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ONDERWERP:
SUBJECT:_____ DIFFUSION OF GASES THROUGH COAL.

AFDELING:
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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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DIFFUSION OF GASES THROUGH COAL.

It is generally realised that the rate of heterogeneous reactions, especially where a porous solid is involved, is very largely if not wholly determined by the rate of diffusion of gaseous reactants to, or of gaseous products from the solid surface.

This applies also to the oxidation of coal irrespective of whether the reaction takes place at ambient temperature (spontaneous heating) or at elevated temperatures (combustion).

It is somewhat surprising, therefore, that, although much fundamental work has been done on spontaneous heating and combustion and work on the porous structure of coal was done in this connection, very little work seems to have been done to establish diffusion coefficients of gases in coal directly.

Reference can only be made to the work of Graham[1] who studied the diffusion of gases in solid slabs of coal. Unfortunately he used gases saturated with water vapour and this makes it very difficult to analyse and interpret his results. His measurements suggest, however, that coal is almost impervious to gases.

Mertin[2] calculated average pore diameters from measurements of the flow rate of hydrogen through solid coal discs. He also found that gases permeate extremely slowly through the mass of the coal substances. Reference may also be made to the studies of Zwietering and others[3] and Joy[4] who calculated a

diffusion coefficient for methane from rate of adsorption data.

Because of this paucity of publications on the subject, it was found necessary to conduct the investigation described in this paper when information on diffusion coefficients of some strongly adsorbed gases was required in the course of other studies on coal at the Institute.

Two methods of approach appeared feasible:

(A) The calculation of diffusion coefficients from the results obtained in adsorption kinetics studies that had already been done at the Institute and,

(B) Direct quantitative measurements of the flow of gases through coal.

The former approach would yield results more rapidly but the latter would have the advantage that the diffusion of gases that are only silghtly adsorbed could also be studied. Furthermore, it could be used to obtain some check on the reliability of the former method.

Coals Used in the Investigation.

The coals used in this investigation may be characterised by typical proximate analyses and data on physical structure applying to the samples actually used as shown in Table 1. Adsorption rate data for coals A, B and C were available from earlier studies[5] and coals B, C and D were used for flow measurements. The porosities and surface areas of these coals had also been determined.[6]

TABLE 1.

Analytical Data on Coals used in the Investigation.

Coal Sample	% Ash	Air-dried Moisture.	He Density.	Porosity[a] cc/gm.	Int.S.Area[b] m^2/gm.
A	24.2	7.5	1.36	0.176	181
D	18.3	5.6	1.36	0.146	161
B	21.8	2.8	1.35	0.121	110
C	13.1	1.8	1.33	0.085	85

a)   Calculated from helium and mercury densities.

b)   Calculated from heat of wetting measurements.[x]

A.   The calculation of Diffusion Coefficients from the Results of Adsorption Kinetics Studies.

The experimental results available for these calculations were confined to those obtained in the study of the adsorption of oxygen and water vapour[8] on coals of varying rank.

Considering the various possibilities of approach, that of Ward[9] appeared to merit close consideration.   Ward had analysed the results of rate of adsorption experiments (hydrogen on copper-oxide) by means of Fick's diffusion law and found that the quantity of gas adsorbed was proportional to the square root of the time.   Barrer[10] applied Ward's findings to the adsorption kinetics in zeolite crystals, and derived the following equation:

$$\frac{Q_t - Q_o}{Q_\infty - Q_o} = \frac{2S}{V} \times \sqrt{\frac{Dt}{\pi}} \quad \dots\dots\dots\dots\dots\dots (1)$$

where D is the diffusion coefficient Q_o, Q_t and Q_∞ are the quantities of the gas adsorbed in a constant pressure system at

the/.............

[x] Maggs[7] and others have established that the heat of wetting per unit area of a coal surface is about 0.1 cal/m^2.

the times o, t and at equilibrium, respectively. S is the external surface area of the sample and V is the volume.

Samples of coal evacuated at 120°C for about 16 hours were always used. It was assumed that the samples had been completely degassed so that Qo = 0.   By plotting $\frac{Qt}{Q\infty}$ against $\sqrt{t}$ the diffusion coefficient can be calculated from the slope of the straight line so obtained.

The volume of a sample is found from the helium density and the surface area can be calculated by a method developed by Barrer[10], the required information being obtained from the $\sqrt{t}$ vs. $\frac{Qt}{Q\infty}$ plots of the low temperature (-185°) oxygen adsorption rate data.   Values of about 1 x 10^{4} cm^{2}/gm. were obtained.

McBain,[11] Damköhler,[12] Barrer and Rideal[13] and Wicke[14] have also proposed equations relating the diffusion process to the adsorption rate.   These equations are formally not very different from the equation derived by Ward and quoted as equation (1) in the modified form suggested by Barrer.

Determination of the Adsorption Rates.

Oxygen adsorption rates were determined in a conventional constant volume adsorption system.   The adsorption of oxygen by coal is an extremely slow process after an initial reasonably rapid stage has been passed.   At 30° and 67 cm Hg. equilibrium was ohly approached after about 100 hours.   Experiments had been done at various constant pressures at 30° and 60° C on about 5 gm. of sample (-60 mesh B.S.S. size).

When plotting $\frac{Qt}{Q\infty}$ against $\sqrt{t}$, curves of the form shown in Fig. 1 were obtained.

FIGURE 1.

RATE OF ADSORPTION OF OXYGEN
BY COAL AT 30°C AND 67 cm.Hg.
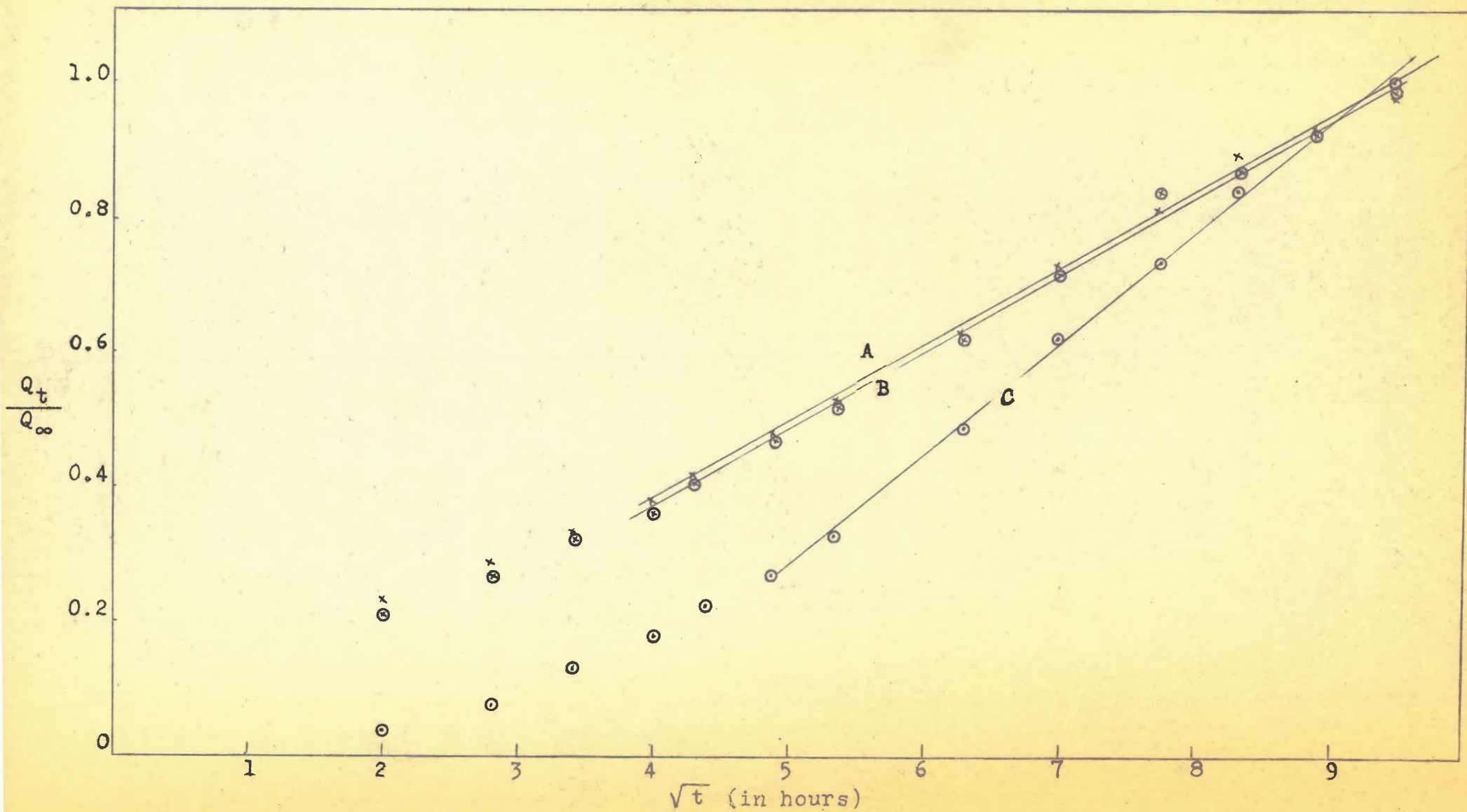
During the initial stages of the adsorption, the $\sqrt{t}$ law is not valid but after about 9 hours a straight line relationship exists and continues throughout until equilibrium is approached. Results computed from data obtained from the straight line region of the curve by means of equation (1) are given in Table 2.

The water vapour adsorption rate measurements were made by means of quartz micro-balances. Before conducting experiments the coal samples (about 1 gm. of coal -60 mesh B.S.S. size) were outgassed in the apparatus by heating to $100^{o}C$ in vacuum to constant weight).

The adsorption of water vapour is more rapid than that of oxygen, about 70% of the equilibrium amount is adsorbed during the first 100 minutes. Thereafter the adsorption is slow, equilibrium being reached after about 24 hours.

The results of experiments conducted at $25^{o}C$ and 21 mm. pressure were used to plot $\sqrt{t}$ against $\frac{Qt}{Q_\infty}$ as shown in Figure 2. These curves are typical of those obtained for the experiments conducted at various temperatures and pressures with water vapour. It will be noted that a straight line relationship exists in the earlier stages of the adsorbtion but that, as might be expected from theoretical considerations, a deviation occurs as equilibrium is approached. Results computed by means of equation (1) from experiments done at $25^{o}C$ are also given in Table 2.

The results indicate that water vapour diffuses about 10 times faster than oxygen at the stated conditions of temperature and pressure.

Since water and oxygen are both fairly strongly adsorbed this difference is probably due to such factors as affinity, degree of coverage and the relative pressure. The effects of temperature and pressure discussed below also demonstrate a

FIGURE 2.

RATE OF ADSORPTION OF WATER
VAPOUR BY COAL AT 25°C AND 2.1 cm.Hg.
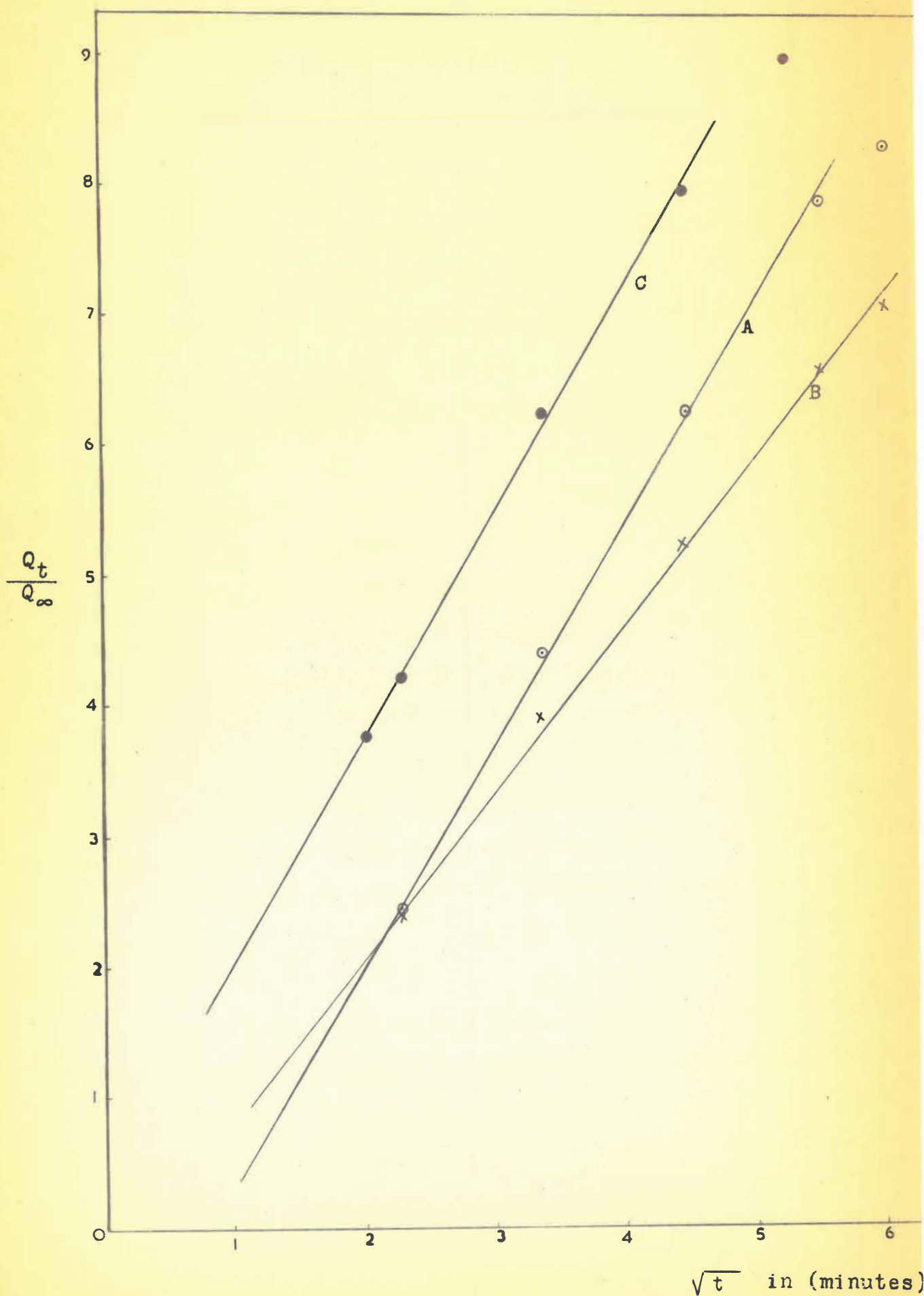
difference in the flow behaviour of oxygen and water vapour.

TABLE 2.

Diffusion coefficients of water vapour (21mm. Hg. and 25°C) and oxygen (30° and 67 cm.) for three different coals.

Sample	Porosity cc/gm	Diffusion coefficient.	
		Oxygen.	Water.
A	.176	4.5×10^{-14} cm^2/sec.	5.2×10^{-13} cm^2/sec
B	.121	4.5×10^{-14} "	4.8×10^{-13} "
C	.085	6.5×10^{-14} "	6.4×10^{-13} "

The Effect of Pressure:

In the case of oxygen, the diffusion coefficient seems to be independent of the pressure. Plots of $\frac{Qt}{Q_\infty}$ against $\sqrt{t}$ for measurements at 10, 40 and 67 cm. Hg. coincide closely.

There is evidence that the predominant pore size of coal is of molecular dimensions which suggests that the flow of oxygen in the gas phase is by molecular streaming which is independent of pressure. But because oxygen is strongly adsorbed, one would expect that surface flow also occurs. It appears however, that although the rate of adsorption increases with pressure, no corresponding increase in the surface flow takes place.

This effect is probably due to the fact that as the pressure increases the surface will become densely occupied thereby preventing the molecules from moving freely across the surface.

Water vapour shows a decided enhanced flow with increased pressure. Results obtained for three different coals are given in Table 3.

TABLE 3.

The Effect of Pressure on the Diffusion Coefficient
of Water Vapour at 25°C.

Sample	Diffusion Coefficient x $10^{13} cm^2/sec.$			
	4.7 mm	10.2 mm	12.2 mm	21.0 mm
B	2.2	2.2	3.3	4.8
C	2.6	3.5	4.5	6.4
A	1.3	2.6	2.4	5.2

Assuming again that the flow is by molecular streaming and surface flow, it seems that in this case the surface flow is dependent on pressure. The relatively weak attractive forces between water and coal and the high dipole attraction between the water molecules may account for the pressure dependence of the water vapour flow.

The Effect of Temperature.

In the experiments conducted at a pressure of 21 mm. Hg. and 25°, 38° and 60°C, it was found that the rate of adsorption of water vapour, as well as the equilibrium amount of water adsorbed, decreased with increase in temperature. However, due to the relative rate of decrease of these quantities, the calculated diffusion coefficient was actually found to increase with temperatures shown in Table 4.

TABLE 4.

Diffusion Coefficient of Water Vapour at 21 mm. Hg.
and Different Temperatures for Three Coal Samples.

Coal Sample	Diffusion Coefficient x 10 ^{13} cm^2/sec.			Average Act. Energy Kilo.cal/mol.
	25°	38°	60°	
B	4.8	5.8	6.4	2.8
C	6.4	7.6	8.2	2.4
A	5.2	6.4	7.4	2.1

By plotting log D against $\frac{1}{T}$ straight lines are obtained the slopes of which correspond to the activation energies given in Table 4.

Since molecular streaming is only dependent on $\sqrt{t}$, and the results clearly indicate an exponential dependence on the temperature, it must be concluded that a considerable proportion of the total diffusion must be by surface flow which is an activated process.

The quantity of oxygen adsorbed at any time, as well as the amount adsorbed at equilibrium, were found to change with temperature in such a way that the $\frac{Qt}{Q_{\infty}}$ vs. $\sqrt{t}$ curves at 30° and 60° for each of the coals studied, coincided closely. However, since there are indications that a definite chemical reaction takes place between oxygen and coal at about 60°C, no further analysis of the results can be made.

The Effect of Porosity.

The coals used for the adsorption rate measurements (A, B and C) provided a fair range of porosities. According to the results in Table 2, the diffusion coefficients of oxygen and water vapour did not change appreciably at the experimental conditions under which the measurements were made.

B.   The Calculation of Diffusion Coefficients from Results of
       Gas Flow Rate Studies.

        Equation (1) yields an overall or total diffusion

coefficient i.e. it includes coefficients for Poiseuille flow,

Knudsen flow and surface diffusion.

        The relative contribution of these processes to the total

flow of a gas depends on various factors such as the pore size, the

size and weight of the diffusing gas molecule and the adsorption

coefficient.

        Poiseuille flow and Knudsen diffusion (molecular streaming)

depend primarily on the pore diameter.   The former occurs in

passages with diameters that are large compared with the molecular

mean free path, and the latter predominates in pores having dia-

meters that are comparable with the mean free path.

        Now, earlier work[6] had proved that a high percentage of

the pore volume of the coals studied was due to pores having

diameters of the order of 20 $\overset{\text{o}}{\text{A}}$ and that much finer pores largely

contribute to the total surface available for adsorption.

        The extremely slow adsorption of gases frequently ob-

served with coal may be due to surface effects in these small pores

and to changes in pore diameter due to adsorption.

        Under such circumstances surface diffusion that depends

on the mobility of the adsorbed molecules may contribute to an

appreciable extent to the total rate of diffusion.

        In recent years attention has been drawn to the quanti-

tative effects which the mobility of molecules in adsorbed layers

have on the total flow of gases and vapours through porous media.

In this connection special attention may be drawn to the work of

Tomlinson and Flood[15] Carman et. al.[16] and Barrer et. al.[17].

Although/.......

Although the available adsorption rate data for oxygen and water could have been analysed by methods proposed by Damköhler[12] and Wicke[14] to obtain information on surface diffusion, it seemed preferable to study diffusion phenomena and especially the influence of surface effects on it by methods based on the direct measurements of flow through the solid material. This would have the advantage of extending the study to less strongly adsorbed gases. Furthermore, actual flow rate measurements through coal would be of practical interest.

The methods of Barrer[17] and Carman[16] were considered. They require more or less the same experimental procedure but Barrer's method involves the measurement of the time taken before a steady state of flow occurs ("time lag"), as well as the measurement of the rate of transport during the steady state. Since it was difficult to follow the course of the transient flow due to the very small flow rate, the measurements of the time lag were liable to error. Therefore, this method was considered to be less suitable for the study of the flow of gases through solid coal than Carman's method which involves only the measurement of the flow during the steady state while the pressures on each side of the plug are kept constant. This method also requires a knowledge of the porosity of the substance of the plug and of the amount of gas adsorbed by the coals at the temperatures and pressures at which the flow measurements were made.

Since the pores encountered in coal are extremely small, the equation proposed by Carman for determining the flow in micropores may be simplified somewhat by neglecting the viscous term for flow in the gas phase.

The equation may be written:

$$P_s = D_s \; \rho \, (1 - \varepsilon) \; \frac{v}{\Delta p} = \frac{WL}{\Delta p A} - \frac{W_1 L}{\Delta p_1 A} \sqrt{\frac{M_1 T_1}{MT}} \quad \ldots \ldots \ldots (3)$$

Where/........

Where P_s is the surface permeability and D_s is the surface diffusion coefficient, ρ is the density of the sample and ε is the porosity.

The pressure gradient across the plug is represented by $\triangle p$ and v is the difference between the quantities adsorbed on each side of the plug at the prevailing pressures. The quantities adsorbed are obtained from isotherms.

The surface permeability is the difference between the total permeability, $\left[\dfrac{WL}{\triangle pA}\right]$ and the "calculated gas permeability",

$$\left[\frac{W_1 L}{\triangle p_1 A} \quad x \quad \sqrt{\frac{M_1 T_1}{MT}}\right].$$

W_1 is the flow rate in ergs./sec. of a non-adsorbed gas with molecular weight M_1. A is the cross sectional area of the plug and L is its length (or thickness).

EXPERIMENTAL PROCEDURE.

The experimental determination of diffusion constants of gases through coal is complicated by a number of factors.

As one object of the investigation was to obtain some information on the flow of gases in the solid coal, it was considered preferable to work on discs cut from solid blocks rather than on compacted plugs of granular coal samples, although the latter would enable one to have a more truly representative sample say, of a coal seam.

On the same grounds one would have to ensure that the test piece was free from cracks or fissures, although it is recognised that these very probably play an important role in the flow of gases in the virgin seam or in lumps of coal e.g. during oxidation (combustion).

The procedure finally adopted for preparing test pieces was to select typical lumps of coal (plus 4") from the run-of-mine coal produced at selected collieries. The lumps were cut along the bedding plane by means of a high speed masonry saw to produce a plane surface. Cores of about 2.6 cm. diameter were then produced from the prepared lumps by drilling holes vertically to the bedding plane with a small diamond core drill.

Discs, 2 - 3 mm. thick, were cut from the cores with a hack saw and these were then ground to the final thickness[x] and diameter (2.6 cm.) on a plate of glass using carborundum grinding powder.

Preliminary experiments proved that the rate of passage of gas through discs of 2 mm. thickness was so low that it was impracticable to use them.

On the other hand discs of about 1/2 mm. thickness had insufficient mechanical strength to withstand the pressure difference that had to be used to ensure flow, and invariably ruptured. This lack of mechanical strength also placed an upper limit on the diameter of the discs.

Practically all the work, therefore, was done on discs of about 1 mm. thickness and a diameter of 26 mm.

All the coals tended to swell to some extent when adsorbing gas or vapour and to contract during outgassing. With coals having air dried moisture contents of the order of 7% and higher, the contraction was so marked that cracks invariably developed in the discs.

The flow rate measurements had, therefore, to be confined to coals having air dried moisture contents below 6% i.e. on samples B, C and D of Table 1.

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[x] Prepared in the Institute's coal petrology section.

Mounting and Testing of Discs.

A glass tube (A in Fig. 3) was flared out at one end to a diameter of 16 mm. and the surface was ground flat. The coal discs were cemented to this tube.

As the outgassing of the discs had to be done at a reasonably high temperature, a cement was required that would not become unduly soft at these temperatures while remaining suffi- ciently plastic at ambient temperature to allow for small expansion and contraction of the coal with adsorption and desorption of vapours or gases.

After trying various cements "Vitacote", having a softening point well above 120°C, was found suitable.

Before sealing on any disc, it was examined under a low power microscope for soundness.

After sealing on, the tube was connected to a vacuum system and the seal and the surface of the disc were tested for leaks by probing with a high frequency leak detector. The tests were made with a short spark length in a darkened room.

Apparatus :

The apparatus used is shown diagramatically in Fig. 3. A represents the glass sample tube to which discs were cemented. This tube was sealed on to the apparatus. The cover tube B with ground glass joint, provided an easy means of getting at and chang- ing sample tubes.

The mercury cut-off C was provided to allow simultaneous evacuation on both sides of the disc. This reduced the pumping time considerably. The cut-off was also used as a manometer.

The coal disc could be maintained at higher than room temperature by slipping a small electrically heated furnace F

FIGURE 3.

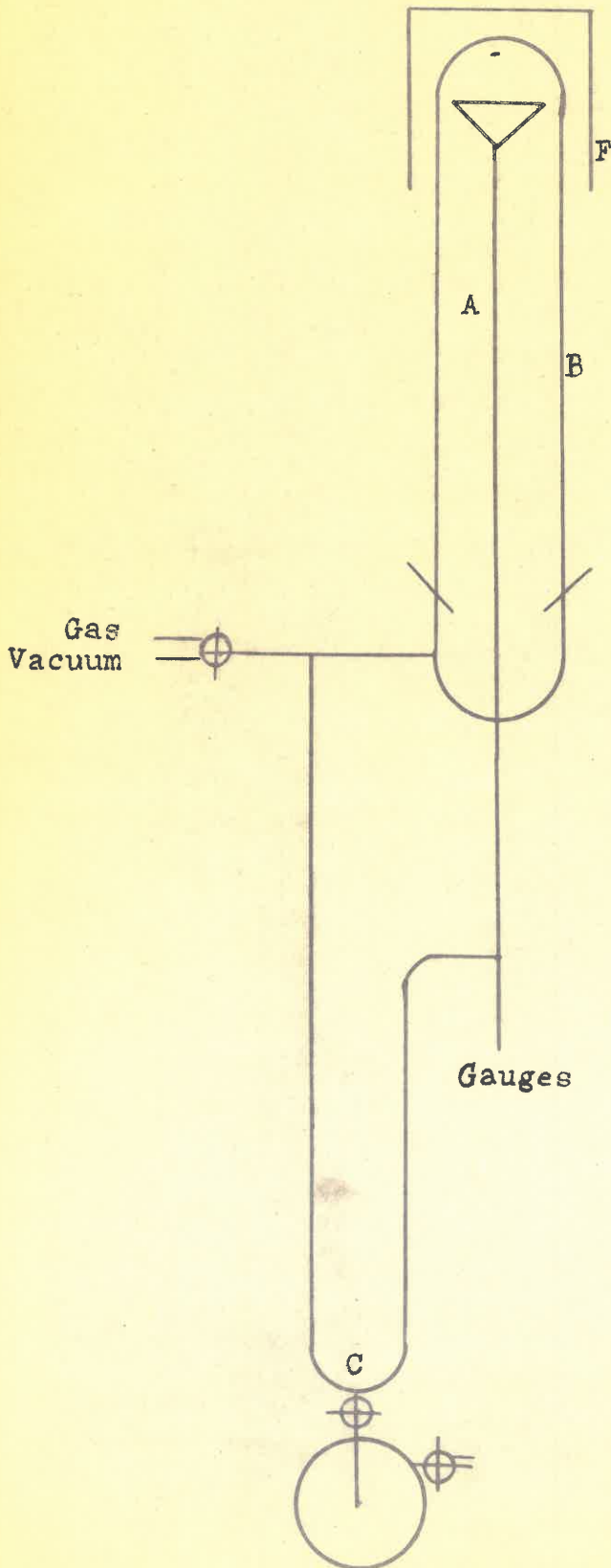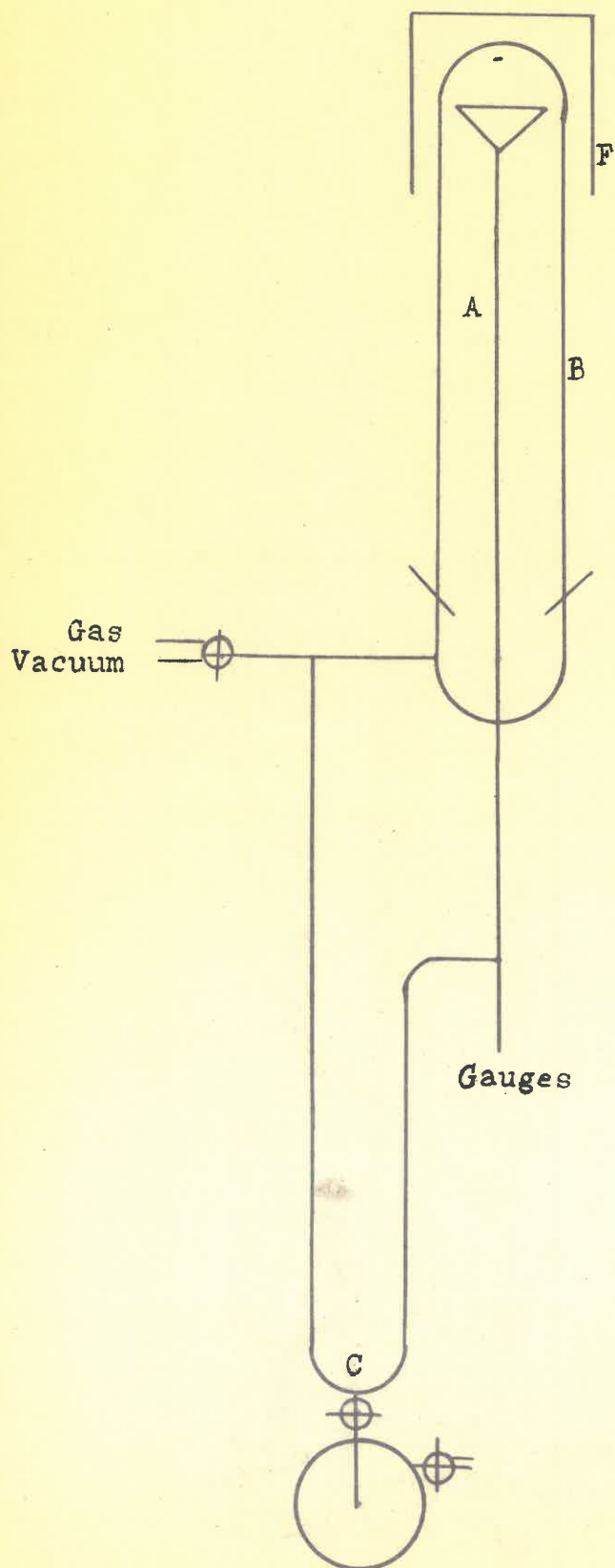APPARATUS USED FOR MEASURING
GAS FLOW RATES THROUGH COAL DISCS.

FIGURE 3.

APPARATUS USED FOR MEASURING
GAS FLOW RATES THROUGH COAL DISCS.

over the tube B.

As the gas flow rate was very low even with 1 mm. coal discs, the apparatus was designed to measure flow rate in terms of the increase in the pressure on the low pressure side of the disc, while the pressure on the other side was kept constant.

Due to the low rate of flow it was found unnecessary to provide an automatic pressure control device on the high pressure side. The pressure on the low pressure side remained so low that the pressure gradient ($\triangle p$) could be considered to be equal to the applied pressure.

To be able to measure such small increases in pressure, use had to be made of a McLeod gauge. In the water vapour experiments a Pirani gauge was also used to measure water vapour pressure.

To obtain the correct setting of the mercury on the calibration mark, a fine adjustment control provided on the mercury reservoir of the gauge was used in conjunction with a cathetometer. The cathetometer was also used to determine the difference in the height of the mercury columns of the McLeod Gauge.

Outgassing of Samples.

A specific disc was usually retained in the apparatus until experiments had been done with all the gases selected for this study.

Outgassing was practised on all fresh samples and between experiments with various gases.

With the apparatus assembled and cut-off C open, the apparatus was evacuated while the coal disc was maintained at 120°C. From time to time cut-off C was closed and the rate of pressure rise on the low pressure side of the apparatus was measured.

The outgassing was considered to be completed when the rate of gas evolution from the coal into the low pressure side was so low that the pressure build-up over a period of 2 hours could not be measured on the McLeod gauge.

It usually took about 2 days to reach this stage of outgassing.

Although this criterion was quite stringent, the results of later experiments suggest that it provided no guarantee that outgassing had been complete or that the surface was always cleaned to exactly the same extent in all the experiments. While such a deficiency would affect the results and their reproducibility it was not practical to continue the outgassing indefinitely.

The Reproducibility of the Measurements:

The theoretical accuracy of the method depends on the accuracy of the pressure measurements and in this case should be about 1%.

Actually, measurements of the flow rates of helium were found to be reproducible to within 2% when doing duplicate determinations on the same disc.

With other gases (that could be absorbed more or less on the coal) the reproducibility was generally not better than 10%. This is probably due to adsorption and desorption effects and to the displacement of gases in the coal not previously removed during outgassing.

Although it was considered impractical to continue with the outgassing much over 50 hours, an effort was made to increase the reliability of the determinations, as far as a coal type was concerned, by doing at least consecutive duplicate runs

with any gas on the same disc and by repeating the duplicate experiment with the same gas using a second disc prepared from the same coal lump or core. The average result of these (at least four) experiments was then used in subsequent calculations.

While no claim is made to high accuracy in the results thus obtained, it is considered that they are reliable enough to indicate trends.

Evaluation and Discussion of Results.

Flow characteristics of Different Gases at Constant Temperature and Pressure.

To determine the diffusion characteristics of different gases in coal, extensive work was done on different plugs of the same coal (B) at 25° and 40 cm. Hg. (water vapour pressure 20 mm.).

The results given in Table 5 represent the average value obtained for three different plugs and duplicate measurements on the same plug.

TABLE 5.

Permeability Coefficients Determined from Flow Rate Measurements on Coal Sample B at 25°C. and 40 cm. Hg. (water vapour pressure 20 mm. Hg.)

Gas	Flow Rate ergs/min. $\times 10^2$	Total Permeability cm^2/sec $\times 10^{11}$	Gas Permeability cm^2/sec $\times 10^{11}$	Surface Permeability cm^2/sec $\times 10^{11}$
H_2	8.1	3.9	3.7	0.2
He	5.4	2.6	2.6	–
CH_4	5.9	2.8	1.3	1.5
H_2O	10.0	4.8	1.2	3.6
N_2	1.8	0.9	0.8	0.1
CO	2.1	1.0	1.0	–
O_2	8.8	4.2	0.9	3.3
CO_2	2.1	1.0	0.8	0.2
Kr	1.1	0.5	0.4	0.1

Adsorption measurements were made on finely crushed coal at the same temperature and pressure to determine the relative affinities of the gases for coal and to evaluate v required for calculating P from equation (3).

These results, and other constants of the gases required in the discussion, are given in Table 6. The values of the molecular diameter[18] are derived from the van der Waals equation.

TABLE 6.

Molecular Constants of the Gases studied and the Amounts of Gas adsorbed by one gram of Coal B at 25°C and 40 cm. Hg.

Gas	Molecular Diameter.	Molecular weight	$P \sqrt{M} \times 10^{11}$	Amount Adsorbed in c.c.
H_2	2.34	2	5.5	0.08
He	2.65	4	5.2	-
CH_4	2.30	16	11.2	7.25
H_2O	2.88	18	20.4	77.0
N_2	3.16	28	4.8	0.41
CO	3.12	28	5.3	0.37
O_2	2.92	32	23.8	13.3
CO_2	3.23	44	6.6	4.1
Kr	3.69	83.8	4.6	3.9

The Effect of the Affinity of the Gas for Coal.

It will be observed that with the exception of methane, water vapour and oxygen, surface flow apparently only plays an insignificant role in the diffusion process.

With /..........

With methane, on the other hand, it is at least as important as the gas phase diffusion and with water and oxygen it is the more important factor.

This relatively large surface flow is probably due to the higher affinities of these gases for coal, as indicated by the amounts adsorbed.

In the case of methane, its relatively small molecular diameter probably has an important bearing on its flow and adsorption characteristics. Thus, comparing it with the higher boiling gases krypton and carbon dioxide, one would not expect that more methane should be adsorbed. It is probable that due to their relative small size, the methane molecules can penetrate pores that are inaccessible to the larger molecules. Although the percentage of pores having diameters of 2 and 3 $\overset{o}{A}$ may be low, they would contribute appreciably to the surface area and the surface flow observed with methane may be due to penetration to such surfaces.

Such surfaces would also be available to helium and hydrogen but no surface flow is observed with these gases, probably because of their very low affinity for coal.

Considering the experiments with water vapour, one must expect the large amount of water absorbed to be due largely to capilliary condensation in the pores at the high relative pressure at which the adsorption was measured (viz. 0.8). The observed amount adsorbed cannot therefore be regarded as a measure of its affinity for the coal relative to that of the other gases.

However, assuming that the heat of adsorption is of the same order of magnitude as the heat of liquefaction of water, one must conclude that the attractive forces between coal and water are greater than those of any of the other physically adsorbed

gases included in this study.   Quite apart from any capilliary condensation effect, one would expect, on this basis, that relatively large quantities of water molecules would be adsorbed by the coal.

The observed high rate of surface flow of water vapour may therefore be ascribed to the comparatively large number of water molecules that are adsorbed and can move across the surface.   The large dipole attraction between water molecules must also have a considerable effect on the flow characteristics of water vapour.

Oxygen is adsorbed in comparatively large quantities by coal at $25^{\circ}C$.   At this temperature chemisorption is probably quite appreciable and the forces binding the chemisorbed oxygen molecules may be expected to reduce their mobility.   These molecules should also obstruct the flow of the more mobile, physically adsorbed molecules.   The observed high rate of surface flow suggests that relatively large quantities of physically adsorbed molecules must be present on the surface, and as a calculation shows that the amount of oxygen adsorbed under the conditions under which the flow measurements were made only covers about 10% of the monolayer capacity of the coal surface, it is clear that enough unoccupied surface area was available for the unhindered flow of mobile oxygen molecules.

The Effect of Molecular Weight of the Gas.

With the gases that are less strongly adsorbed, surface diffusion makes only a small contribution to the total observed flow.   These gases are therefore transported mainly in the gas phase.

Considering/....

Considering only the gases (He, H_2, CO and N_2) where the surface flow contributes less than 10% of the total flow, it is found that the observed total permeability varies roughly as the reciprocal of the square root of the molecular weight. This is the relationship to be expected with molecular streaming and it may be concluded that the flow in the gas phase is mainly governed by a mechanism of the nature of that postulated by Knudsen.

In the third column of Table 6, the product $P\sqrt{M}$ for all the gases are given. It is seen that the gases with higher affinities deviate from the general trend of dependence on the molecular weight probably because of the relatively large contribution of surface diffusion.

The effect of reduction of pore radii on the gas phase diffusion during the course of adsorption cannot be studied by this method but it is likely that it has a considerable influence on the flow characteristics of gases in coal in which the predominant pore sizes are of molecular dimensions.

On the other hand, coal also has pores with dimensions large enough for bulk diffusion to take place. However, the results clearly indicate that this type of flow does not govern the overall diffusion.

The Effect of the Molecular Size of the diffusing Gas:

Since molecular streaming and surface flow are dependent on the radii of the pores, it could be expected that the flow would be affected if there were a large number of pores with radii approximating those of the diffusing gases.

Considering the gases H_2, He, N_2 and CO whose diameters range from 2.3 to 3.2 Å and which are only slightly adsorbed, (so that the effect of a variation in pore radii consequent on adsorption is excluded), it is found that the value of $P\sqrt{M}$ is fairly constant.

This/........

This seems to indicate that no molecular sieve effects arise in the gas phase and that there are relatively few pores of these dimensions in coal.

However, since the large surface area of coal is mostly located in these micropores, enhanced surface flow is observed with adsorbed molecules such as methane whose dimensions are such that these surfaces are accessible to them.

The Effect of Pressure on the Diffusion:

Experiments were conducted at constant temperature and at pressures (Δp) ranging from 2 to 60 cm.Hg.

With the gases having a small surface flow such as helium, hydrogen, nitrogen and carbon monoxide the pressure appeared to have no effect on the rate of flow.

With the other gases the results were found to fluctuate so much that it was impossible to establish any trend.

The Effect of Temperature:

The rate of flow of most gases increased only slightly with temperature and due to the difficulty in reproducing results no general relationship could be established.

However, with helium the reproducibility was better and values of the diffusion coefficient calculated from measurements made at 25° and 85°C (on coal B) were found to be 2.6×10^{-11} and 2.8×10^{-11} cm^2/sec. respectively. This represents an increase of about 7.7% over this temperature range whereas dependence on $\sqrt{T}$, as required for molecular streaming, would require an increase of about 9%. Although the agreement cannot be considered to be good, the results indicate that the diffusion of helium is not exponentially dependent on temperature.

A fairly/.......

A fairly large increase in the flow rate is observed with water vapour and methane in the temperature range 25° to $60^{\circ}C$. The values of the total and surface diffusion coefficients obtained at various temperature are given in Table 7.

TABLE 7.

The Effect of Temperature on the Diffusion of Methane and Water Vapour at 40 cm and 2 cm Hg pressure respectively.

Gas	Total Permeability Coefficient.			Activation energy in Kilo Cal/mol.	Surface Permeability Coefficient.			Activation energy in Kilo Cal/mol.
	25°	38°	60°		25°	38°	60°	
Methane	2.8	3.1	3.6	2.5	1.5	1.8	2.0	2.8
Water	4.8	5.0	6.0	2.2	3.6	3.8	4.2	1.6

By plotting log P against $\frac{1}{T}$ for the surface permeability coefficients the slopes of the best average straight lines through the points indicate that the activation energy for methane is and 2.8 kilo cal/mol for the total permeability and surface permeability respectively. For water vapour the values are 2.2 and 1.6 kilo cal/mol respectively.

The Effect of Porosity of the Coal.

The study of the effect of porosity on gas flow is complicated by the fact that surface and gas permeabilities depend on the porosity in different ways.

According to the theory [16] the gas permeability should decrease rapidly with a decrease in porosity and the surface permeability should increase with decreasing porosity. The net effect will therefore, be determined by the relative contribution of the surface and gas flows to the total flow.

Furthermore, if the permeating gas is adsorbed, another complication is introduced by the possible reduction in the pore diameter and porosity in the course of the adsorption process.

In view of these difficulties the flow behaviour of only the slightly adsorbed gases, with which relatively little surface flow and adsorption occur, were studied on three coals of varying porosities.

In Table 8 the values for the total permeabilities are given for coals with porosities ranging from 0.15 to 0.08. With this range of porosities a four-fold variation could be expected. From the results given in Table 8 no definite relationship can be established although a decrease in the permeability is observed with decreasing porosity.

TABLE 8.

The Effect of the Porosity of the Coal on the
Flow Rate of some Gases at 25°C and 40 cm.Hg.
Pressure.

Gas	Permeability Coefficient cm^2/sec $\times 10^{11}$		
	Porosities cc/gm		
	0.146	0.121	0.085
He	2.9	2.6	2.2
N_2	1.1	0.9	0.8
CO	1.0	1.0	0.8
Kr	0.6	0.5	0.3

Comparison between the Diffusion Coefficients obtained by the Different Methods.

To be able to compare the results obtained by the adsorption and flow rate methods it is necessary to convert the permeabilities obtained by the latter method to diffusion coefficients.

Since/..........

The surface diffusion coefficient may be calculated by means of equation (3) and since it is assumed that the gas flow is independent of the surface flow, the gas diffusion coefficient is numerically equal to the gas permeability.

In Table 9 the values of the total diffusion coefficients obtained for oxygen and water vapour by the two methods are listed. These results indicate a considerable disparity between the values by the different methods.

TABLE 9.

Total Diffusion Coefficients for Oxygen and Water Vapour.

Gas	Total Diffusion Coefficients $cm^2/sec.$	
	Flow Rate Method	Adsorption Rate Method.
O_2	1.14×10^{-11}	4.5×10^{-14}
H_2O	1.24×10^{-11}	4.8×10^{-13}

In the case of oxygen the flow rate method yields values that are higher by a factor 10^3 and for water, by a factor 10^2.

The differences in the experimental conditions, such as the degree of coverage, aggregate - state of the sample and in the case of oxygen, the pressure, cannot account for the large difference in the diffusion coefficients.

It therefore, seems probable that the higher flow rate in the solid plug is due to microcracks and fissures which are

destroyed/......

destroyed when the coal is ground to a finely sub-divided state. This flow through cracks etc. may be expected to play an even more important role in larger lumps or even the seam of coal.

Conclusions.

The total diffusion coefficient for a number of gases is of the order of 10^{-13} cm^2/sec. for powdered coal and 10^{-11} for flow in a solid plug. These values compare favourably with those of Zwietering and Joy who obtained values of 10^{-12} cm^2/sec calculated from methane adsorption rates. Graham obtained a value of 10^{-8} for the permeation through a solid slab of coal. From these results it may be concluded that the coal substance is almost impermeable to gases and that the higher permeation rates observed with solid plugs are due to microcracks and fissures in the coal.

A comparatively large surface flow is observed with strongly adsorbed gases such as oxygen and water vapour. The enhanced flow of methane can be ascribed to a higher surface area available to its relatively small molecules. The flow of these gases is activated with activation energies of 2 to 3 kilo cal/mol.

The flow of less strongly adsorbed gases is probably governed by molecular streaming because it is independent of pressure but is related to the temperature and molecular weight by the expression $\sqrt{\frac{T}{M}}$. The flow of these gases also increases with porosity.

The diffusion coefficient of water has been found to increase with increased pressure but the oxygen flow seems to be independent of the pressure. The flow characteristics of oxygen are complicated, however, by the fact that it is chemisorbed.

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