be the particle radius. At 303 K, D equaled 3.9×10^{-12} cm^2/sec. Diffusion was activated, having an activation energy of about 4.3 kcal/mole.

Walker *et al.* (1966a) showed that the interpretation of the meaning of the activation energy calculated for diffusion in porous solids from Arrhenius plots must be guided by the nature of the diffusion process. There are two models of importance for diffusion in porous solids: the occluded gas model and the adsorption-free gas model. In the occluded gas model, the rate of diffusion is proportional to $\partial C/\partial x$, C being the concentration of occluded gas and x the distance in the diffusing direction. In the adsorption-free gas model, gas diffuses via "free" molecules, with gas adsorbed on the walls of the pores acting as a reservoir which replenishes the free gas space. The rate of diffusion is proportional to $\partial C_f/\partial x$, where C_f is the concentration of free gas.

The relation between C_f and the total gas concentration C is

$$C = C_f\epsilon + f(C_f) \tag{19}$$

where ϵ is the open porosity within the particles of the solid which is filled with gas of concentration C_f and $f(C_f)$ is the adsorption isotherm. If C_s is the amount of adsorbed gas at saturation and if the Langmuir isotherm for nondissociative adsorption applies, then

$$C = C_f\epsilon + [KC_f/(1 + KC_f)]C_s \tag{20}$$

where K is the equilibrium constant of adsorption. At relatively low pressures and high temperatures, KC_f will be small; the Langmuir isotherm reduces to a Henry's law form (amount adsorbed proportional to pressure) and

$$C_f = C/(\epsilon + KC_s) \tag{21}$$

It is then readily shown that the effective diffusion coefficient $\bar{D}$ is given by

$$\bar{D} = D/(\epsilon + KC_s) \tag{22}$$

where D is the true diffusion coefficient (independent of pressure). For activated diffusion $D = D_0 \exp(-\Delta H_0^{\ddagger}/RT)$, where $\Delta H_0^{\ddagger}$ is the enthalpy of activation (or activation energy) and D_0 the preexponential rate factor. The equilibrium constant K can be put as $K = K_0 \exp(-\Delta H_0/RT)$, where ΔH_0 is the enthalpy of adsorption.

The overall temperature dependence of the apparent diffusion coefficient for the adsorption-free gas model is

$$\bar{D} = \frac{D_0 \exp(-\Delta H_0^{\ddagger}/RT)}{\epsilon + C_s K_0 \exp(-\Delta H_0/RT)} \tag{23}$$

At low temperatures and high pressures where the quantity of adsorbed gas is high relative to the amount of free gas, ϵ can be neglected, giving

$$\bar{D} = (D_0/C_s K_0) \exp[-(\Delta H_0^{\ddagger} - \Delta H_0)/RT] \tag{24}$$

At higher temperatures where the quantity of adsorbed gas is small,

$$\bar{D} = (D_0/\epsilon) \exp(-\Delta H_0^{\ddagger}/RT) \tag{25}$$

For the occluded gas model, the true diffusion constant is obtained and

$$D = D_0 \exp(-\Delta H_0^{\ddagger}/RT) \tag{26}$$

applies under all conditions.

It is clear that in any investigation of activated diffusion it is necessary to determine which model applies before a precise meaning can be assigned to the overall energy of diffusion. Walker *et al.* (1966a) indicate that there are several guides which can be used, including the following:

(i) When making measurements over a temperature range, it is possible that Eq. (24) will hold at lower temperatures and Eq. (25) will hold at higher temperatures. Thus the Arrhenius plot of log $\bar{D}$ versus $1/T$ will not give a straight line.

(ii) For Eq. (24) to apply, it is necessary for a van't Hoff plot of $\log(V_e - V_0)$ versus $1/T$ to be a straight line, where $V_e - V_0$ is the quantity of gas adsorbed or desorbed at equilibrium for a given pressure differential.

(iii) For Eq. (24) to apply, it is necessary for the amount of adsorbed gas to be greater than the amount of free gas in the pores. At the same time, the rate of diffusion is assumed to be controlled by the passage of free gas molecules over an activation energy barrier. If molecules can pass directly over the activation energy barrier from their adsorbed position, then the occluded gas model applies. (This is activated surface diffusion with the rate-controlling energy barrier occurring at certain positions in the surface geometry and not between every adsorption position. For example, adsorbed molecules may be able to move freely over the surface of the cavities in the coal but not freely through the holes connecting the cavities.)

Unfortunately, for most diffusion studies on coal, insufficient information has been made available to choose between the occluded gas model and the adsorption-free gas model. For the studies of Joy (1958) and Zwietering *et al.* (1956), linear Arrhenius plots and curved van't Hoff plots were found, suggesting that the occluded gas model is applicable. In these cases, it appears that the activation energies reported are the true activation energies for methane diffusion.

Walker *et al.* (1966b) consider, theoretically, the diffusion of rare gases between the basal planes of graphite. These workers show that activated diffusion begins when the distance between basal planes falls below approximately the sum of the kinetic diameter of the diffusing species and 1.6 Å. Density measurements on coals—for example the benzene densities are higher than the *n*-hexane densities (Franklin, 1949)—suggest that the apertures in coal are slit-shaped. If one further speculates that the slit-shaped apertures are formed by the approach of the planar building blocks in coals and chars and that these building blocks can be approximated by the basal planes of graphite, then estimates can be made as to what distance of their approach would result in activated diffusion of methane. Since methane has a kinetic diameter of 3.8 Å, this slit thickness is estimated to be 5.4 Å. Considering that the repulsive potential varies inversely with the twelfth power of distance, according to the Lennard-Jones potential, small decreases in slit thickness below 5.4 Å will produce very large increases in the activation energy for methane diffusion—so large, in fact, that activated diffusion of methane can only be measured experimentally for a narrow range of aperture sizes. That is, the activation energy quickly becomes so large and *D* so small that it is not practical, in the laboratory, to make measurements.

Nandi and Walker (1970) studied methane diffusion from coals of different rank and for several anthracites of different particle size. Methane was first adsorbed onto the particles at a pressure of about 1.6 atm and at temperatures ranging from 60 to 227°C prior to making desorption runs. As the particle size of two anthracites was decreased from 42 × 65 to 100 × 150 mesh, the activation energy for diffusion decreased from 5.4 to 4.4 kcal/mole in one case, and from 4.8 to 3.9 kcal/mole in the other case. The reason for this effect is not understood. For six anthracites of 100 × 150-mesh particle size, the activation energy for diffusion increased from 3.5 to 5.2 kcal/mole as their volatile matter content increased from 4.2 to 9.0%. For six bituminous coals, ranging in volatile matter content from 19.7 to 40.5%, the activation energy for methane diffusion showed no trend. However, values were significantly higher than for the anthracites, ranging from 6.5 to 7.6 kcal/mole. Nandi and Walker (1966) previously reported that activation energies were higher for diffusion of argon from bituminous coals than from anthracites.

Nandi and Walker (1975) further looked at methane diffusion from three coals of varying rank at temperatures between 0 and 50°C and loading pressures between 3 and 28 atm. The three coals were a medium volatile bituminous coal (PSOC-135), a HVA bituminous coal (PSOC-171), and an anthracite (PSOC-177). Adsorption isotherms for the three coals are given in Fig. 6. With decreasing rank, the isotherms became more linear. Figures 7 and 8 show desorption rate plots for two of the coals at 25°C. For the anthracite, slopes of the plots increased with increasing initial methane loading pressure. For the HVA coal, the slope was independent of methane charging pressure. Figure 9 shows that the diffusion parameters for the anthracite and medium volatile bituminous coal increased linearly with increasing methane concentration in the coal. As discussed earlier, various reasons have been given for diffusion coefficients being a function of concentration. One suggestion is that coal monotonically expands as adsorption increases. However, Nandi and Walker (1975) concluded that this explanation did not hold for this study, since Moffat and Weale (1955) find that anthracite expands less on adsorption than do bituminous coals. In the study of Nandi and Walker, the extent of concentration dependence paralleled the extent to which the adsorption isotherms deviated from linearity.

Nandi and Walker (1975) showed the possible effect of working at elevated pressures on the activation energy calculated for methane diffusion. For the anthracite sample, where adsorption was very high, the activation energy was 8.4 kcal/mole. For the HVA coal, where adsorption

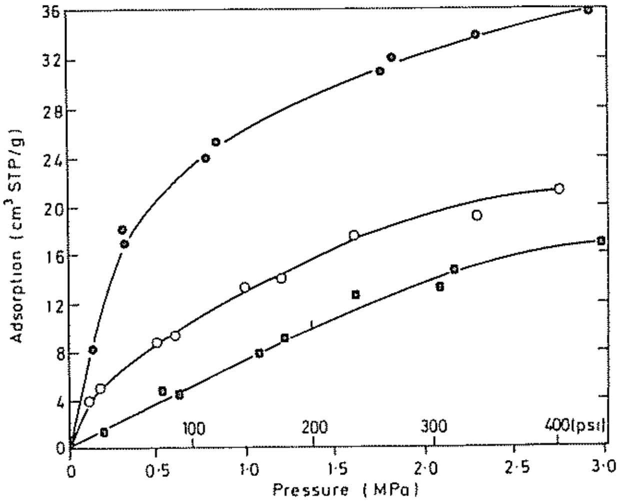

Fig. 6 Adsorption isotherms of methane on 40 × 70-mesh coals at 25°C. ◉, PSOC-177; ○, PSOC-135; ▣, PSOC-171. [From Nandi and Walker, *Fuel* 54, 81 (1975) by permission of the publisher, IPC Business Press, Ltd.]

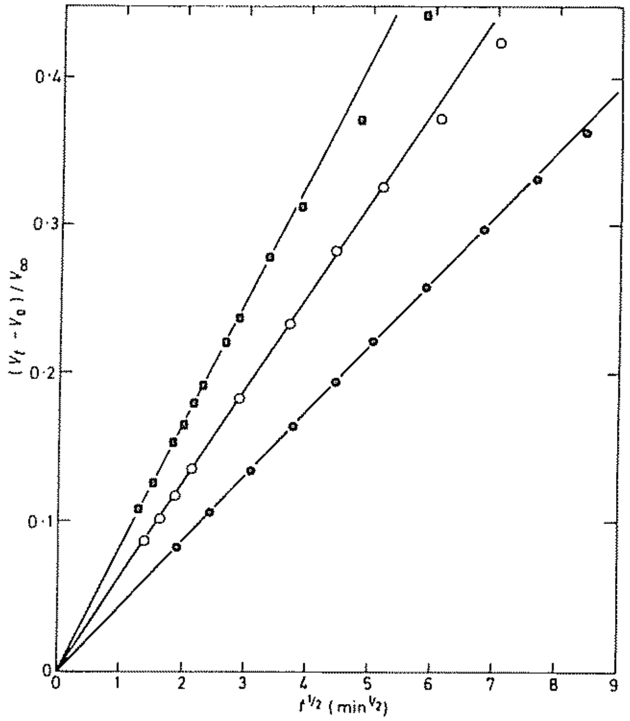

Fig. 7 Plots for unsteady state diffusion of methane from 40 × 70-mesh coal PSOC-177 at 25°C for different initial methane pressures: ●, 45 psi; ○, 109 psi; ▨, 245 psi. [From Nandi and Walker, *Fuel* **54**, 81 (1975) by permission of the publishers, IPC Business Press, Ltd.]

was reasonably small, the activation energy was 6.3 kcal/mole. It is recalled that Nandi and Walker (1970) found, from methane diffusion at low pressures, that the activation energy for diffusion from anthracites was less than that for diffusion from bituminous coals. It was suggested that the reported activation energy of 8.4 kcal/mole, in fact, consisted of the true activation energy $\Delta H_0 \ddagger$ plus the enthalpy of adsorption ΔH_0, as given in Eq. (24). If a value of 4.8 kcal/mole is taken for ΔH_0 (Joy, 1958), the true activation energy for methane diffusion in the anthracite will be 3.6 kcal/mole. This value is consistent with that found by Joy (1958), Zwietering *et al.* (1956), and Nandi and Walker (1970) for methane diffusion in anthracites at low (about atmospheric) pressures.

Nandi and Walker (1975) also studied the effect of particle size on diffusion parameters. They found that the parameter doubled with decreasing particle size between 4 × 5 and 40 × 70 mesh. But if r_0 was taken as the average particle radius in a sieve fraction, the diffusion

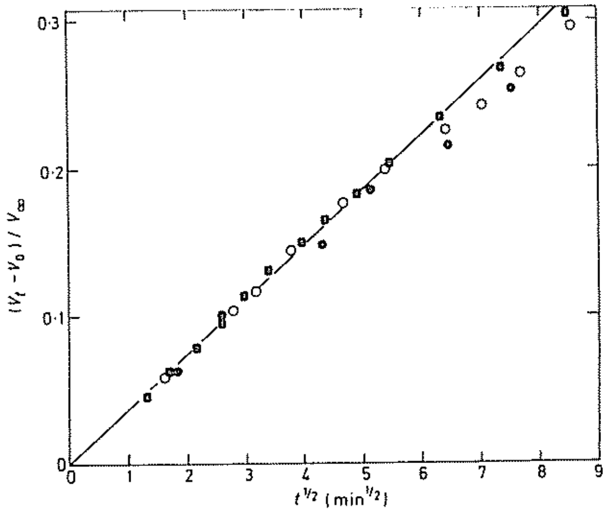

Fig. 8 Plot for unsteady state diffusion of methane from 40 × 70-mesh coal PSOC-171 at 25°C for different initial methane pressures: ◉, 78 psi; ○, 148 psi; ▣, 293 psi. [From Nandi and Walker, *Fuel* 54, 81 (1975) by permission of the publishers, IPC Business Press, Ltd.]

coefficients decreased 50 times with decreasing particle size. Clearly, the diffusion distance does not decrease as rapidly as particle radius, but r_0 does decrease somewhat with decreasing particle size in the range studied. Nandi and Walker (1975) suggested that this reduction in r_0 is caused by an increasing production of more closely spaced cracks as coal is ground more finely in particle size.

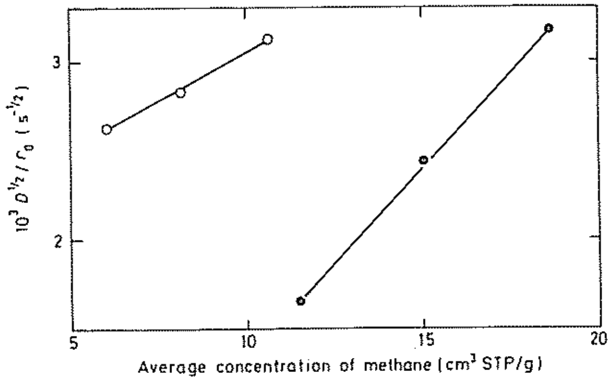

Fig. 9 Effect of average methane concentration during unsteady flow out of 40 × 70-mesh coals—◉, PSOC-177 and ○, PSOC-135—on diffusion parameter. [From Nandi and Walker, *Fuel* 54, 81 (1975) by permission of the publishers, IPC Business Press, Ltd.]

Taking r_0 equal to the particle radius does give an upper limit for the diffusion coefficient. Nandi and Walker (1975) found D for the 40 × 70-mesh size fractions of the three coals to vary from 5 to 25 × 10^{-10} cm^2/sec at 25°C.

3. *Methane Diffusion in Chars*

When thermosetting coals (those that soften little or none) are heated in an inert atmosphere, there are two major occurrences. First, volatile matter is released, resulting in further opening of the pore structure and making molecular diffusion in the particles more rapid. Second, at a higher temperature some of the cross-links between the planar regions in coal are broken and these planar regions grow in size and improve in their alignment. This results in a decrease in the average aperture size in the solid, a decrease in the rate of molecular diffusion in the particles, and an increase in activation energy for diffusion. Thus chars act, more or less, as molecular sieve materials to methane diffusion. The behavior depends on the starting coal and the heat treatment conditions to which it is exposed.

The fact that coal chars are molecular sieve materials means that small amounts of carbon burn-off (gasification) can markedly change the diffusion rates of molecules within char particles. This was shown most graphically by Patel *et al.* (1972). They first converted a 42 × 65-mesh

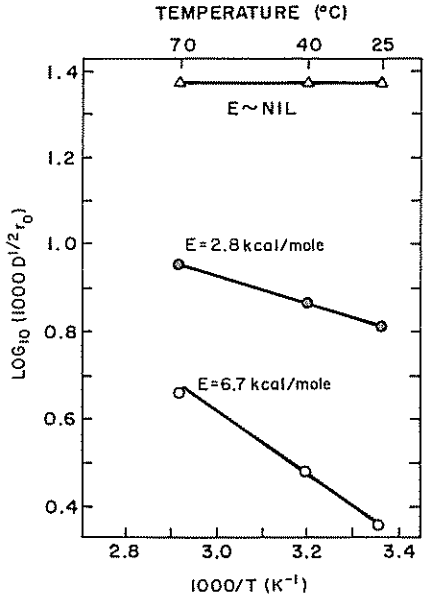

Fig. 10 Diffusion parameters for methane flow into 42 × 65-mesh calcined anthracite as a function of diffusion temperature and anthracite burn-off: ○, 6.9%; ◉, 8.0%; △, 9.1%. [From Patel *et al.*, *Fuel* **51**, 47 (1972) by permission of the publishers, IPC Business Press, Ltd.]

fraction of anthracite to a char by heating in nitrogen to 950°C. They then gasified the char in air at 425°C to various levels of burn-off, prior to measuring methane diffusion into the particles between 25 and 70°C. Figure 10 shows the dramatic effect of increasing carbon burn-off from only 6.9 to 9.1%. At 6.9% burn-off, methane diffusion is strongly activated. Burn-off to 8.0% decreases the activation energy for diffusion, and burn-off to 9.1% converts methane transport in the char to Knudsen diffusion with its weak $T^{0.5}$ dependence on temperature. Results of this type must be made available and taken into account if the mathematical modeling of gasification processes is to be successful.

Recently Kamishita (1976) has shown that the process opposite to gasification, i.e., carbon deposition, also has a pronounced effect on methane diffusion rates in chars. Methane diffusion in a lignite char produced at 855°C was found to be nonactivated. However, the deposition of 2.6% by weight carbon into the pores of this char, by the cracking of methane at 855°C, resulted in subsequent methane diffusion being activated (4.7 kcal/mole). Even though the total open porosity in the original lignite char was 35.6%, deposition of enough carbon to fill only a small fraction of that total pore volume produced a dramatic change in the nature of the diffusion process. This is consistent with coal chars also being aperture–cavity materials. Small additions of carbon to the aperture radically change rates of molecular transport in the char, even though the cavity size has undergone an insignificant fractional decrease in size.

B. Flow through Solid Disks

Sevenster (1959) studied methane flow through a disk of bituminous coal at average pressures close to atmospheric. He reported a permeability at room temperature of about 10^{-11} cm²/sec. This low value indicates that the rate-controlling process was transport through apertures of molecular dimensions.

Karn *et al.* (1970) studied the flow of methane and helium through disks of high volatile A bituminous coal at inlet pressures of from 20 to 760 torr and outlet pressures close to zero. Samples were cut parallel and perpendicular to bedding planes in the coal seam. Room temperature permeabilities found along the bedding plane were 873×10^{-10} cm²/sec for helium and 1.2×10^{-10} cm²/sec for methane—or a ratio of 800. Permeabilities across the bedding plane were about half these values, with the ratio of helium to methane remaining the same. If flow were solely by Knudsen diffusion, the ratio of the helium to the methane permeabilities would be given by the square root of the ratio of their molecular weights or equal to 2. From the high ratio found, the authors concluded that molecular sieving of methane was occurring. This was supported by an activation energy for methane diffusion of 13.6 kcal/mole, either along or across the bedding plane, calculated from flow measurements made from room temperature to 100°C. This activation energy is significantly higher than any value reported from measurements on the unsteady state diffusion of methane from ground coals.

Thimons and Kissell (1973) studied flow of methane and helium through disks of three bituminous coals at room temperature and inlet pressures ranging from 515 to 2060 torr. By measuring flow rate versus pressure differential and confirming that the plots were linear, these authors confirmed that no Poiseuille flow through cracks was taking place. Again the ratios of helium to methane permeabilities were greater than 2—ranging from about 100 for Pittsburgh seam coal to only 3–4 for Pocahontas and Hartshorne coals. Methane permeabilities were much higher than those found by Sevenster (1959) or Karn *et al.* (1970), ranging from about 10^{-6} cm^2/sec for the Pittsburgh seam coal to 2×10^{-5} cm^2/sec for the other two coals. When coverted to diffusion coefficients, the values ranged from about 5×10^{-5} cm^2/sec for the Pittsburgh seam coal to 2×10^{-4} cm^2/sec for the other two coals. The authors found that permeabilities for methane saturated with water were markedly reduced—in some cases to a tenth of those found in dry methane.

Thimons and Kissell (1973) compare the permeabilities measured on disks of coal in the laboratory with those determined in seams of the same coals. Permeabilities for the seams ranged from 8.3 cm^2/sec for the Pittsburgh coal to 0.5 cm^2/sec for the Hartshorne coal. Not only were the permeabilities of methane in the seams much larger than values found in the laboratory but their order was reversed. The authors conclude that flow in coal beds primarily takes place through cracks, whereas the flow in disks is primarily through the pore structure.

Thimons and Kissell (1973) measured lag times to reach steady state flow of methane across disks 3.6 mm thick. Lag times ranged from about 10^6 sec for the Pittsburgh seam coal to 5×10^3 sec for the Pocahontas and Hartshorne coals. Clearly the Pittsburgh seam coal contained a higher percentage of blind pores.

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