SUMMARY.

A STUDY OF THE FACTORS INFLUENCING THE PHYSICAL PROPERTIES OF COKE FOR BLAST FURNACE PRACTICE.

by

R. Kennedy, B.Sc. A.R.T.C.

The behaviour of coking coals heated through the plastic swelling range has been investigated. Uniform heating of the samples was obtained by the dielectric method. Earlier work(1) along similar lines had suggested that the rate of swelling could be expressed as a function of the rate of gas evolution minus the rate of escape of gas through the plastic envelope and that the latter would be related to the permeability of the envelope. The quantitative analysis of the results was handicapped because no independent estimate of the volumetr rate of evolution of volatile matter could be made. A satisfactory method for making this determination has now been developed.

The expression previously used relating rate of swelling press and rate of gas evolution has been modified to

$$\frac{dv}{dt} = R - \frac{8\pi.Pd.}{l} A$$

where $\frac{dv}{dt}$ = volume rate of expansion (cm^3/min.)

R = volume rate of gas evolution (cm^3/min.)

Pd = applied pressure (atm.)

π = permeability coefficient.

A = cross sectional area (cm^2)

l = effective thickness (mm.)

Rates of expansion and rates of gas evolution have been measured for 4 coals over a range of applied pressures. Variables such as particl size grading, rate of heating and mass of sample have also been examin

Permeability coefficients, calculated from the above expressi decrease rapidly with increasing pressure. Values reached a constant (minimum) at much the same applied pressure for the coals examined, although the minima varied considerably from coal to coal. Particle size grading, within limits, did not affect the results. Rate of heating did but in the opposite sense to what was expected. Similarl the mass of the sample unexpectedly had a marked effect on the calcula permeability coefficient.

The only possible explanation for this seems to be that plastic coal has dilatant properties; under increasing rates of shear the structure becomes less "dense" and permeability increases. Proof of this hypothesis will not be easy but the fact that the permeability coefficient increases with increase in the rate of swelling is of considerable significance. It implies a self compensating swelling mechanism which must have considerable bearing on the pressures developed by coal in the coke oven. There the thickness (mass) and the rate of temperature increase of the swelling layer are inversely proportional to one another and a more thorough investigation of these two interrelated variables seems desirable.

(1) J.W.Taylor. Thesis for Ph.D., Glasgow University 1952.

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RANKIN KENNEDY, B.Sc., A.R.T.C.

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CHAPTER I.

INTRODUCTION.

INTRODUCTION.

The importance of the properties of metallurgical coke with regard to its suitability for use in the blast furnace may be judged by the extensive literature on the various aspects of this subject. Despite the number of investigations which have been made, however, there is still no unanimity on the question of which particular properties are of prime importance, or on how these properties should be assessed(1,2). At one time interest centred on the chemical properties of coke and in particular on its combustibility and reactivity (3,4), but the more recent view is that such factors are of secondary importance to the physical properties of the coke, which have been shown to have an appreciable effect on the efficiency of furnace operation (5,6,7). Particular attention has been devoted to measurements of coke strength (1,8), size and size grading (9) and bulk density, but investigations of the more fundamental properties such as true and apparent density, porosity and cell structure have also been made.

The fact that the exact effect of the physical characteristics of coke on blast furnace performance is still uncertain is due mainly to the difficulty of setting up criteria to define the performance of the blast furnace and of correlating such criteria with coke properties as evaluated by the various methods of testing used. In this connection it has been noted by Mayers(10) that the most profitable lines of investigation on coke are probably those concerning the mechanism of coke production rather than methods of influencing specific coke properties, since a fuller knowledge of the fundamental processes involved should assist in a more satisfactory interpretation of the data available on both coke properties and their effect on furnace operation. It is to this aspect of the problem that the present work has been devoted.

The physical properties of coke are closely connected with the changes occurring during the so called "plastic range", shown by all coking coals, to a greater or lesser degree, in the temperature range between 350 and 500°C during the carbonization process. At the beginning of this stage softening of the coal material causes the original coal particles to coalesce and swelling then takes place due to entrapment of the volatile products of thermal decomposition in the plastic mass. At higher temperatures progressive decomposition of the "fluid constituents" present leads to a decrease in plasticity and eventually a rigid semi-coke is produced, having a new cellular structure. There is general agreement that this transient low temperature stage of the coking process is of prime importance in determining the structure and properties of the final coke obtained at higher temperatures. Thus Davies and Mott(11) have expressed the opinion that "although in the latter stages of carbonization the coke cell walls harden, the porosity alters and cracks and fractures appear, these changes have a less profound influence than the reactions occurring during the plastic range." It is for this reason that the great majority of investigations into the coking behaviour of coals have been based on a study of this "plastic" state. [It is realised that the use of the terms "plasticity" and "plastic" may be questioned from a strict rheological standpoint, since the behaviour of such a substance as bituminous coal in the process of thermal decomposition is exceedingly complex. The above terms, however, are used in the present work purely to describe the coal material when it is in a state exhibiting flow characteristics, for want of a more exact rheological nomenclature.]

The attainment of plasticity during carbonization is an essential characteristic of coking coals and variations in the coking properties of different coals are attributed to the degree of plasticity which they develop; non coking coals show this property to only a slight extent or not at all. Various types of test have been employed to measure, directly or indirectly, the plasticity of coking coals and the aim of such investigations has been to correlate the data obtained with coke quality and coal composition and to give some insight into the coking behaviour and coking mechanism of coal in general. An excellent review of the literature on this subject has been given by Brewer(12), and it is proposed only to mention a few of the more important tests below. Agglomerating and agglutinating tests are commonly used in practice, while more fundamental methods of assessing plasticity include investigations of rheological properties in various types of plastometer, penetrometer and extrusion tests, and measurements of resistance to gas flow. Studies of the plastic state based on the swelling properties of coal are perhaps the most numerous of all the methods employed and such investigations will be discussed in greater detail in the following Chapter with reference to the present work.

Various theories have been put forward to explain the plastic and coking properties of coals. These properties were originally attributed to the presence of certain "coking constituents" in the coal material which became fluid on heating and were considered to be effective in binding the remainder of the coal substance together. Several investigators, including Wheeler and his co-workers(13) identified the "coking constituents" with certain fractions of the extract obtained from bituminous coal by the action of organic solvents, since it was found that the coal residue after extraction had lost its coking power. Different workers in this field used different solvents and opinions also varied as to which fractions of the extract obtained were responsible for the coking and swelling properties. Thus while Wheeler(13) attributed these properties to the chloroform soluble portion of the extract be obtained with pyridine, Fischer(14) thought that the coking constituents were the petroleum ether soluble fractions of benzene extracts. Attempts to relate the amount of extract obtained from various coals with their general coking characteristics were unsuccessful and the general theory of the presence of definite coking constituents was further undermined by the investigations of Broche and Schmitz(15) and Shimmura(16) who found that the coking and swelling properties were dependent on the properties of the extract and the residual coal material. Mott(17) concluded that the conception of coke formation being due to the finding of about 90% of the coal substance by a small amount of agglutinant was misleading. It has been noted recently by Kreulen(18), that many of the results obtained by coal extraction methods can be explained when it is realised that extraction actually involves colloidal dispersion of the coal substance in liquids of progressively lower surface tension, a view which has also been stressed by Lahiri(19).

In recent years it has been generally realised that coal is colloidal in nature(20) and the methods of colloidal chemistry have led to a more promising approach to coal structure and behaviour. Measurements of the internal surface of coals(21) by heats of wetting in methanol showed that the relationship between rank and heat of wetting formed a catenary, the coking coals being found to lie in the minimum region of the curve. Coking coals therefore appear to be characterised by low internal surface or low porosity. Determinations of the variation of heat of wetting during carbonization(22) indicated that with coking coals the internal surface rose to a slight maximum corresponding to the initial contraction temperature of the coal in the Sheffield Laboratory Coking Test(23) and then fell throughout the softening and swelling period reaching a minimum at a temperature corresponding approximately to the maximum swelling temperature of the coal. This reduction in internal surface was clearly associated with the plastic range since it was found to a lesser degree in weakly caking coals but did not occur with completely non-caking coals. The internal surface, however, never fell to zero even in coals which became highly fluid in the plastic range, which precludes any explanation of plasticity on the basis of melting or fusion of the coal substance.

Hirst(24) likened coal to an isogel, the micelles of which are composed of aggregates of varying degrees of polymerisation, the heaviest aggregates being situated in the centre or nucleus and surrounded by progressively less complex molecular units. He postulated that on heating, the smaller molecular units of the coal micelle attained a degree of mobility due to thermal vibration and that they acted as "boundary lubricants", allowing relative movement of the larger micelle nuclei and resulting in plasticity of the coal material. The movement of the micelles under the action of these mobile constituents would lead to their cohesion with a resultant decrease in the internal surface of the coal, and the gradual formation of a more rigid structure. Thus at higher temperatures the latter effect together with progressive decomposition and evaporation of the available boundary lubricants would result in loss of plasticity. The degree of plasticity attained during the above process will obviously depend on the extent to which the micellar nuclei are free to move under the action of the plasticising molecules, while the period during which these lubricants are effective will depend on the ease with which they can evaporate and hence on the openness of the coal structure. Hirst therefore considered the properties of coking coals to be due to their compact structure, i.e., low porosity, and to their micellar nuclei being of relatively simple shape, both these factors contributing to a high degree of plasticity. He regarded the coking coals to be intermediate in structure between lower rank coals which he suggested had a more open structure and more complicated irregularly shaped micelles which were less mobile, and higher rank coals in which it was probable that coking power diminished due to increasing linkage of the micelle nuclei by covalent carbon bonding.

In a recent paper(25) Berkowitz emphasised the fact that coking coals were found to have low porosities. He suggested that softening and swelling of the coal material were two more or less independent processes the former being due to mobility of the coal micelles and the latter being related to the pore structure of the coal. Intumescence was attributed to the development of gas pressures within the coal pores, due to the disparity in the rate at which gas was generated and the rate at which it could diffuse to the exterior, governed solely by the pore structure. Thus the degree of intumescence was dependent on the porosity of the coal and the amount of volatile matter disengaged from the coal during the swelling range.

Although several points of Berkowitz's theory have been criticised(19), it would appear that an interpretation of the swelling of coals in relation to their porosity and rates of volatile evolution offers an interesting line of study. Such an approach has, in fact, been made by Taylor(26) who proposed the calculation of permeability values for plastic coal from the results of swelling tests. The preliminary findings of Taylor, which will be discussed in the following Chapter proved promising and the present work is devoted to a fuller investigation of the swelling process from this point of view.

CHAPTER II.

SWELLING MEASUREMENTS.

SWELLING MEASUREMENTS.

The fact that all coking coals tend to show swelling during the plastic state and the importance of this phenomenon in relation to the coking process and the quality of coke were recognised at an early date and studies of the swelling behaviour of coal are probably the most numerous of all investigations into the plastic and coking properties of coals.

Early workers noted the variation in the degree of swelling of coke buttons obtained by rapid carburisation of small coal samples in volatile matter determinations, a criterion which has now been standardised and adopted in classifying coals by their B.S. swelling number(27); the value of this test as a measure of coking power is, however, dubious(28). Several workers devised more accurate dilatometric tests to measure the volume change during heating. Probably the most widely adopted of these is the Sheffield Laboratory Coking Test devised by Mott(23) and his co-workers in the course of extensive investigations on the coking behaviour of coal. Mott showed that there was a relationship between the percentage of swelling in this test and both coal composition and coking properties. For coals of approximately the same hydrogen content, the volume change was found to increase with increasing carbon percentage, the curve showing a definite increase in gradient at about 85 - 86% C, corresponding to the markedly superior coking quality of coals with carbon contents above this value. In a later work(29) a graphical correlation was shown between ultimate hydrogen and carbon contents and swelling power for a wide range of coals and an approximate mathematical relationship between these variables was also derived.

In tests of the above type the "free" swelling of the coal under no applied load or swelling under a slight added load is determined. The extent of "free" swelling, however, may be quite different from the volume change observed when the coal is heated under an applied pressure while, if the coal is entirely prevented from increasing in volume considerable pressures may be built up in the plastic mass due to entrapped volatile decomposition products.

The importance of the pressure built up within the plastic layer as a factor affecting coke quality has been emphasised by several workers (30,31). Foxwell(31) pointed out that this pressure led to greater cohesion of the softened coal particles binding them together so that there would be greater bonding and higher strength in the final coke produced. It has in fact been shown by Blayden, Noble and Riley(30) that the application of pressures of up to 40 lb./sq.in. during the plastic range resulted in a marked improvement in the strengths of cokes produced from weakly coking coals.

In coke oven practice free swelling of the coal charge is prevented by the oven walls and if high swelling coals or blends are carbonized there is a danger that the pressure exerted by the confined coal may be sufficient to cause damage to the coke oven walls. Numerous laboratory tests have therefore been developed to study the pressure developed during coking, with a view to determining which coals are likely to be "dangerous" in practice. Such methods may be divided into two main groups, namely those which determine the volume change under constant applied pressure(32) and those in which the pressure required to prevent expansion of the coal is measured(33). The results obtained with various tests, however, showed considerable lack of agreement as to which coals should be regarded as dangerous and the general unreliability of such measurements has led to the adoption of larger scale tests in experimental moveable wall ovens(34,35) for investigations of this type. Since the laboratory tests were designed to simulate conditions in the coke oven, unidirectional heating of the coal sample was used. Taylor(36) pointed out that, since the whole coal sample was not at the same temperature under such conditions, the results obtained are due to the combined effects of both swelling and subsequent semi-coke contraction and are therefore of little significance with regard to the properties of the actual plastic layer. There are, indeed, few measurements of expansion pressures which are not liable to criticism on the above grounds, although Davies and Mott(37), using a very low heating rate and small coal samples probably obtained practically isothermal conditions.

Thus the main obstacle to any fundamental study of the plastic state has been that, due to the low thermal conductivity of coal, conventional methods of heating lead to temperature gradients in the coal sample, and the isolation of the various stages of the plastic range is rendered difficult, if not impossible, since initial softening and contraction, swelling and subsequent collapse, and shrinkage of semi-coke formed all occur within a relatively short temperature range.

In developing a method of studying the swelling properties of coal which would not be subject to the above limitations, Taylor(26) established an experimental technique employing dielectric heating to obtain isothermal conditions in the coal sample. The theory of the dielectric heating method may be described briefly as follows:-

The coal sample is placed between two metal plates to which an alternating voltage is applied, the whole unit forming a capacitor which is continually charged and discharged in each voltage cycle. When the applied field is of radio frequency, materials such as coal which have large unsymmetrical or polar molecules are strongly heated under such conditions. This is due to the molecules of the dielectric becoming polarised and tending to align themselves in the applied field, the highly damped nature of the continual reorientation causing the molecular displacement (D) to lag behind the alternation of the applied field (F). The resultant phase difference between (F) and (D) leads to a loss of energy in the dielectric resulting in generation of heat.

The heat or power generated in the dielectric material is given by the expression

$$P_V = w.Ko.\varepsilon . \tan \delta . F^2$$

where P_V is the power generated per unit volume of material

w " " angular frequency

Ko " " capacity of free space

ε " " dielectric constant

δ " " angle of phase difference between (F) and (D)

F " " field strength.

From the above equation, it will be seen that the heating effect is proportional to the square of the field strength, so that in order to obtain uniform generation of heat the field strength must be constant throughout the sample. This may be achieved by a suitable arrangement of the electrodes which should be parallel and equal in area, while the slight variation in field strength at, and radiation loss from, the outer surface of the coal sample is compensated for by a resistance furnace surrounding the sample and electrodes.

Taylor(26) succeeded in applying this method of heating to the study of the swelling behaviour of coals and experiments were carried out using both constant volume and constant pressure techniques, the results obtained by the latter method of investigation proving to be most interesting. Using a Scottish Kingshill coal, Taylor found that the rate of volume increase was practically constant over a considerable range of temperature during swelling and that a significant variation in swelling rate was obtained under different applied pressures. Initial increase in pressure resulted in an increase in the rate of swelling of the coal sample, until at higher applied pressures the swelling rate was found to decrease again.

Taylor considered that during swelling an equilibrium existed between the rate of generation of volatile products, the rate at which gas was entrapped in the plastic mass, i.e., the rate of swelling, and the rate at which gas escaped from the plastic coal, the latter being a function of the applied pressure and the "permeability" of the plastic coal material. He expressed the relationship by the equation

$$R - \frac{dv}{dt} = P_a \cdot S \qquad \text{..............(1)}$$

where R	is the volume rate of generation of volatile decomposition products in c.c. at N.T.P. per minute.
$\frac{dv}{dt}$	is the rate of swelling in c.c. at N.T.P. per minute, obtained by correcting the measured swelling rate to N.T.P.
P_a	is the applied pressure in atmospheres, i.e., the pressure difference between the inside and outside of the plastic mass causing gas escape.
S	is the permeability of the plastic coal mass in c.c. at N.T.P. per atmosphere per minute.

In order to calculate permeability values from the above equation, however, the value of R must be obtained.

Taylor explained the observed variation in swelling rate by postulating that an initial increase in applied pressure reduced the permeability of the coal mass, leading to an increase in the rate of swelling. At higher pressures, however, the swelling rate would be expected to decrease due to a constant permeability value being attained when all the small pores in the mass had been sealed by flow of plastic coal. Taylor pointed out that if this were the case and if the above equation were satisfied the graphical relationship between swelling rate and applied pressure should become linear and of negative gradient and that the value of R could be obtained by an extrapolation of this portion of the curve to zero applied pressure.

Using a value of R determined in this way Taylor calculated permeability values for the Kingshill coal; his actual results will be considered later in relation to those of the present work. The limited number of results he obtained, however, allowed of only an approximate estimation of R, since a truly linear relationship between $P(d)$ and $^{dv}/_{dt}$ at high pressures was not definitely established. Thus while Taylor concluded that the swelling properties of a coal could be expressed in terms of two relatively fundamental properties of the plastic coal, namely its permeability and rate of generation of volatile matter, he also noted that further investigation along these lines was desirable to confirm such an interpretation.

The objects of the present investigation were therefore as follows:-

To apply the dielectric heating technique to further coals, to ascertain whether their swelling rate/pressure relationships are capable of interpretation on the basis suggested above, and if so, to determine permeability values for a range of coking coals.

To study the effect of various variables, notably heating rate, on the swelling characteristics and permeability.

To devise, if possible, a direct experimental method for the determination of the volume rate of generation of volatile matter from coal during the plastic stage.

CHAPTER III.

EXPERIMENTAL APPARATUS.

EXPERIMENTAL APPARATUS.

A photograph of the experimental apparatus is shown in Fig.1 and a diagrammatic sketch showing the main features of the apparatus is given in Fig.2. Fundamentally the apparatus is the same as that used by Taylor(26) although several alterations and additions have been made.

The coal sample, contained in a suitable refractory crucible is placed between two metal electrodes which are connected to a radio frequency generator forming a condenser unit in which heat is generated by the alternating field. The crucible and electrodes are enclosed in a small resistance furnace which serves to prevent radiation loss from the periphery of the crucible, and allows an inert atmosphere to be maintained round the coal sample. Pressure is applied to the coal through the top electrode and any alteration in the sample volume during heating causes movement of the electrode. This movement is magnified and recorded on a revolving drum. In this way the swelling of the coal under constant pressure during the "plastic" range may be studied.

The apparatus is described in detail below under the following headings:- (a) Radio Frequency Generator, (b) Crucible and Thermocouples, (c) Heating Chamber, (d) Pressure System, (e) Swelling Recorder.

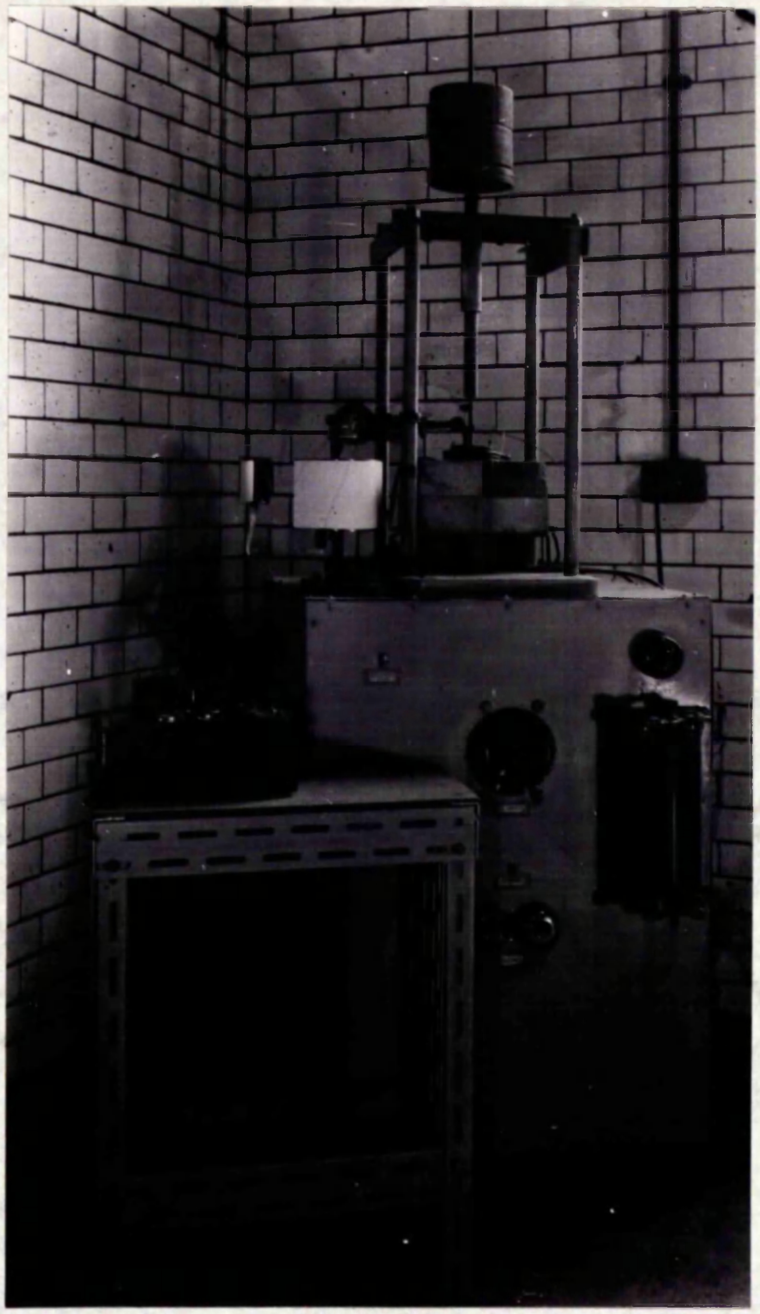


FIG. 1.

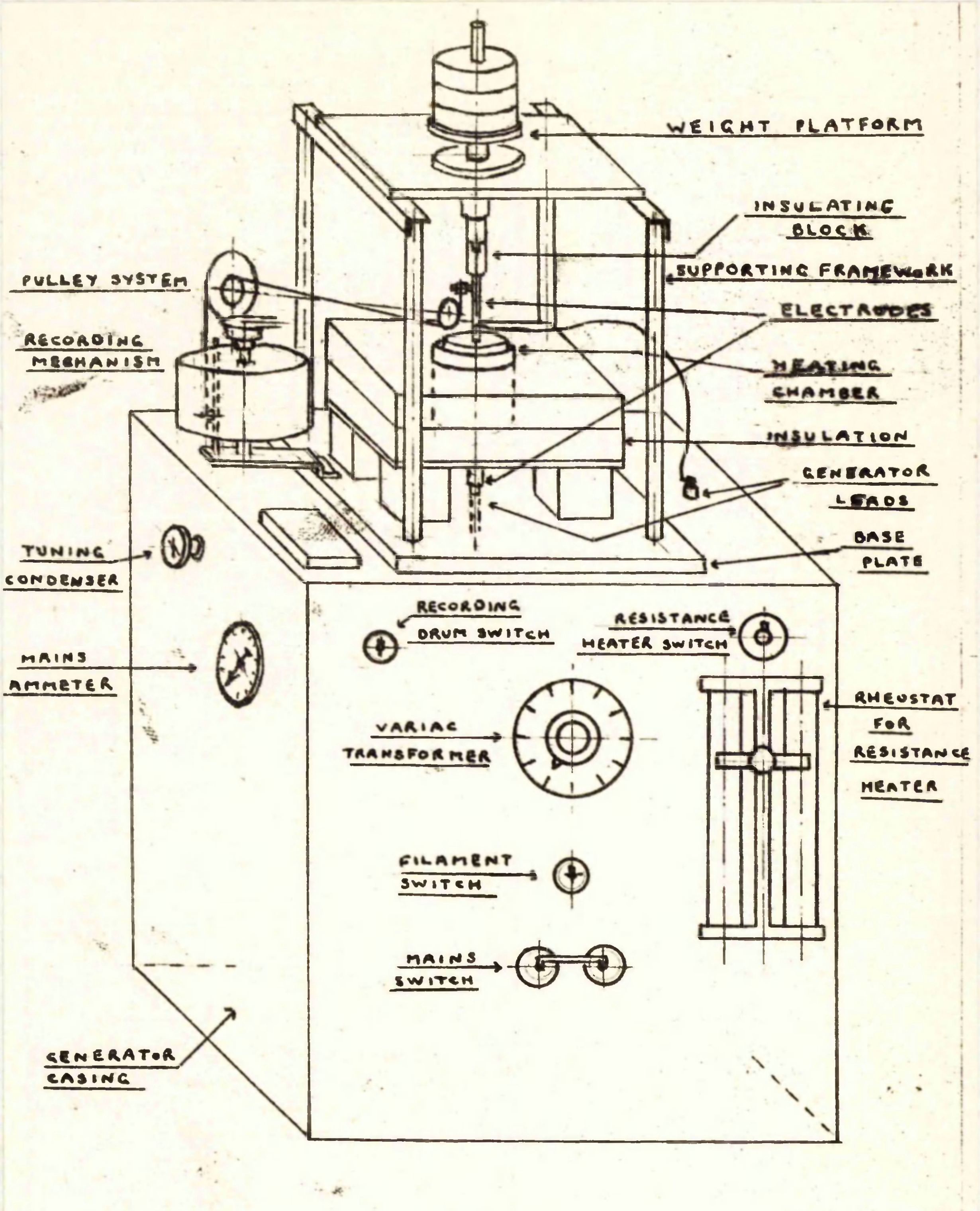

WEIGHT PLATFORM
INSULATING BLOCK
SUPPORTING FRAMEWORK
PULLEY SYSTEM
ELECTRODES
RECORDING MECHANISM
HEATING CHAMBER
INSULATION
GENERATOR LEADS
BASE PLATE
TUNING CONDENSER
RECORDING DRUM SWITCH
RESISTANCE HEATER SWITCH
MAINS AMMETER
RHEOSTAT FOR RESISTANCE HEATER
VARIAC TRANSFORMER
FILAMENT SWITCH
MAINS SWITCH
GENERATOR CASING

FIG. 2

(a) Radio Frequency Generator.

The necessary high frequency alternating field is supplied by a valve generator, operating at a frequency of approximately 50 megacycles per second, with an output of some 200 watts.

The generator is encased in the lower cabinet of the assembly shown in Figs. 1 and 2, and from the circuit diagram shown in Fig.3, it can be seen that the two valves operate on the push-pull principle. The power output to the electrodes is controlled by the variable condenser in the load circuit and by the Variac transformer voltage control shown in Figs. 2 and 3. The former allows the load circuit to be suitably turned to the generator and a fine control of the heating rate is then obtained by adjustment of the voltage control.

The power output leads leave the generator casing at the points (L_1) and (L_2) (Fig.4). The central lead passes through the heavy base plate (A), and makes direct contact with the bottom fixed electrode (C), while the other lead is connected to the upper moveable electrode (F) by the flexible connection (B).

(b) Crucible and Thermocouples.

The crucible used to contain the coal sample has to meet two main requirements, namely; (i) sufficient strength to withstand pressures of up to 90 lb./sq.in. at a temperature of 600°C, and (ii) suitable dielectric properties, so that heat is not preferentially generated in the crucible material, instead of the coal.

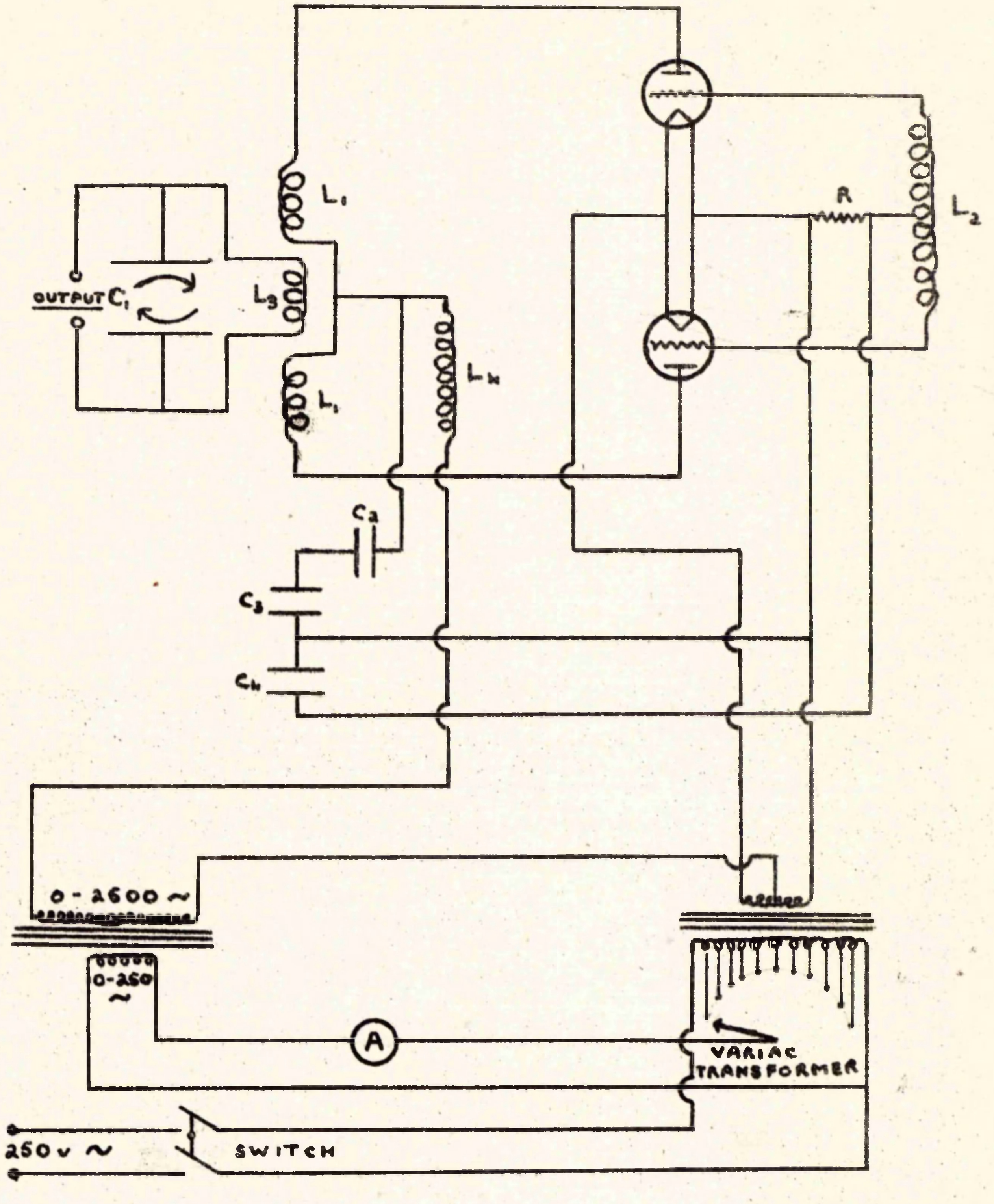

OUTPUT
C1
L3
L1
L1
L4
L2
R
C2
C3
C4
0-2600 ~
0-250 ~
A
VARIAC TRANSFORMER
250 v ~
SWITCH

FIG. 3

The development work carried out by Taylor(26) led to the use of a crucible made from a $3\frac{1}{2}$ inch length of Mullite tubing, of 2 inch inside diameter. A thermocouple sheath passes through two diametrically opposite holes bored in the tube, $\frac{3}{4}$ inch from one end, allowing the temperature at the centre of the coal sample to be obtained. Originally 5 mm. diameter silica tubing was used for the sheaths. Under high pressures, however, this proved very liable to fracture and 6 mm. diameter fused alumina sheathing was substituted.

The coal sample is confined above and below by perforated refractory discs of alundum cement, ground to fit neatly into the ends of the mullite tube. Closely fitting circles of asbestos paper, placed between the alundum discs and the coal, prevent escape of coal through the perforations in the discs during the "plastic" range, while allowing free escape of the evolved volatile products. The crucible arrangement is shown in Figs. 5 and 6.

Temperature readings are taken at two points by 22 S.W.G. chromel-alumel thermocouples, positioned as shown diagrammatically in Figs. 4 and 5. One thermocouple passes through the sheath which traverses the crucible, recording the temperature at the centre of the coal sample. The junction of the second thermocouple is on the same horizontal level as the first but is situated at the periphery of the crucible, between the crucible and the heating chamber wall. This thermocouple allows the temperature of the heating chamber to be controlled so that there is no radiation loss from the surface of the crucible. Because of its symmetrical position with respect to the

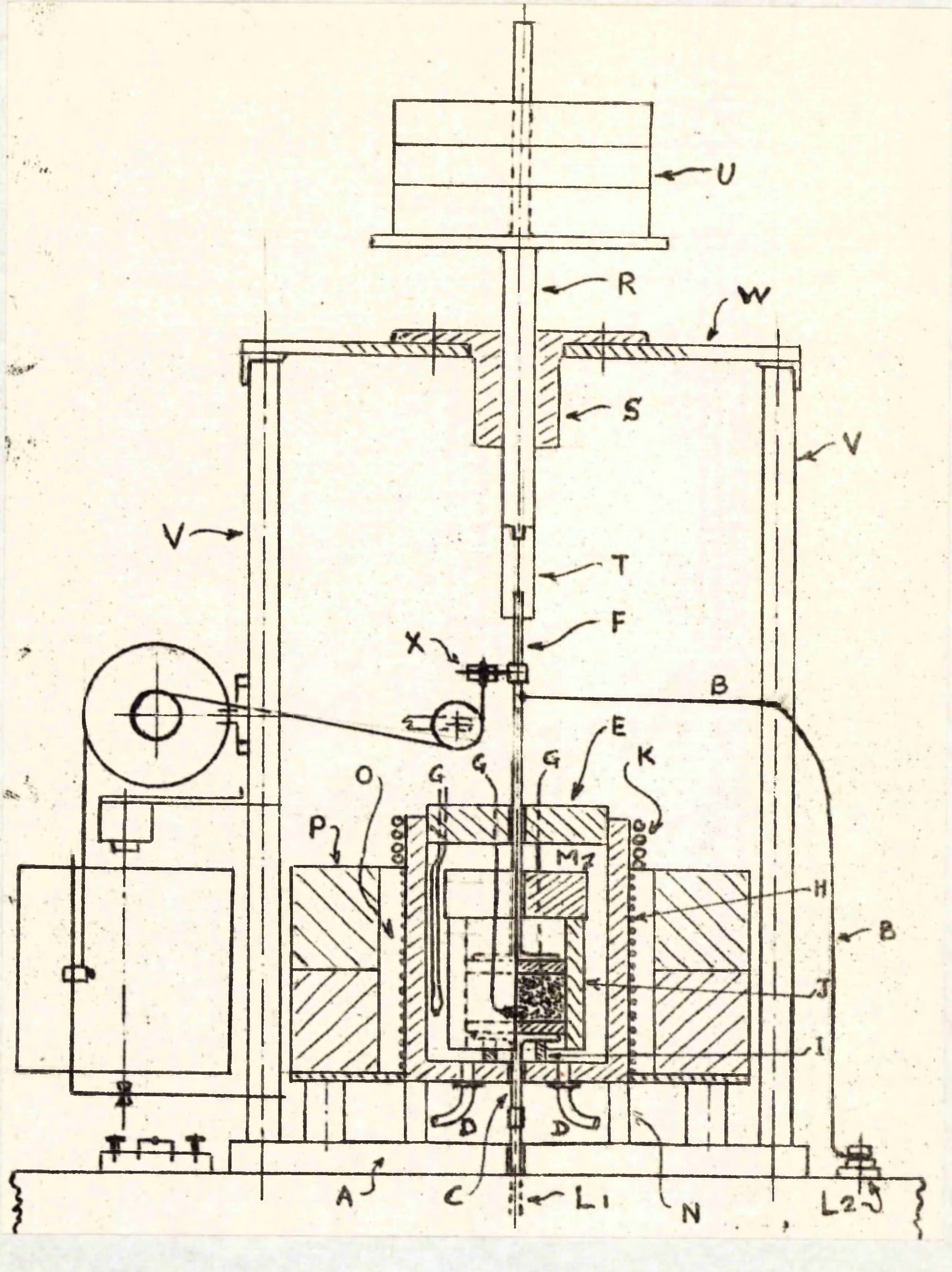


FIG. 4

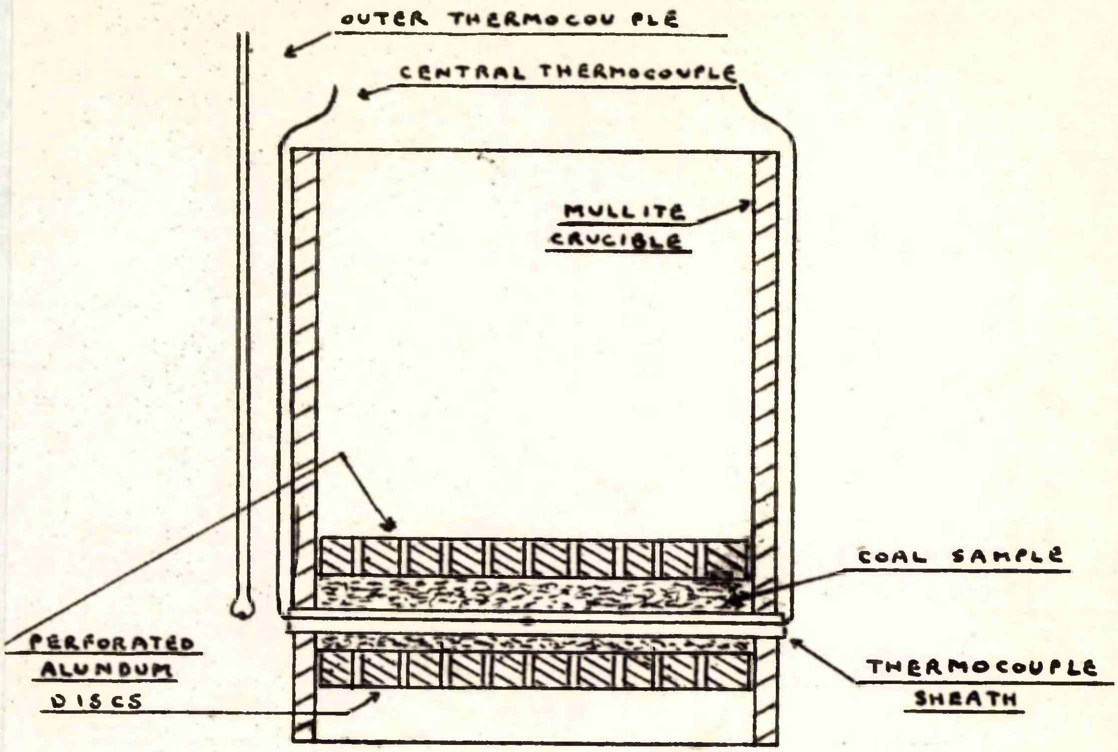

OUTER THERMOCOUPLE
CENTRAL THERMOCOUPLE
MULLITE CRUCIBLE
COAL SAMPLE
PERFORATED ALUNDUM DISCS
THERMOCOUPLE SHEATH

FIG. 5

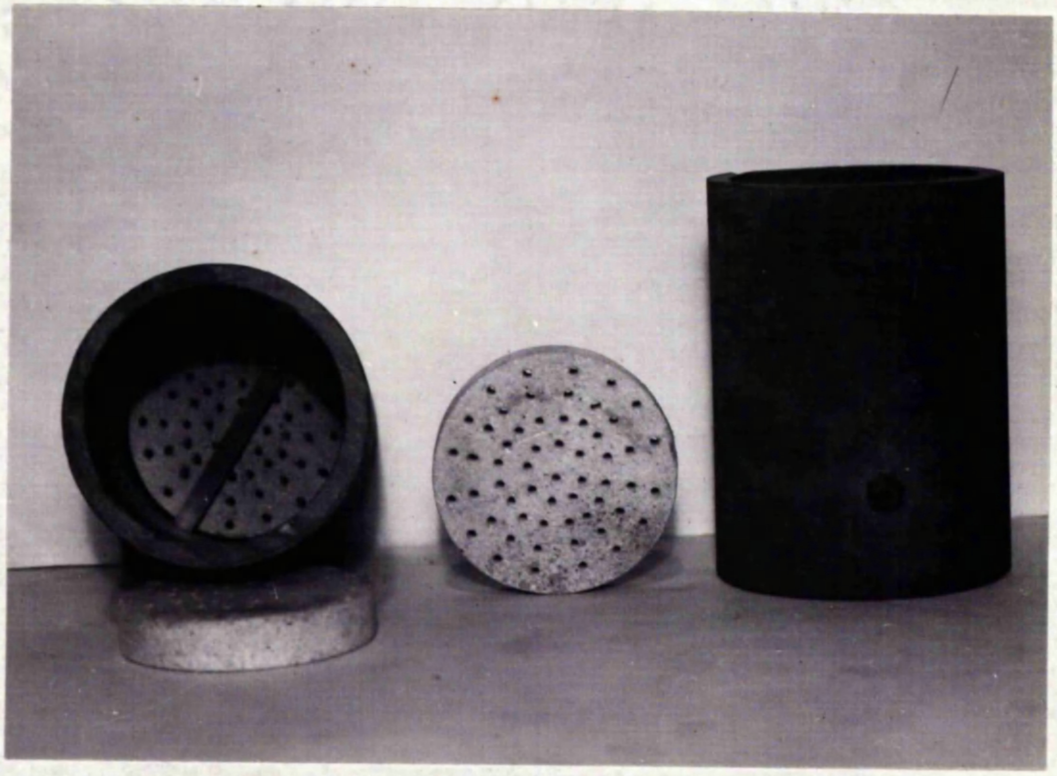


FIG. 6

high frequency field, the central thermocouple was found to record the same millivoltage irrespective of whether the field was off or on. The peripheral couple, however, tended to pick up induced high frequency currents which affected the readings obtained on the potentiometer. To obviate this effect and prevent damage to the potentiometer a filter circuit was interposed between the thermocouple and the instrument.

(c) Heating Chamber.

The chamber, in which the coal sample is heated, is machined from a solid block of steatite (hydrated magnesium silicate). It is cylindrical in shape, being 6 inches deep and $2\frac{3}{4}$ inches internal diameter (Fig.4). The bottom electrode (c) passes through a central hole in the base of the steatite pot and makes direct contact with the central lead (L_1) from the generator. Two further, diametrically opposite holes (D) in the base accommodate fused alumina tubes through which nitrogen is introduced to the chamber. The tubes and the electrode are sealed into the pot with a cement of water glass and alundum, the joints being completely gas tight.

The electrodes have flat 2" diameter heads which fit neatly into the Mullite crucible, as shown in Fig.4. The electrode heads are of mild steel but the stems are made of "Invar" alloy to reduce any error due to thermal expansion of the electrodes during the test. The upper electrode has a longer stem than the lower one and carries a short horizontal arm(X) which is attached to the volume recording device.

The top of the heating chamber is closed by a rubber bung(E) which has a central hole, carrying a silica sleeve, through which the stem of the upper electrode passes, there being sufficient clearance to allow free movement of the electrode in the sleeve. The thermocouple leads from the crucible also pass through the bung by holes (G) near the circumference . Oxygen free nitrogen is passed into the base of the heating chamber at the rate of 200 c.cs./minute, and passes out through the narrow annular space between the top electrode and the silica sleeve, which provides the only outlet for the gas. This clearance is approximately 1/32" and the quantity of gas passing ensures a sufficient linear velocity of escaping gas to maintain an inert atmosphere inside the chamber.

The outer surface of the heating chamber carries an electrical resistance winding(H) which is used to maintain the steatite pot at the same temperature as the inner crucible, thus preventing loss of heat from the crucible by radiation and compensating for any variation of the high frequency field strength at the periphery of the coal sample. The temperature of the winding is controlled by the rheostat shown in Fig.1 and 2.

The head of the bottom electrode is supported about 1 inch above the base of the heating chamber by a stool(I), so that the assembled crucible (J) is in the centre of the hot zone of the resistance winding. A water cooling coil (K) is wound on the upper part of the steatite pot to prevent overheating of the rubber bung (E) and the insulating block (M) prevents excessive radiation of heat to the bung.

The heating chamber is supported on the base plate(A) by four stools (N), and is surrounded by insulation consisting of an anulus of crushed brick (O) and insulating bricks(P).

(d) Pressure System.

Originally pressure was applied to the coal by means of an hydraulic system, shown in Fig.7. By adjustment of the screw valve(A) pressure was applied, via the oil reservoir (B) to the piston (C) and thence to the coal sample. The pressure was measured by the gauge (D) which was graduated from 0 to 1000 lb./sq.in. This reading, however, was sixteen times greater than the pressure on the coal, owing to the difference in area of the piston head and the coal sample, so that the range of pressure actually available was from 0 to 62·5 lb./sq. in.

After the first series of experiments, on the Easton coal, it was decided, for reasons which will be discussed later, to use a direct gravity load on the coal. The present arrangement can be seen in Fig.4. The platform and rod (R) slides in the sleeve (S) which is bolted to the supporting framework of the apparatus so that the rod is positioned directly above the central hole in the base plate through which the central generator lead emerges. The sliding rod connects with the top electrode through the insulating block (T) which is composed of "mycalex" high frequency insulating material.

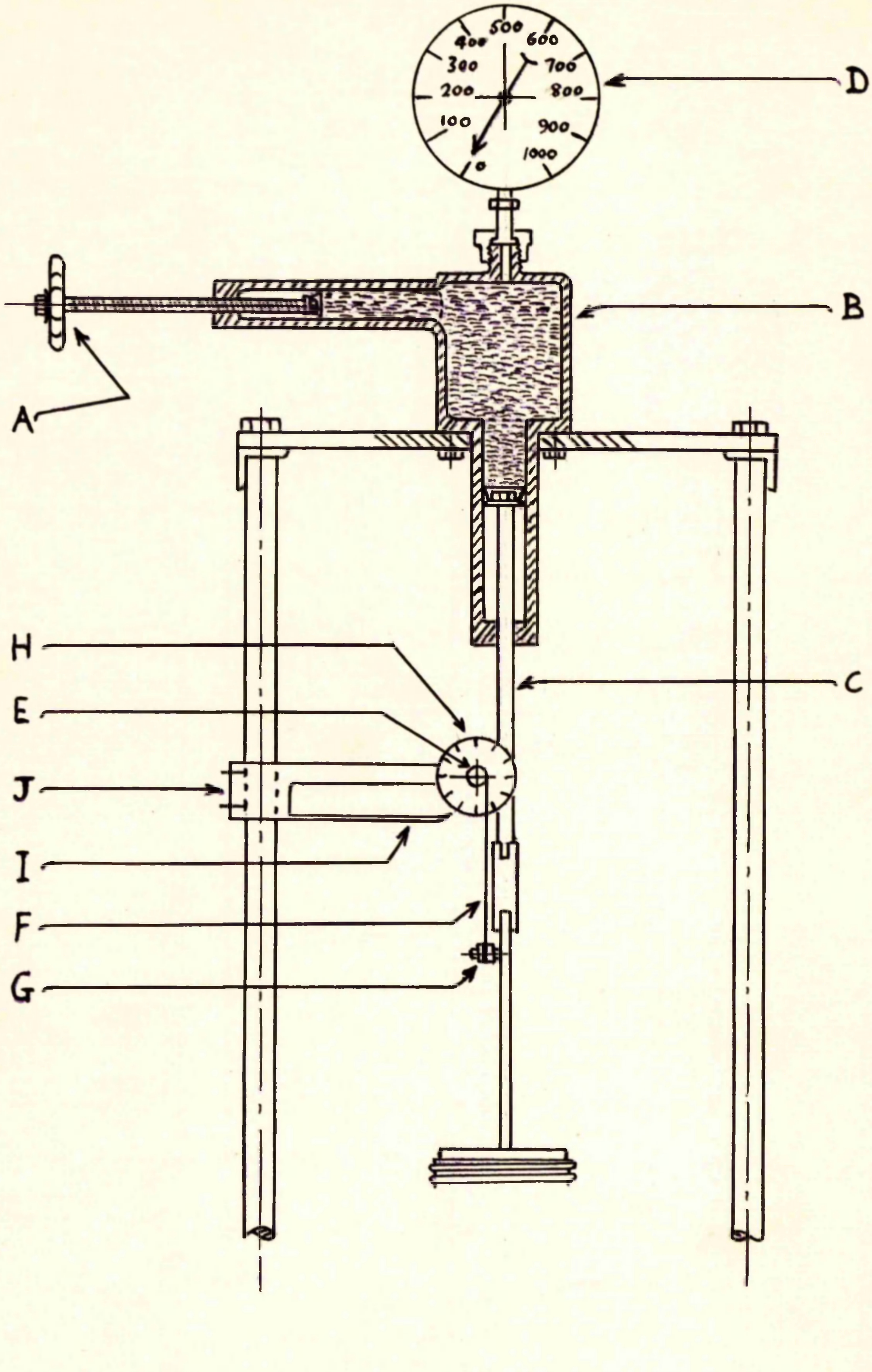


FIG. 7.

The desired pressure is applied to the coal through the top electrode by placing lead weights (U) on the upper platform. Accurate positioning of the guide sleeve (S) ensures practically frictionless movement of the rod and weights during swelling of the coal sample.

A series of lead weights were cast and machined so that they were equivalent to pressures of 2.5, 5 and 10 lb. per sq. inch on the coal. In this way any load between 5 and 90 lb./in.sq., by increments of 2.5 lb. per in. sq., can be applied to the coal.

The supporting framework which carries the weight platform consists of four vertical, 1 inch diameter iron bars which are screwed into the base plate (A) and tied at the top by four cross struts (W) to which the guide sleeve is bolted. The structure is very robust and quite rigid under the maximum pressure used.

(e) Volume Recorder.

Any alteration in the volume of the coal sample during heating causes a corresponding vertical movement of the top electrode which carries a small horizontal arm (X Fig.4) from which the movement is transferred to the recording device.

The first form of volume indicator, shown in Fig.7, consisted of a spring loaded rotating drum (E) connected to the arm of the electrode by a thin metal wire (F) and insulating sleeve (G). A 2½ inch diameter graduated dial (H) mounted on the drum spindle served to magnify the rotation of the drum and readings of the pointer (I) were noted at regular intervals during heating. The indicator was attached to the main framework by a support and clamp (J).

This arrangement was superceded by the recording device shown in Fig.8, which provides a permanent record of the swelling characteristics of the coal.

A cord (A), attached to the side arm of the top electrode (B) by a small "mycalex" insulating sleeve (c), passes under a pulley (D) directly below the side arm and is wound on to the smaller of two co-axial pulleys (E). A further cord (F) wound on the larger pulley (C) is attached to a weighted recording pen (H) which slides on the vertical guide I. Thus any movement of the top electrode results in a vertical movement of the recording pen, the movement of the pen in relation to the electrode being in direct proportion to the diameters of the co-axial pulleys. A ratio of 3 to 1 was found to be suitable for the majority of coals and sample sizes used.

The recording pen traces a line on the paper covered drum (J) which is revolved at a constant speed of 1 revolution per hour by the small synchronised motor (K). In this way a graphical record of the swelling characteristics of the coal is obtained.

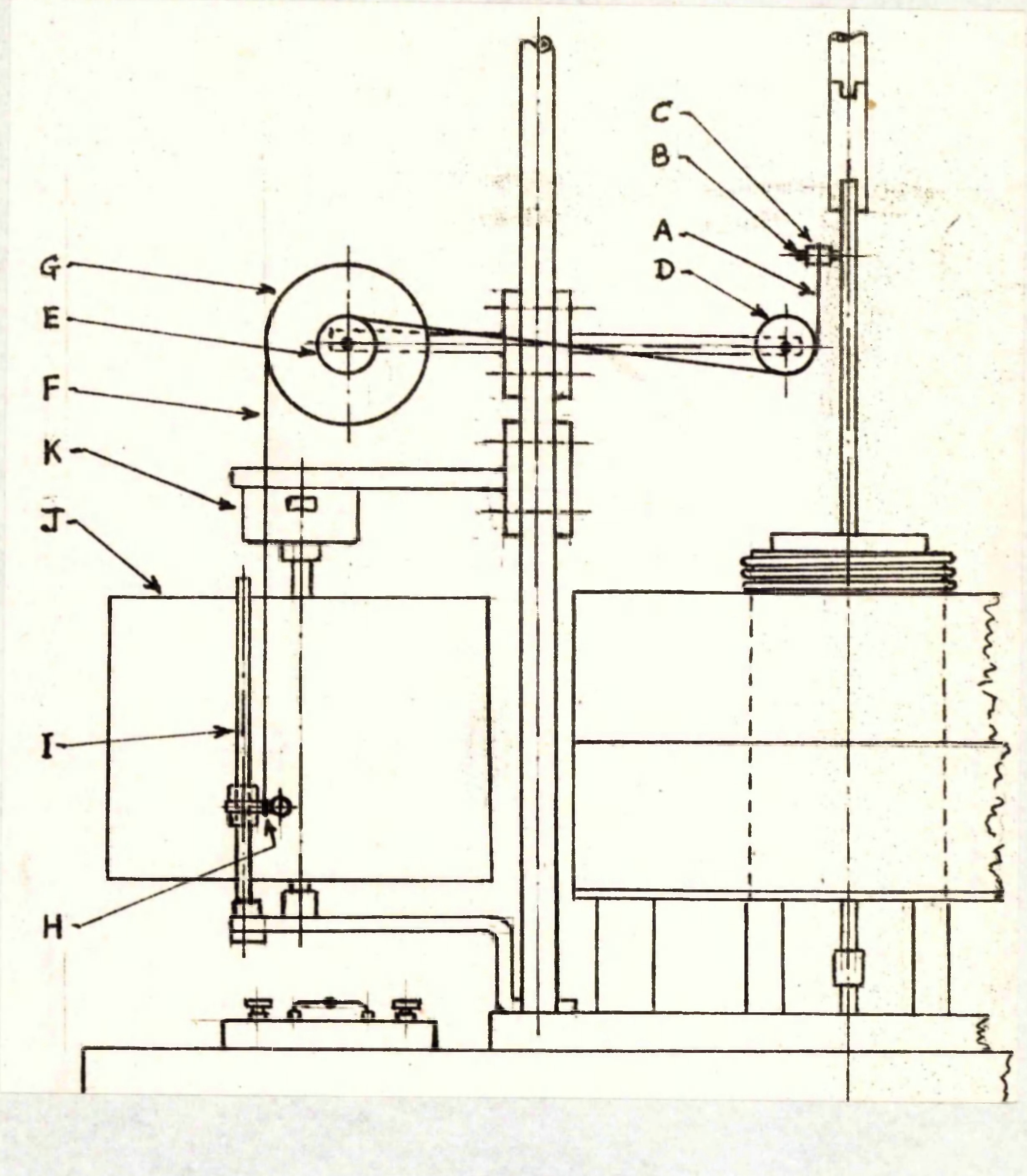


FIG. 8

CHAPTER IV.

EXPERIMENTAL TECHNIQUE.

EXPERIMENTAL TECHNIQUE.

The fact that coal is a complex organic material which is also heterogeneous in composition makes any investigation of its properties extremely difficult. This is especially the case in a study of the fundamental processes involved in the formation of coke, based on the behaviour of coking coals in the "plastic" range, since decomposition of the coal material is occurring throughout the period in which measurements can be made. In such an investigation consistent results can be obtained only by the adoption of a rigidly standardised experimental technique, and considerable attention was paid to this feature of the present work.

Sampling and Storage of Coal.

In order to minimise the effect of the heterogeneity of the coal material it would have been desirable to crush the bulk coal sample finely, so that successive test samples would have a representative petrographic composition. The serious effect of oxidation during storage on the swelling and coking properties of coal has, however, been noted by several authors (38,39,40) and it has been shown(38) that small particles of coal are more seriously affected in this respect than larger sizes. Because of this it was not considered advisable to store the coal in a finely divided condition, since it was imperative that the bulk sample could be kept for a considerable period of time without deterioration. In view of this a compromise was made and a bulk sample of $-\frac{1}{2}$" + $\frac{1}{4}$ " material used, since this allowed a sufficiently large number of increments to be taken for each experimental test to ensure a representative sample, while avoiding the greater susceptibility to deterioration of smaller sizes.

The coal was therefore crushed to pass a ½" sieve, care being taken to prevent excessive breakage. All the -¼" fraction was then removed by screening and discarded together with any predominantly shale like material, the -½" + ¼" fraction being retained for use in the experimental tests.

Spooner and Mott(38) noted that even 1" to 2" lumps of coal could show a serious loss of swelling power on storage for a period of 20 weeks. Since, in the present work, tests on any one coal extended over a comparable period, steps were taken to reduce the rate of oxidation of the bulk sample. It was originally intended to store the coal in vacuo. On one occasion in the early part of the work, however, a leakage of air into the vacuum system occurred due to failure of the vacuum pump. The effect of this on the coal proved to be extremely serious, the swelling power then being much lower than that of another part of the same original sample which had been stored in air for several weeks. In view of this observation and the difficulty of maintaining a suitably vacuum tight system over a long period,the coal was thereafter stored in an atmosphere of nitrogen subsequent to evacuation to remove as much adsorbed oxygen from the coal as possible. In order to avoid exposure of the whole bulk sample to air every time a test sample was taken,successive parts of the bulk sample, sufficient for about ten tests, were removed as required and stored separately, also under nitrogen and the actual test samples were taken from these portions. The coal storage vessels were re-evacuated and refilled with nitrogen each time a sample was removed. The advisability of this procedure was shown by the fact that on two occasions during work on the Hartley Dross coal, the part of the bulk sample in use showed a serious loss of swelling power, while a further portion of the bulk sample still retained its original swelling properties. It was found that the coals used could be stored in this way for several months with no detectable deterioration in the swelling properties of the bulk samples.

Since the swelling properties might have been affected by variation in the size grading and packing density of successive samples, the test samples were prepared according to a standard particle size grading. In theory any standard grading could have been used, but since Bennett(41) has shown that the Rosin-Rammler(42) size distribution equation holds for broken coal, this type of grading was adopted. The Rosin-Rammler equation is expressed as $R = 100e^{-\left(\frac{x}{\bar{x}}\right)^{n}}$, where R is the cumulative percentage on a sieve of aperture x, $\bar{x}$ the absolute size constant is the value of x for which R becomes $\frac{100}{e}$, and n is the distribution constant. An aggregate with a maximum particle size of - $\frac{1}{8}$", and a distribution constant n = 1 was chosen, the sample being composed of the following fractions:-

$-\frac{1}{8}" + \frac{1}{16}"$	16.8%	-36 + 72 mesh	29.3%
$-\frac{1}{16}"$ + 16 mesh B.S.S.	15.2%	-72 + 100 mesh	2.3%
- 16 + 36 mesh	30.0%	- 100 mesh	6.4%

A standard sample weight of 15 gms. was used in the main series of tests, the samples being prepared in the following manner:-

25 gms. of coal were taken, care being exercised that a representative sample was obtained. It was found that 25 gms. of coal were required to ensure that a sufficient amount of the various size fractions was obtained for a 15 gm. composite sample. The coal was first reduced to $-\frac{1}{8}"$ and the required weight of $-\frac{1}{8}" + \frac{1}{16}"$ material was taken. All the remaining material was then crushed to $-\frac{1}{16}"$ before screening on a 16 mesh B.S.S. sieve and weighing the $-\frac{1}{16}"$ + 16 mesh fraction. The remaining size fractions were then obtained in a similar manner in successive stages. By the adoption of this method of progressive crushing and screening, excessive breakage of the more friable constituents of the coal was avoided and the tendency for such material to be concentrated in the lower size fractions reduced.

After weighing out, the various size fractions were thoroughly mixed and fed into the Mullite crucible, described earlier, in which the bottom alundum disc and asbestos paper had been fitted, care being taken to avoid segregation of the coal. The sample was lightly tamped down in the crucible and the upper asbestos and alundum discs were then inserted. Crushing and assembly of the sample for each test was standardised to occupy a period of one hour to avoid variation in the time for which the crushed coal was exposed to air.

The assembled crucible was evacuated overnight for 16 hours. The vacuum was then broken with nitrogen and the crucible was placed in the heating chamber of the apparatus, as shown in Fig.4 (Chapter III). The heating chamber was then flushed out with nitrogen for 15 minutes before heating was commenced.

Test Procedure.

A constant pressure method was employed in all the present work on the swelling properties, i.e., the coal samples were heated at a constant rate under a constant pressure, the variation of sample volume with temperature being recorded.

In the technique originally employed, pressure was applied to the coal by means of an hydraulic system and the volume change was noted by a small revolving dial, as described earlier (Chapter III). This method was used in the work on the Easton coal, the results of which will be given later (Chapter V).

A slight pressure was first applied to the coal sample and the zero reading of the volume recording dial was noted. Heating was then commenced, the desired heating rate being maintained as closely as possible throughout the test. The required pressure was applied when a temperature of 300°C was reached and thereafter kept constant by adjustment of the hydraulic valve till the swelling period was completed. In a few of the early tests pressure was not applied to the coal sample until swelling actually commenced. This variation in procedure was found to result in a higher initial swelling temperature being recorded, but there was no noticeable effect on the rate of swelling of the sample and the former method of applying pressure was generally adopted since it involved fewer adjustments at the beginning of the swelling period.

It was found, however, that the above technique was not particularly successful. Owing to the fact that the heating rate tended to vary markedly during the swelling range, frequent temperature readings and appropriate supply voltage adjustments had to be made to maintain a steady rate of temperature rise. The pressure valve also required continuous adjustment due to the swelling of the coal sample leading to an increase in the applied hydraulic pressure and readings of the volume indicator dial had to be taken at 1/2 minute intervals to obtain a reasonably accurate record of the swelling characteristics. Thus the number of readings and adjustments required during the swelling range proved to be greater than could be conveniently or accurately made. As a result considerable variation of heating rate occurred in many of the tests carried out owing to the fact that a continuous check on the temperature rise was impracticable.

It was therefore decided to make certain alterations to the apparatus before work began on a second coal. The hydraulic pressure was replaced by a direct load on the coal and a recording drum mechanism was also incorporated to record the swelling characteristics graphically, as already described in Chapter III. Thus adjustments of the pressure and readings of the sample volume were no longer required during the swelling period and greater attention could be devoted to the maintenance of the desired heating rate throughout the test. It was, in fact, found that accurate control of the temperature was now possible and this was reflected in an improvement in the reproducibility of the test results.

The standard procedure used in the remainder of the present work is detailed below.

After assembly of the crucible on the heating chamber of the apparatus, a load of 5 lb./sq.in. was applied to the coal sample, the cord of the drum recorder was attached to the upper electrode and the zero position of the recording pen marked on the recorder chart. The heating chamber having been flushed out with nitrogen for 15 minutes to expel all air, the generator was switched on and heating commenced. Temperature readings of the inner and outer thermocouples were taken at 5 minute intervals during the early stages of the test and the desired rate of temperature rise obtained by variation of the voltage supplied to the valve generator. The current supplied to the outer resistance heater was controlled by a rheostat, the temperature of the outer thermocouple being kept just below that of the inner so that radiation loss from the surface of the crucible was minimised.

When a temperature of 300°C was reached, the load on the coal sample was increased to the desired value for the test, except of course, in the case of tests at 5 lb./sq.in., and from this point until the completion of the run the temperature of the inner thermocouple was taken at 1/2 minute intervals. The initial contraction, or softening temperature of the coal sample was indicated by a slight downward motion of the recording pen. The recording drum was set in operation at this stage and rotated at a constant speed throughout the remainder of the test.

Heating was continued for some time after the maximum swelling temperature of the sample had been reached until the recording pen showed no further movement indicating solidification of the plastic coal. Some of the experimental tests, however, were curtailed by leakage of the plastic coal round the retaining discs. After completion of the test the generator was switched off and the recording drum stopped, the crucible being allowed to cool before it was removed from the heating chamber. The semi coke produced was carefully extracted and examined to ensure that there were no signs of non-uniform heating of the samples.

Details of a typical test are shown in Table 1 and the swelling curve obtained is reproduced in Fig.9. From the swelling graph the initial (I.S.T.) and maximum (M.S.T.) swelling temperatures are found and the swelling rate is calculated from the gradient of the linear portion of the curve as shown in Table I.

TABLE I.

Test B1. Sample Prepared 2/11/53.
Tested 3/11/53.

Pressure 5 lb./sq.in. Heating Rate 2.5°C/min.

15 gm. coal sample Crucible No.2.

Time (mins).	Temperature °C		Heating Rate °C/min.	Time (mins).	Temperature °C		Heating Rate °C/min.
	Inner	Outer			Inner	Outer	
0	20.0	20.0	0.0	90	258.4	253.8	2.6
5	40.7	28.1	4.1	95	271.3	268.2	2.6
10	54.3	35.0	2.7	100	283.9	281.1	2.5
15	67.5	48.6	2.6	105	297.1	295.5	2.6
20	80.7	63.4	2.6	110	309.0	308.3	2.4
25	94.8	82.1	2.8	115	322.1	320.0	2.6
30	107.0	100.2	2.5	120	334.7	333.2	2.5
35	120.2	118.7	2.6	125	347.2	245.1	2.5
40	132.9	133.0	2.5	130	359.9	359.0	2.5
45	145.3	146.5	2.5	135	373.0	370.9	2.6
50	157.6	157.0	2.5	140	385.6	383.0	2.5
55	169.6	168.5	2.4	145	398.7	397.0	2.6
60	181.5	180.1	2.4	150	411.4	409.8	2.5
65	194.0	192.3	2.5	155	424.1	423.2	2.5
70	205.9	203.8	2.4	160	437.2	436.8	2.6
75	218.1	215.2	2.6	165	449.8	448.0	2.5
80	231.1	228.5	2.6	170	462.5	460.1	2.5
85	245.2	240.4	2.7				

Recording Drum Started 137 mins. Stopped 171 mins.

Additional Pressure Applied - (none)

From swelling graph I.S.T. at 146 mins. i.e. 401.4°C.
M.S.T. at 161 mins. i.e. 439.7°C

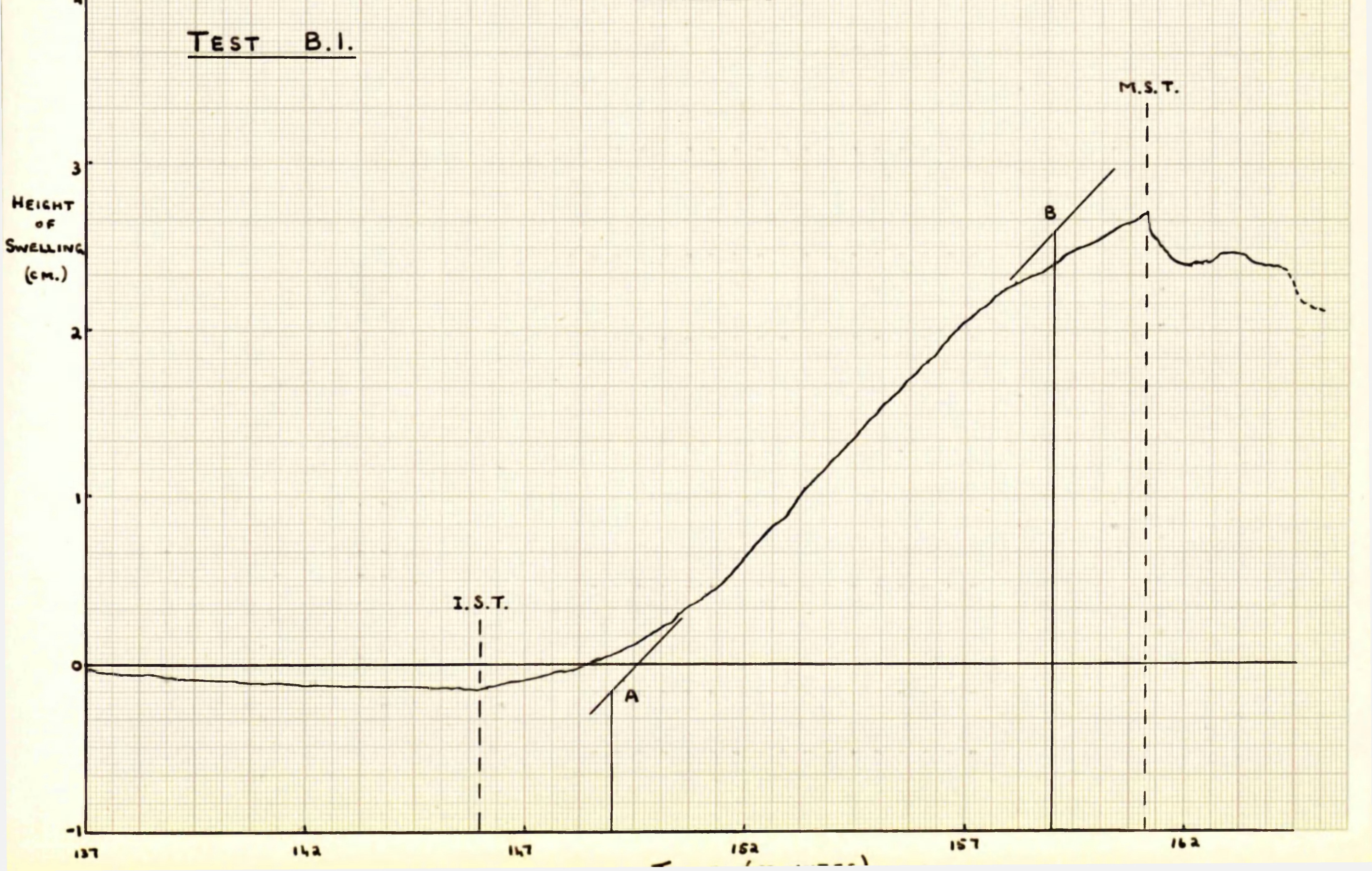
Swelling Rate (from gradient A-B) ≡ 2.74 cm. in 10 mins.
Area of crucible = 20.0 cm^3.

$$\therefore \frac{dv}{dt} = \frac{2.74 \times 20.0}{10} = 5.48 \text{ cc./min.}$$

Absolute
Pressure = 1.34 atms. Mean Temp. 695°K

$$\therefore \frac{dv}{dt}_{\text{NTP}} = 2.89 \text{ cc./min.}$$

FIG. 9


TEST B.I.
HEIGHT OF SWELLING (CM.)
4
3
2
1
0
-1
137
142
147
152
157
162
I.S.T.
M.S.T.
A
B

Except where otherwise stated, the above procedure was closely followed in all the experimental work described in the following Chapter.

CHAPTER V.

EXPERIMENTAL WORK AND RESULTS.

EXPERIMENTAL WORK AND RESULTS.

In the present work the relationship between swelling rate and applied pressure has been studied for various coals and the influence of rate of heating on the swelling characteristics has also been investigated, together with the effect of such variables as coal particle size and sample weight. A detailed account of the work on the various coals and the results obtained is given below.

Coals Tested.

The main part of the experimental work was carried out with three coals, two of which, namely Easton and Hartley Dross were of Scottish origin, the third, Backworth, being a Northumberland coal. The proximate and ultimate analyses and British Standard Swelling Nos. of these coals are given in Table 2, together with details of the Kingshill and Sacriston coals studied by Taylor(26), which will be referred to later. Very little data was obtained on the swelling behaviour of the sixth coal listed, the Welsh Cwymtillery but all six coals were used in the volatile evolution experiments which will be dealt with in the following Chapter.

Easton Coal.

The Easton coal was the first to be used in the present investigation and, as already noted in Chapter IV, the technique employed in this early work was not so satisfactory as that adopted later, in that considerable variation in heating rate occurred during swelling in several of the experimental runs. Numerous tests were carried out under applied pressures of up to 62·5 lb./sq.in. (4·25 atmospheres), the maximum pressure

TABLE 2.

Coal	Series Letter	Source	Proximate Analysis(dry) VM%	FC%	Ash%	Ultimate Analysis(Parr) C%	O%	H%	N%	B.S. Swelling No.
Easton	E	Scottish	32.1	60.2	7.7	85.70	7.63	5.23	1.43	3
Hartley Dross	H	Scottish	30.9	67.0	2.1	86.70	5.73	5.25	2.11	$7\frac{1}{2}$
Backworth	B	Northumberland	37.8	60.3	1.9	86.20	6.38	5.52	1.78	$7\frac{1}{2}$
Kingshill	K	Scottish	34.2	61.7	4.1	84.84	8.01	5.42	1.73	4
Sacriston	S	Dirham	28.5	66.8	4.7	89.48	3.78	5.16	1.56	8
Cwymtillery	C	Welsh	28.8	65.1	6.1	89.18	4.22	5.12	1.43	8

possible with the hydraulic system then in use, the desired heating rate in each case being 2·5°C/min. The swelling characteristics of the coal were represented graphically by plotting the volume indicator readings, suitably corrected to give the sample volume in c.c., against time. It was found that, where large variations in heating rate had occurred, irregular swelling curves were obtained and, since no definite swelling rate could be measured, the results of such tests were neglected. Reasonably linear swelling curves were obtained, however, in those tests in which the rate of heating had been nearly constant over the plastic range. The heating rates in such tests varied between 2·25 and 2·75°C/min. Subsequent work on other coals showed that the swelling rate decreases with lower heating rates. The relationship is not strictly linear, but may be considered to be approximately so without appreciable error over a small range of heating rate. The above results were therefore calculated to a mean heating rate of 2·5°C/min. on this basis in order to account for the variation from test to test.

The results of the series of tests on the Easton coal are contained in Table 3. For ease of reference the tests are listed and numbered in order of increasing applied pressure, as are the results shown later in Tables 4, 5 and 6. This is not, however, the order in which the tests were performed, the pressures applied in successive tests being chosen at random. This was considered advisable since any variation in swelling properties obtained with increasing pressure cannot then be attributed to progressive changes in the swelling power of the coal during storage.

TABLE 3.

Easton Coal

15 gm. samples. Heating Rate 2.5°C/min.

R = 24.6 cc NTP/min. Mean Temperature 705°A

Test No.	P(d) at.	I.S.T°C	M.S.T.°C	Measured $\frac{dv''}{dt}$ cc./min.	$\frac{dv}{dt}$ cc.NTP/min.	S	π
E1	0.42	415	443	1.60	0.88	56.5	2.04
E2	0.42	416	443	2.55	1.40	55.2	1.95
E3	1.28	418	445	2.78	2.45	17.3	0.584
E4	1.70	417	443	3.52	3.68	12.3	0.391
E5	2.13	412	443	3.18	3.86	9.7	0.302
E6	2.55	419	444	3.65	5.02	7.7	0.225
E7	2.55	422	448	3.62	4.97	7.7	0.226
E8	2.98	413	440	3.00	4.62	6.7	0.200
E9	3.40	414	450	3.40	5.79	5.5	0.150
E10	3.83	414	443	3.32	6.20	4.8	0.133
E11	3.83	415	438	3.17	5.93	4.9	0.136
E12	4.25	417	452	3.14	6.30	4.3	0.118

TABLE 4.

Kingshill Coal.

15 gm. samples.

Heating Rate 2.5°C/min.

R = 25.6 cc NTP/min.

Mean Temperature 700°A

Test No.	P(d) at.	I.S.T°C.	M.S.T°C.	Measured $\frac{dv''}{dt}$ cc./min.	$\frac{dv}{dt}$ cc.NTP/min.	S	π
K1	0.08	407	430	1.40	0.59	314	11.60
K2	0.42	412	437	2.47	1.37	57.6	2.06
K3	1.50	407	432	4.72	4.60	14.0	0.431
K4	2.57	407	437	6.24	8.68	6.58	0.164
K5	3.40	410	442	5.68	9.71	4.67	0.109
K6	4.25	415	443	4.65	9.51	3.79	0.090

The results obtained by Taylor(26) for the Kingshill coal, using a similar procedure, are given in Table 4 and the relationship between the swelling rate, $^{dv}/_{dt}$ in c.c. at N.T.P. per minute, and the applied pressure, P(d) in atmospheres, which he obtained is compared with that of the Easton coal in Figure 10. The increase in swelling rate with initial increase in applied pressure, noted by Taylor, was also found for the Easton samples, but no inflexion in the curve was obtained at the highest pressure used, although it will be seen, from Figure 10, that the swelling rate values appear to be approaching a maximum.

As already discussed in Chapter II, Taylor(26) expressed the swelling process by the equation

$$R - \left(\frac{dv}{dt}\right) = P(d) \cdot (s) \qquad \dots\dots\dots\dots \qquad (1)$$

where (s) is the "permeability" of the coal mass and R is the volume rate of generation of volatile products during swelling. The values of R for the Kingshill and Easton coals were determined experimentally as described in Chapter VI, and hence the permeability, (s) in c.c. N.T.P./ atmosphere/min., of the coal samples in the various tests was calculated, the results being shown in Tables 3 and 4. It should be noted that the permeability figures shown in Table 4 are not the same as those obtained by Taylor, since he estimated the value of R by extrapolation of the swelling rate/pressure graph, as shown by the dotted line in Figure 10. This extrapolation has been found to give a lower value for R than that determined experimentally.

FIG. 10

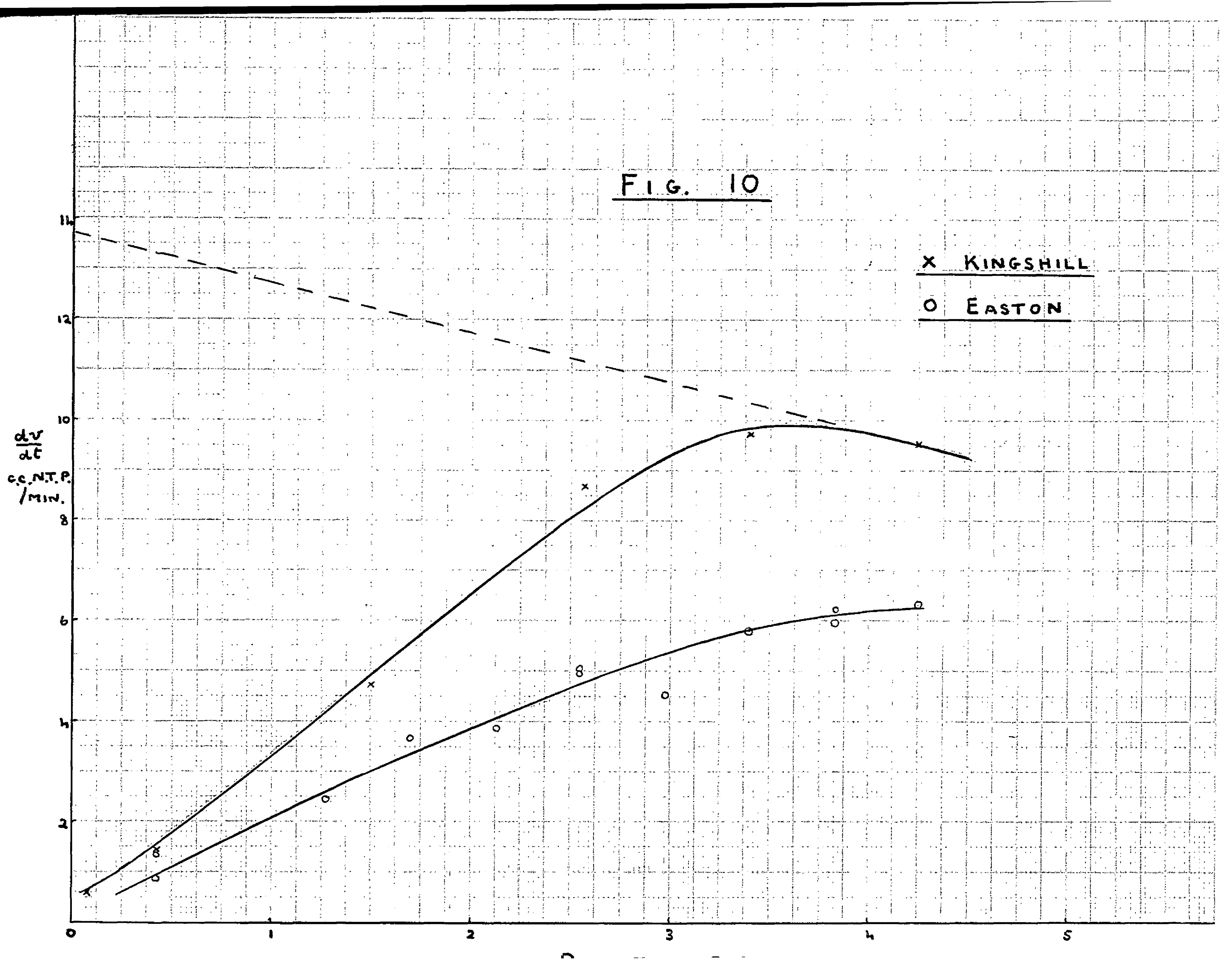


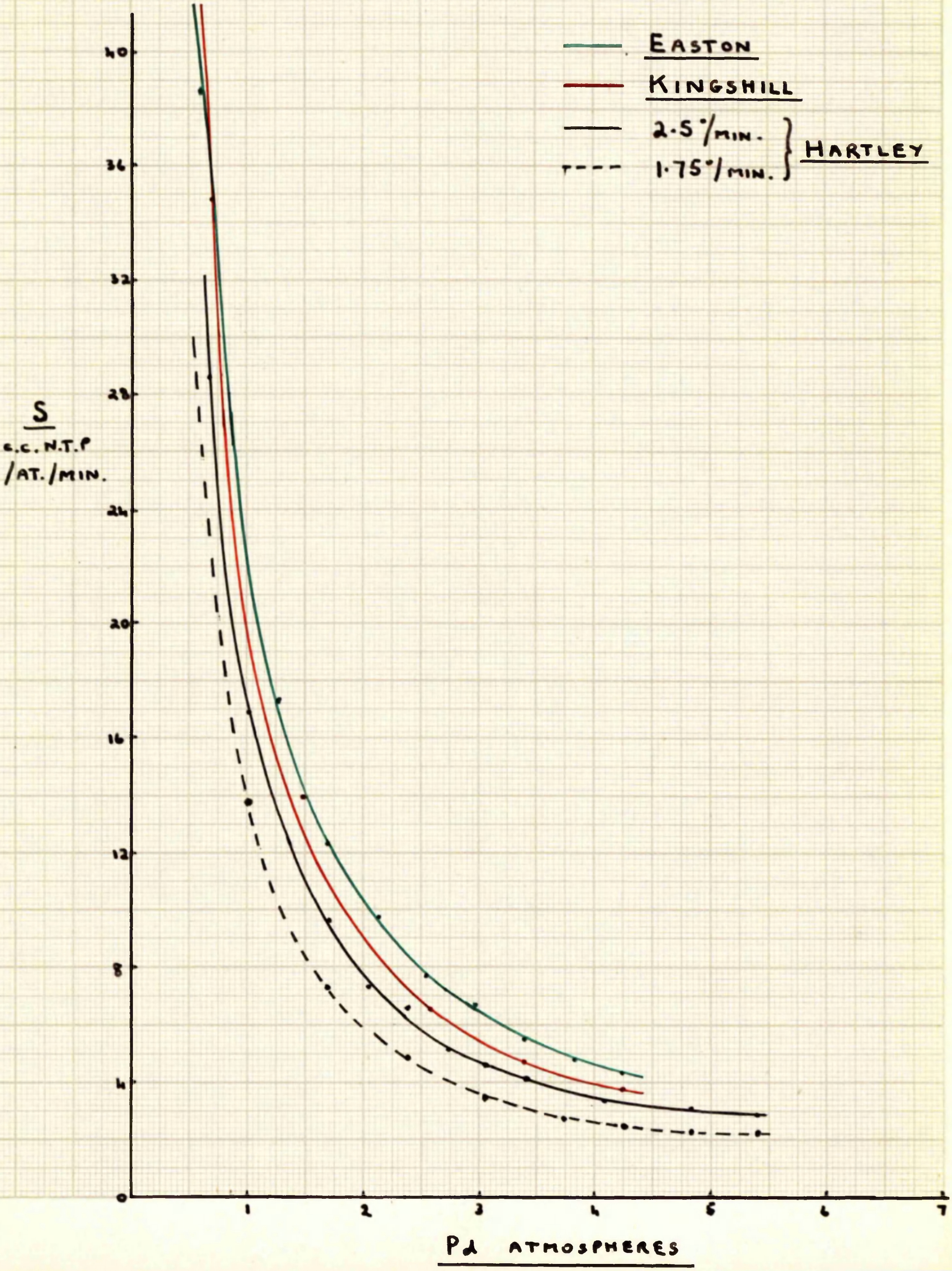
Figure 11 shows the variation of (s) with applied pressure for the Kingshill and Easton coals. It is not intended to discuss the results obtained at this stage, beyond noting that the curves are very similar, a minimum(s) value being approached in both cases. The significance of the value of π , the permeability coefficient, shown in Tables 3 and 4, will also be discussed subsequently in Chapter VII.

In view of the difficulty experienced in maintaining the correct heating rate in the experimental work on the Easton coal, and since it was also desirable to employ higher applied pressures, the alterations to the apparatus already described in Chapter IV were undertaken, before further series of tests were attempted. This work occupied several weeks and at the end of this period it was found that the Easton coal had suffered a serious loss in swelling power. A sample of a second coal, namely Hartley Dross was therefore obtained.

Hartley Dross.

Preliminary tests on the Hartley Dross, using the modified apparatus, showed that the heating rate during the test could now be controlled within narrow limits. It was also possible to measure the swelling rate of the sample much more accurately from the recorded swelling graph than from the volume indicator readings obtained previously. Because of these improvements the general reproducibility of the results obtained was considerably greater than in previous tests.

FIG. 11


EASTON
KINGSHILL
2·5°/MIN.
1·75°/MIN.
HARTLEY
S
c.c. N.T.P
/AT./MIN.
40
36
32
28
24
20
16
12
8
4
0
1
2
3
4
5
6
7
Pd ATMOSPHERES

It was noted that in all the experimental tests the heating rate tended to increase when swelling commenced and that the power input to the generator had to be reduced at this stage. This effect was similar to that which led to variation in the heating rate during swelling in the experiments on the Easton coal. Unfortunately it is impossible to tell whether this tendency is due to variation in the dielectric properties of the coal sample or results from a heat evolution during coking, which might be expected from the work of Tettweiler(43) who reported that Ruhr coals showed exothermic heats of coking.

In the work on the Hartley coal, some difficulty was encountered due to deterioration of the swelling power of the coal during storage. As already described in Chapter IV, the test samples were taken, not from the main bulk sample, but from smaller portions of it stored separately, in order to minimise exposure of the main sample to air. On two occasions the portion of the bulk sample in use showed a marked decrease in swelling power, accompanied by an increase in the initial swelling temperature of the coal. The loss of swelling power occurred very suddenly, there being no indication of any gradual deterioration in previous test samples. It was found that the remainder of the bulk sample still retained its original coking properties, so that further tests on another portion of the main sample were possible. Investigation of this coal was, however, ultimately terminated by a similar decrease in the swelling power of the bulk sample. Rose and Sebastian(44), in a study of oxidation during storage, also noted sudden deterioration in the coking properties of some coals. It was found that a considerable increase in oxygen content could occur with little change in agglutinating power, while rapid decreases in the agglutinating value were obtained with no appreciable change in oxygen content.

The relationship between swelling rate and applied pressure was studied with the Hartley Dross at two different heating rates, 1·75 and 2·5°C/min., both series of tests being carried out concurrently, so that the swelling power of the coal would be strictly comparable in the two sets of experiments. Details of the results and the calculated permeability values are given in Table 5. From the swelling rate/pressure curves shown in Figure 12 it is evident that a definite inflexion occurs at an applied pressure of about four atmospheres and that the swelling rate thereafter shows a progressive decrease with increasing pressure.

There is a striking similarity in the variation of swelling rate with pressure for the two heating rates used. Lower swelling rates are obtained in the lower heating rate tests, the difference between the rates of swelling being approximately constant over the whole pressure range so that the curves are almost parallel, (see Figure 12). The other notable feature of the result is that the permeability of the coal mass is lower at lower heating rates as may be seen from the permeability graphs for the Hartley Dross coal in Figure 11.

Since a satisfactory technique had now been established and consistent results obtained with the Hartly Dross, it was decided to carry out similar test series on other coals.

TABLE 5.

Hartley Dross

15 gm. samples.
R = 20.0 cc NTP/min.

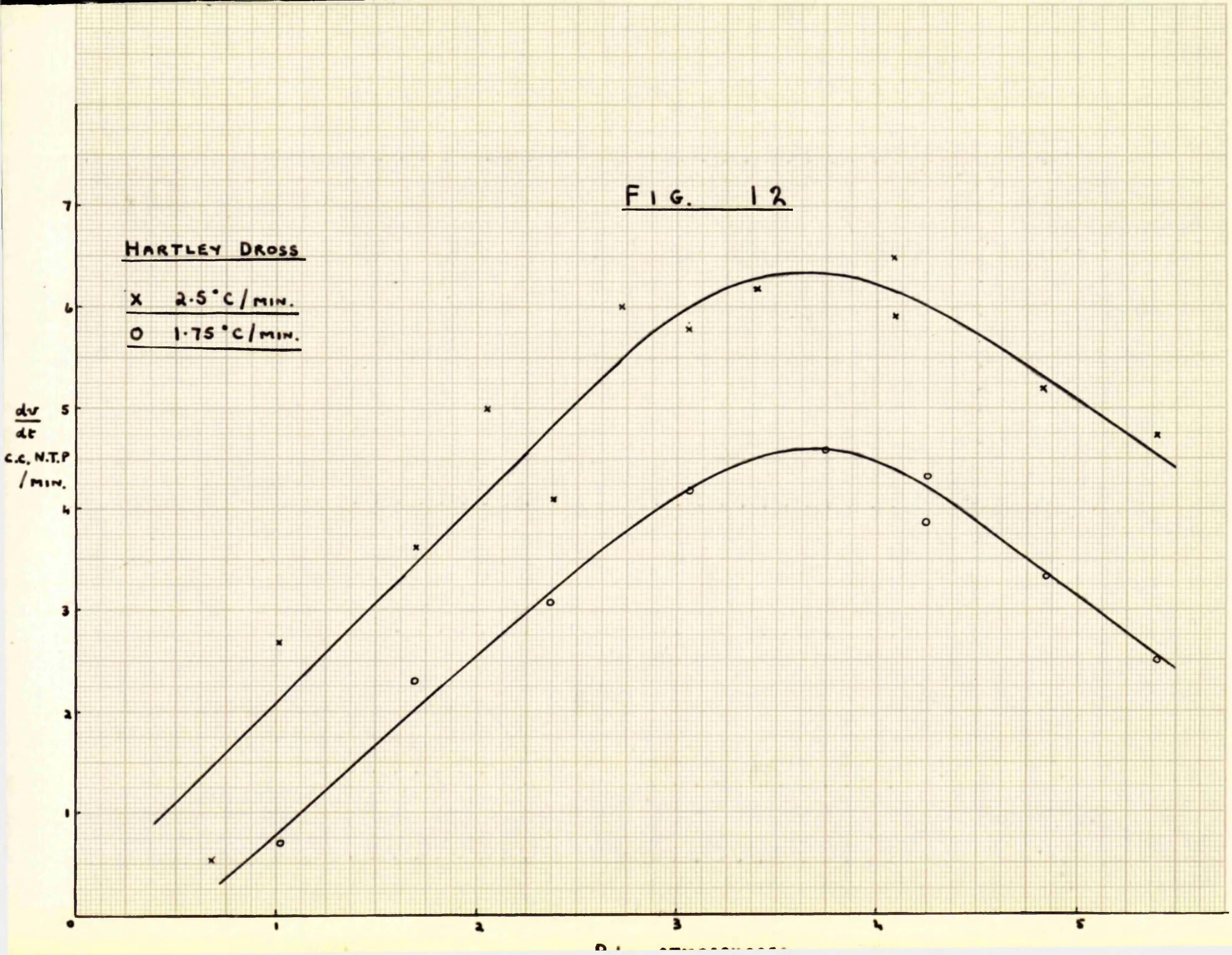
Heating Rate 2.5°C./min.
Mean Temperature 715°A.

Test No.	P(d) at.	I.S.T. °C.	M.S.T. °C.	Measured $\frac{dv^*}{dt}$ cc/min.	$\frac{dv}{dt}$ cc.NTP/min.	S	π
H1	0.68	427	443	0.86	0.55	28.6	0.990
H2	1.02	429	455	3.51	2.71	16.9	0.520
H3	1.70	423	454	3.53	3.64	9.60	0.280
H4	2.04	425	455	4.32	5.01	7.34	0.196
H5	2.38	430	456	3.19	4.12	6.67	0.189
H6	2.72	428	456	4.27	6.02	5.14	0.128
H7	3.06	431	462	3.74	5.80	4.64	0.117
H8	3.40	432	459	3.70	6.20	4.06	0.100
H9	4.08	423	452	3.36	6.51	3.30	0.079
H10	4.08	430	-	3.05	5.91	3.45	0.086
H11	4.83	430	458	2.34	5.21	3.06	0.080
H12	5.40	430	458	1.95	4.75	2.83	0.077

Heating Rate 1.75°C/min. R = 14.7 cc/min. Mean Temperature 710°A

Test No.	P(d) at.	I.S.T. °C.	M.S.T. °C.	Measured $\frac{dv^*}{dt}$ cc/min.	$\frac{dv}{dt}$ cc.NTP/min.	S	π
H13	1.02	425	440	0.93	0.72	13.7	0.482
H14	1.70	421	442	2.24	2.32	7.27	0.227
H15	2.38	423	447	2.38	3.09	4.88	0.143
H16	3.06	423	448	2.68	4.19	3.43	0.091
H17	3.74	422	450	2.53	4.60	2.70	0.069
H18	4.25	427	451	1.93	3.89	2.55	0.069
H19	4.25	424	447	2.18	4.40	2.42	0.063
H20	4.83	424	442	1.50	3.36	2.37	0.068
H21	5.40	423	441	1.02	2.51	2.26	0.068

FIG. 12



Cwymtillery Coal.

It had been intended to use a Welsh Cwymtillery coal on the next part of the experimental work. Initial tests on this coal, however, showed that its swelling properties could not be determined by the technique used for the other coals tested. Shortly after the initial swelling temperature was attained in the experimental tests the rate of heating suddenly decreased and the temperature of the sample remained practically constant, even when the power input was increased to the maximum possible. This effect was found in all the tests which were attempted and further investigation of the swelling characteristics of the coal was therefore impossible.

A pronounced endothermic reaction during coking could account for the observed decrease in heating rate, but such an explanation is unlikely in view of the increased heating rate obtained with the other coals and the work of Tettweiler(43) who found the heat of coking to be exothermic for a wide range of coals. It was also found that while variation of the power input to the generator had no effect, the temperature of the coal sample could be raised by increasing the current supplied to the resistance furnace surrounding the crucible. This behaviour can only be attributed to an alteration in the dielectric properties of the coal sample and a resultant failure of the applied high frequency field to produce further heating, but no explanation for such an alteration in the properties of this particular coal has been obtained.

Backworth Coal.

The Backworth coal was the last to be investigated in the present work. The behaviour of this coal was similar to that of the Easton and Hartley Dross, in that there was a tendency for the heating rate to rise during swelling. Some difficulty was experienced, however, in confining the coal in the crucible at high pressures, since the plastic mass appeared to become very fluid and tended to escape round the sides of the retaining discs. In some tests escape occurred shortly after the initial swelling temperature and no measurement of the swelling rate could be made, but in several cases, even although escape took place towards the end of the test and the maximum swelling temperature was not reached, the swelling rate was determined from the portion of the swelling graph obtained.

Two complete series of tests were carried out at heating rates of 1.75 and 2.5°C/min., under applied pressures of up to six atmospheres. This involved a direct load of about $2\frac{1}{2}$ cwts. on the upper electrode and higher pressures than this were found to be impracticable; indeed some of the crucibles used failed during the high pressure tests. The results of the experimental tests on the Backworth coal are given in Table 6, and tl corresponding swelling and permeability graphs are shown in Figures 13 and 14, from which the general similarity in the behaviour of the Backworth coal to that of the Hartley Dross (see Figures 12 and 11) is evident.

It was intended to perform a further series of tests on the Backworth coal at a heating rate of 3.75°C/min. In several of these tests, however, unexpectedly low swelling rates were obtained; the

TABLE 6.

Backworth Coal

15 gm. samples
R = 25.9 cc NTP/min.

Heating Rate 2.5°C/min.
Mean Temperature 695°A

Test No.	P(d) at.	I.S.T. °C.	M.S.T. °C.	Measured $\frac{dv''}{dt}$ cc/min.	$\frac{dv}{dt}$ cc. NTP/min.	S	π
B1	0.34	401	440	5.48	2.89	67.7	2.18
B2	0.34	402	436	5.74	3.02	67.3	2.15
B3	1.02	398	434	5.30	4.20	21.3	0.645
B4	1.70	400	445	4.92	5.21	12.2	0.354
B5	2.72	404	-	4.55	6.65	7.08	0.191
B6	2.72	403	449	4.73	6.91	6.97	0.185
B7	3.74	403	-	4.34	8.08	4.76	0.119
B8	3.74	399	-	4.32	8.04	4.77	0.119
B9	4.25	401	-	4.62	9.53	3.85	0.088
B10	4.83	404	-	3.84	8.79	3.54	0.085
B11	5.51	405	-	3.50	9.08	3.05	0.072
B12	6.08	406	-	2.98	8.28	2.90	0.072
Heating Rate 1.75°C/min. R = 19.1 cc NTP/min. Mean Temperature 687°A							
B13	0.34	398	431	4.13	2.20	49.7	1.59
B14	0.34	399	430	4.33	2.31	49.3	1.57
B15	1.70	392	423	3.94	4.23	8.74	0.247
B16	2.72	392	-	3.56	5.26	5.09	0.134
B17	2.72	393	431	3.62	5.34	5.05	0.132
B18	3.74	401	439	3.21	6.05	3.49	0.086
B19	4.83	404	445	2.92	6.75	2.55	0.060
B20	5.51	387	426	2.33	6.03	2.37	0.058
B21	6.08	399	430	1.91	5.37	2.26	0.059
Heating rate 3.75°C/min. R = 37.8 cc NTP/min. Mean Temperature 715°A							
B22	0.34	415	-	4.68	2.39*	-	-
B23	1.70	412	-	6.27	6.46	18.4	0.604
B24	2.72	414	-	5.98	8.49	10.8	0.302
B25	3.74	424	-	2.88	5.20*	-	-
B26	4.83	416	486	4.98	11.09	5.5	0.140
B27	5.51	421	-	3.46	8.60*	-	-

* Very poor curves and indications of uneven heating.

FIG. 13

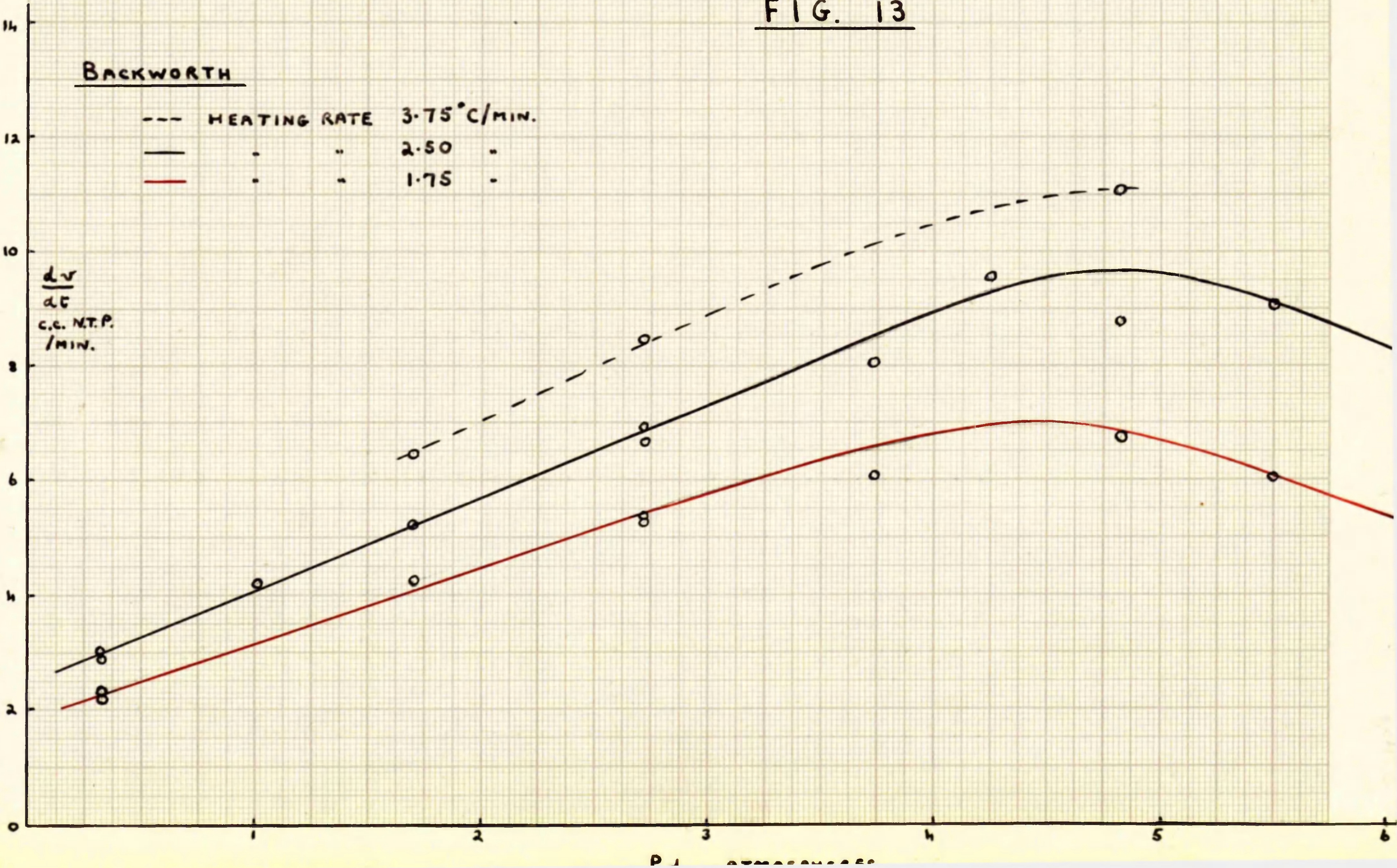
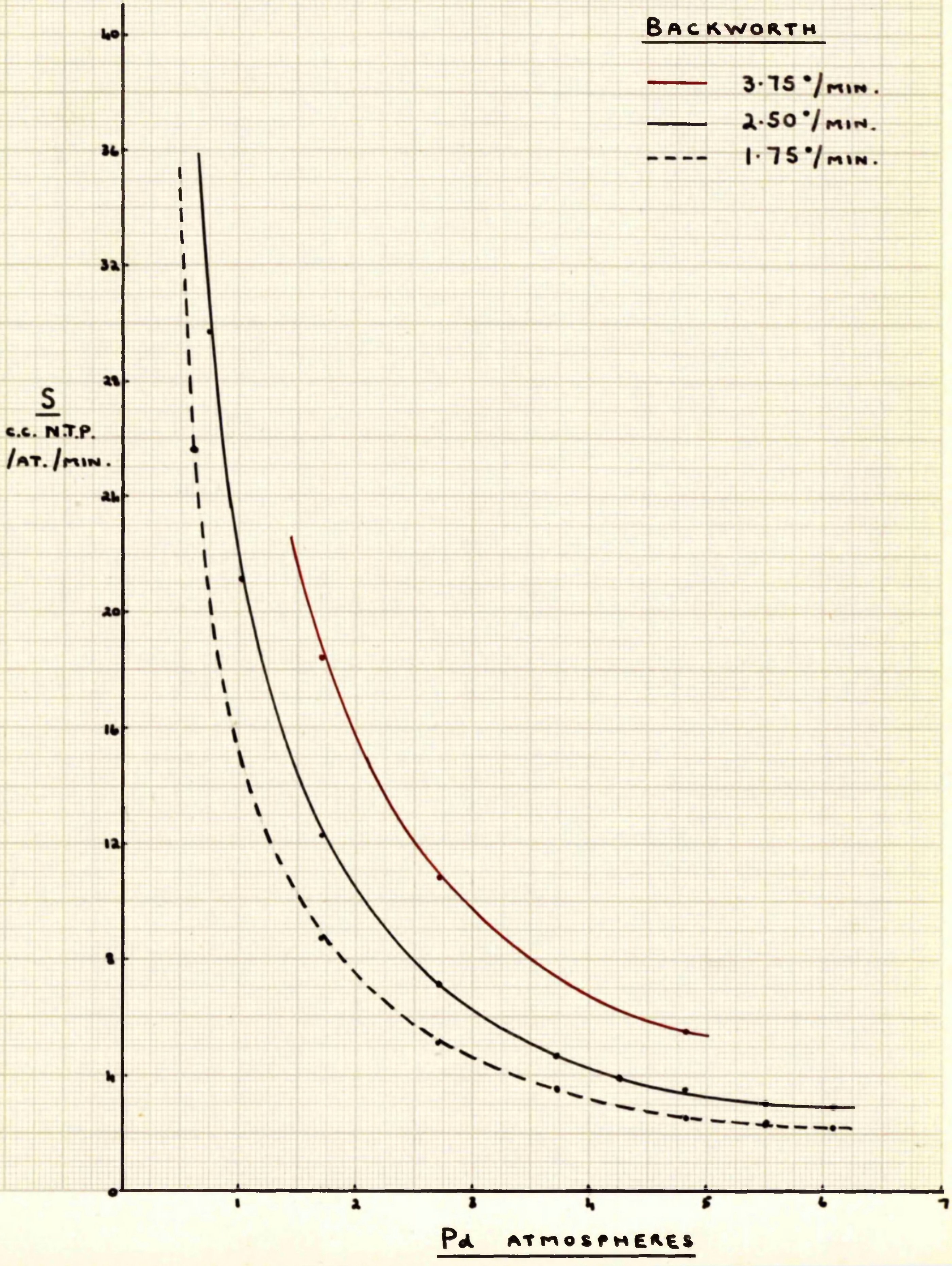

BACKWORTH
--- HEATING RATE 3·75°C/MIN.
" " 2·50 "
" " 1·75 "
dv/dt c.c. N.T.P. /MIN.
14
12
10
8
6
4
2
0
1
2
3
4
5
6

FIG. 14


BACKWORTH
3·75°/MIN.
2·50°/MIN.
1·75°/MIN.
S
c.c. N.T.P.
/AT./MIN.
0
4
8
12
16
20
24
28
32
36
40
1
2
3
4
5
6
7
Pd ATMOSPHERES

swelling curves were also irregular and difficulty was experienced in maintaining regular heating. Subsequent examination of the semi coke produced in such tests showed that there were definite signs of uneven heating of the coal sample, part of which had a greyish overheated appearance, while the upper layers of the sample showed incomplete fusion of the original coal particles. This was the first occasion on which such an effect had been observed.

The results of six tests at the high heating rate are included in Table 6. In tests B 23, 24 and 26, there was no indication of uneven heating and, as shown in Figures 13 and 14, the results of these tests confirm the general variation in swelling rate and permeability found at lower heating rates. Non uniform heating, however, occurred in the other three tests (B 22, 25 and 27) and the swelling rates obtained are actually lower than in corresponding experiments at a heating rate of 2·5°C/min. In view of this tendency and since it was also found to be difficult to prevent leakage of plastic coal round the retaining discs in high pressure, high heating rate tests, the series of experiments at 3.75°C/min. was not completed.

The Backworth coal was also used in a number of tests in which the effect of coal particle size and packing density was investigated. The swelling properties of 15 gm. samples of - 3/32" + 1/16" and -36 + 100 mesh coal were compared and the effect of packing density was also studied by testing a composite sample of 65% - 3/32" + 1/16" and 35% - 36 + 100 mesh material, which corresponds approximately to the maximum packing density obtainable with two different particle sizes(45), since the voids between the larger grains are occupied by the smaller particles when the ratio of particle diameters is about 10 to 1, as above. In order to minimise variation in the petrographic composition of the coarse and fine samples used, about 25 gms. of coal were taken for each test and crushed to below the upper size limit required so that in each case the test sample taken corresponded to the largest size fraction of the crushed coal. These results are given and discussed in Chapter VII.

The effect of sample weight was the final variable to be studied, 7.5, 15 and 30 gm. samples of Backworth coal of the usual size grading being tested. The results of these experiments (see Table 20, Chapter VII), will be discussed at a later stage. In some of the tests in which 30 gm. samples were used non uniform heating of the coal sample was again observed. It would appear that, since this effect has only been found at high heating rates and with large samples, i.e., when the power requirements are high, non uniform heating may be an indication, not of the failure of dielectric heating as such but rather of the inadequacy of the generator at present in use.

Before proceeding to the discussion of the results obtained in this part of the work, it is proposed to describe, in the following Chapter, the supplementary work which was carried out on the determination of the rate of generation of volatiles from coal during the plastic range.

CHAPTER VI.

DETERMINATION OF RATE OF EVOLUTION OF VOLATILE MATTER.

DETERMINATION OF THE RATE OF EVOLUTION OF VOLATILE MATTER.

If the view is taken that permeability is a controlling factor in the swelling behaviour of coking coals, then the time rate of generation of volatile matter in the plastic mass, which for simplicity will be referred to as R, becomes of primary importance, the extent of swelling being determined by these two factors.

Taylor(26) expressed the swelling mechanism by the equation $R - \frac{dv}{dt} = P(d). S$, and in order to obtain values for (S), the permeability of the coal, R was determined indirectly from the graphical relationship between $\frac{dv}{dt}$, the rate of swelling in cc NTP/min., and the applied pressure P(d), as described earlier in Chapter 2. Evaluation of R by this method is unsatisfactory, since it presupposes a strictly linear variation of gas escape with applied pressure, which supposition is difficult to confirm accurately from the experimental results. It is obvious that a direct determination of R would be of considerable value in interpreting the data obtained from the swelling tests and in providing evidence on the validity of the above approach to the swelling mechanism.

The main problem to be faced, in devising an experimental technique for a direct determination of R, is that the oil and tar vapours produced from the coal tend to be unstable and, if pyrolysis or condensation of these vapours takes place, the measured evolution rate will not correspond to that obtaining during swelling of the plastic coal.

Several workers have investigated the evolution of volatile matter from coal. Two main types of determination have been made, those in which the rate of loss of weight is found(46,47), and those which determine the amount and constitution of the vapour and gases evolved (48,49,50). A value could be obtained for R from results of the former class, if the average molecular weight of the volatile products were known. Any estimation of the molecular weight, based on the constitution of the complex gases, oil and tars evolved, would, however, be liable to serious error and could give only a very approximate value of R. The method which has been adopted in investigations of the second type is similar in principle to the Gray-King coal assay test, (51) in which the moisture, tar and oil vapours evolved are condensed and the volume of permanent gases only is determined. It was evident, therefore, that a different approach would be required to determine the volume rate of generation of volatile products corresponding to that occurring within the plastic coal during swelling.

The principle of the method adopted for this determination in the present work is essentially simple. The coal sample is heated in an inert atmosphere in a long vertical metal cylinder which contains a number of close fitting but not, of course, gas tight, horizontal baffles. The effect of these baffles is to prevent rapid diffusion of the heavier constituents of the volatile matter evolved from the coal, in the base of the crucible, with the less dense inert atmosphere in the upper part of the crucible. Thus the heavy oil and tar vapours do not escape from the crucible and condense, but displace an equal volume of inert gas from the crucible into a gas measuring burette.

Experimental Apparatus.

The apparatus is shown diagrammatically in Fig.15. The crucible (A) was machined from a free cutting aluminium alloy and had an internal depth of 6", with an internal diameter of $1\frac{3}{8}$" and $\frac{3}{16}$" wall thickness. The upper $\frac{1}{2}$" of the crucible was tapped to accommodate the screwed cap (B) which carries the long exit tube (C). The fifteen circular internal baffles were of aluminium and were separated by aluminium spacers (E).

Aluminium was chosen as the crucible material for several reasons. High thermal conductivity is desirable to facilitate the maintenance of an even temperature over the entire crucible length and aluminium also has the required resistance to attack by the gases and vapours produced from the coal, especially those containing sulphur. The only disadvantage of aluminium is its relatively low melting point, but care was taken that the temperature of the crucible never exceeded 550°C.

A vertical electric furnace (F) consisting of a 2 inch internal diameter refractory tube, wound with Nichrome resistance wire to give a long even hot zone, and surrounded by insulating bricks (G) was used in this part of the work. The crucible was supported centrally in the hot zone by insulating stools (H) and the upper part of the furnace tube was also filled by insulating brick (I) to prevent temperature gradients at the top of the crucible. Temperature readings were taken by a 22 S.W.G. chromel-alumel thermocouple (J) which fitted into a recess in the base

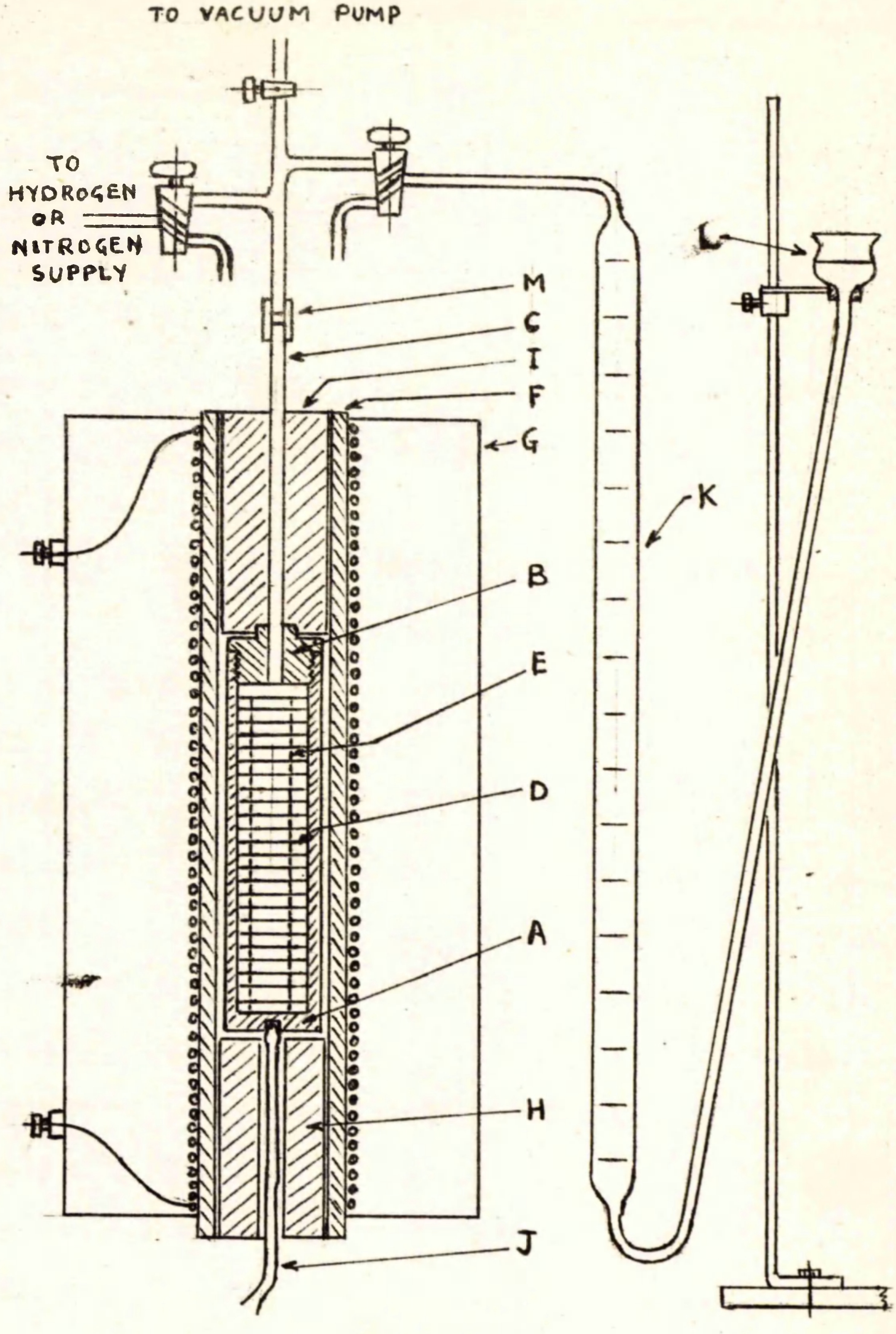

TO VACUUM PUMP
TO HYDROGEN OR NITROGEN SUPPLY
M
C
I
F
G
B
E
D
A
H
J
K
L

FIG. 15.

of the aluminium crucible. The gases evolved passed out through a narrow bore aluminium tube (C) and were collected in the gas burette (K) via the tap system shown in Fig.15, the volume of gas in the burette being measured by the use of the levelling bottle (L). The rate of heating was controlled by a variac transformer connected to the furnace winding circuit.

Experimental Technique.

The size of coal sample used must necessarily be small, since the volume of volatile products must not be so great that condensible vapours escape from the crucible. Another consideration in this connection is that a small coal sample gives a thin layer of coal on the bottom of the crucible and this is advantageous in obtaining even heating of the sample. Obviously, however, with a very small coal sample, the volume of volatile products would become too low to give an accurate estimation. Preliminary investigation showed that a sample weight of between 0.5 and 1.0 gms. gave reproducible results and a suitable rate of volume increase to allow accurate readings to be made. A standard sample size of 0.75 gm. was adopted thereafter.

It was also found that the coal sample tended to agglomerate . This is undesirable, since free escape of the volatile matter generated is essential. Inert material was mixed with the coal to overcome this effect, various additions being tried. Silica sand was found to segregate easily from the coal particles, while aluminium powder, which it was thought would also increase the thermal conductivity of the sample, tended to sinter. The most satisfactory addition, which was generally adopted for the estimations, was 0.5 gm. of finely powdered graphite powder, intimately mixed with the coal.

The effect of coal particle size was also investigated. No significant variation was found in the results obtained using different size ranges between 16 and 100 mesh (B.S.S.) and samples of - 36 + 72 mesh were used in all subsequent experiments.

The standard procedure used in the experimental determinations is detailed below. A representative sample of +1/4" coal was crushed, 0.75 gm. of - 36 + 72 mesh material being taken and thoroughly mixed with 0.5 gm. of fine graphite powder. The mixture was placed in the aluminium crucible and the aluminium baffles were inserted. The top of the crucible was then screwed tightly into place, a jointing compound being applied to the joint faces to ensure a completely air tight seal. The assembled crucible was placed in the furnace and attached to the gas burette by the rubber connection (M), shown in Fig.15. The crucible was then evacuated by opening the tap to the vacuum pump and the temperature of the furnace was raised at the desired heating rate till a temperature of 150°C was attained. Evacuation was then stopped and the inert atmosphere admitted to the crucible. Hydrogen was used as an inert atmosphere in the majority of experiments carried out, but nitrogen was employed in some determinations, and it was found that the resulting values obtained for R were not affected by this alteration in procedure. Heating was continued and readings of gas volume and temperature were taken alternately at suitable intervals till the temperature had reached 550°C and the coal sample had passed through the plastic range.

Experimental Results.

A specimen set of readings and the method of calculation employed to determine the volume rate of volatile evolution are shown in Table 7.

The first four columns of the Table show the experimental temperature and gas volume readings at alternate minute or two minute intervals. The temperature corresponding to each of the volume readings (Column A) is then taken as the mean of the temperature readings before and after it. Since the volume of the aluminium crucible is known, the volume at N.T.P. of the gases occupying the crucible may be calculated (Column B) for each of the above temperatures and the total volume of gases in the system is then obtained (Column D) by summation of Column B and Column C, which shows the gas burette volume connected to N.T.P. The total volume is then plotted against temperature as shown in Fig.16, and from the gradient of the straight line portion of the curve the rate of increase in volume, i.e., the rate of evolution of volatile products, is obtained in cc per °C and hence in cc/minute as shown in Table 7.

It will be noted that in the above calculation the assumption is made that all the gas in the crucible is at the same temperature, and no correction is applied for the temperature gradient in the connections between the crucible and burette. Any correction for the latter effect would be very small, and the above method of calculation may be justified by the fact that blank tests in which no coal was used gave substantially constant values for the total gas volume throughout the experiment.

TABLE 7.

Backworth Coal Test No. BV9.

Heating Rate 2.5°C/min. 0.75 gm. coal. 0.5 gm. graphite.

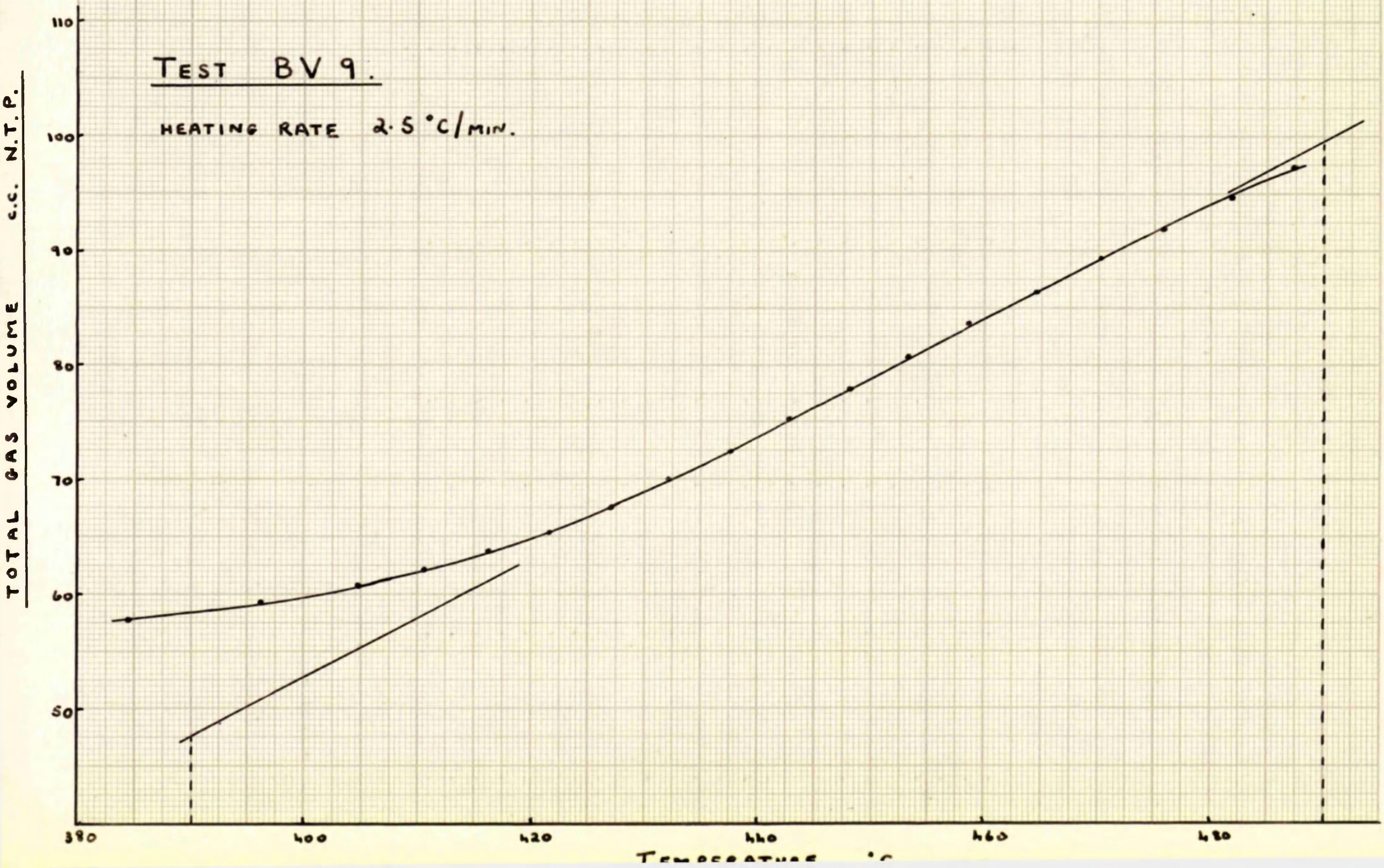
Time (mins.)	Temp. °C.	Time (mins)	Volume c.c.	A Temp °C.	B cc NTP	C cc NTP	D cc NTP
122	300.3	124	4.7	305.7			
126	311.2	128	6.3	316.6	45.40	5.90	52.30
130	322.4	132	8.0	328.0	45.60	7.45	53.05
134	334.0	136	9.7	339.4	44.75	9.05	53.80
138	345.1	140	11.5	350.6	43.95	10.70	54.65
142	356.2	144	13.3	361.7	43.20	12.40	55.60
146	367.4	148	15.0	373.1	42.50	14.00	56.50
150	378.8	152	17.1	384.5	41.75	15.95	57.70
154	390.4	156	19.5	396.2	41.05	18.20	59.25
158	402.1	159	21.7	404.9	40.50	20.20	60.70
160	407.8	161	23.4	410.6	30.20	21.80	62.00
162	413.5	163	25.4	416.3	39.85	23.70	63.55
164	419.2	165	27.6	421.8	39.55	25.70	65.25
166	424.4	167	30.2	427.0	39.25	28.15	67.40
168	429.6	169	33.0	432.1	39.00	30.80	69.80
170	435.0	171	36.0	437.6	38.70	33.60	72.30
172	440.2	173	39.2	442.8	38.40	36.70	75.10
174	445.4	175	42.6	448.0	38.15	39.70	77.85
176	450.6	177	45.9	453.2	37.90	42.70	80.60
178	456.0	179	49.4	458.8	37.60	46.00	83.60
180	461.6	181	52.8	464.5	37.30	49.10	86.40
182	467.4	183	56.1	470.2	37.00	52.30	89.30
184	473.1	185	59.3	475.9	36.75	55.20	91.95
186	479.1	187	62.5	481.9	36.45	58.20	94.65
188	484.9	189	65.4	487.8	36.20	60.90	97.10
190	490.7						

From graph, gradient of line = $\frac{52}{100}$ cc/°C $= \frac{52 \times 2{\cdot}5}{100}$ cc/min.

$=$ 1·3 cc/min. for 0.75 gm.

R $=$ 26 cc/min. for 15 gm.

FIG. 16



TEST BV 9.

HEATING RATE 2·5 °C/MIN.

Determinations of the Rate of Evolution of Volatile Matter were carried out on the six coals listed in Table 2 (Chapter V); i.e., all the coals whose swelling characteristics have been studied. Several determinations were made on each coal and it was found that the results showed a high degree of reproducibility and that a reasonably linear rate of evolutions was obtained over a considerable temperature interval. A standard heating rate of 2.5°C/min. was employed for the main series of tests, but the effect of varying heating rates on the rate of evolution was also investigated with the Hartley Dross and Backworth coals. The results obtained are summarised in Table 8 and will be discussed subsequentl

Effect of Pressure on the Rate of Evolution.

Since the swelling tests described in previous Chapters were carried out at pressures of up to seven atmospheres, a series of experiments was undertaken to determine whether the volume rate of evolution of volatileswas affected by pressures of this order.

The method used was essentially the same as that employed in the previous experiments although alterations had of course to be made to the apparatus to allow a pressure to be maintained in the crucible. Since it was doubtful whether the aluminium crucible used previously was capable of withstanding the necessary pressure at high temperatures an aluminium bronze crucible was used, the pressure in the crucible being regulated by the pressure gauge and valve system shown in Fig.17. The assembled crucible was first evacuated and then filled with nitrogen under pressure, via the valve (A). The crucible was then heated as before and the

TABLE 8.

Coal	Test No.	Heating Rate °C/min.	Inert Gas.	Temp. *	R cc NTP/ min (15 gm sample)	Average R
Easton	EV 1	2.5	H_2	425	24.6	24.6
	EV 2	-	H_2	428	24.8	
	EV 3	-	H_2	427	24.6	
Kingshill	KV 1	2.5	H_2	422	25.6	25.6
	KV2	-	H_2	422	25.4	
	KV 3	-	N_2	424	25.6	
Hartley Dross.	HV 1	2.5	H_2	440	20.4	20.0
	HV 2	-	H_2	440	19.4	
	HV 3	-	H_2	441	20.2	
	HV 4	-	H_2	439	19.8	
	HV 5	-	N_2	438	20.0	
	HV 6	1.75	H_2	434	14.7	14.7
	HV 7	-	H_2	435	14.7	
Backworth	BV 1	2.5	H_2	426	25.6	25.9
	BV 2	-	H_2	422	26.0	
	BV 3	-	H_2	425	25.8	
	BV 4	-	N_2	424	26.4	
	BV 5	-	N_2	424	26.0	
	BV 6	1.75	H_2	420	19.0	19.1
	BV 7	-	H_2	420	19.2	
	BV 8	3.75	H_2	430	37.8	37.8
	BV 9	-	H_2	428	37.8	
	BV 10	5.0	H_2	435	49.6	49.4
	BV 11	-	H_2	437	49.2	
Sacriston	AV 1	2.5	H_2	450	24.4	24.4
	AV 2	-	H_2	448	24.6	
	AV 3	-	H_2	448	24.2	
	AV 4	-	H_2	450	24.6	
Cwymtillery	CV 1	2.5	H_2	443	23.2	23.2
	CV 2	-	H_2	440	23.2	

* The temperatures shown are those at which the gradient of the volume increase graph becomes approximately linear.

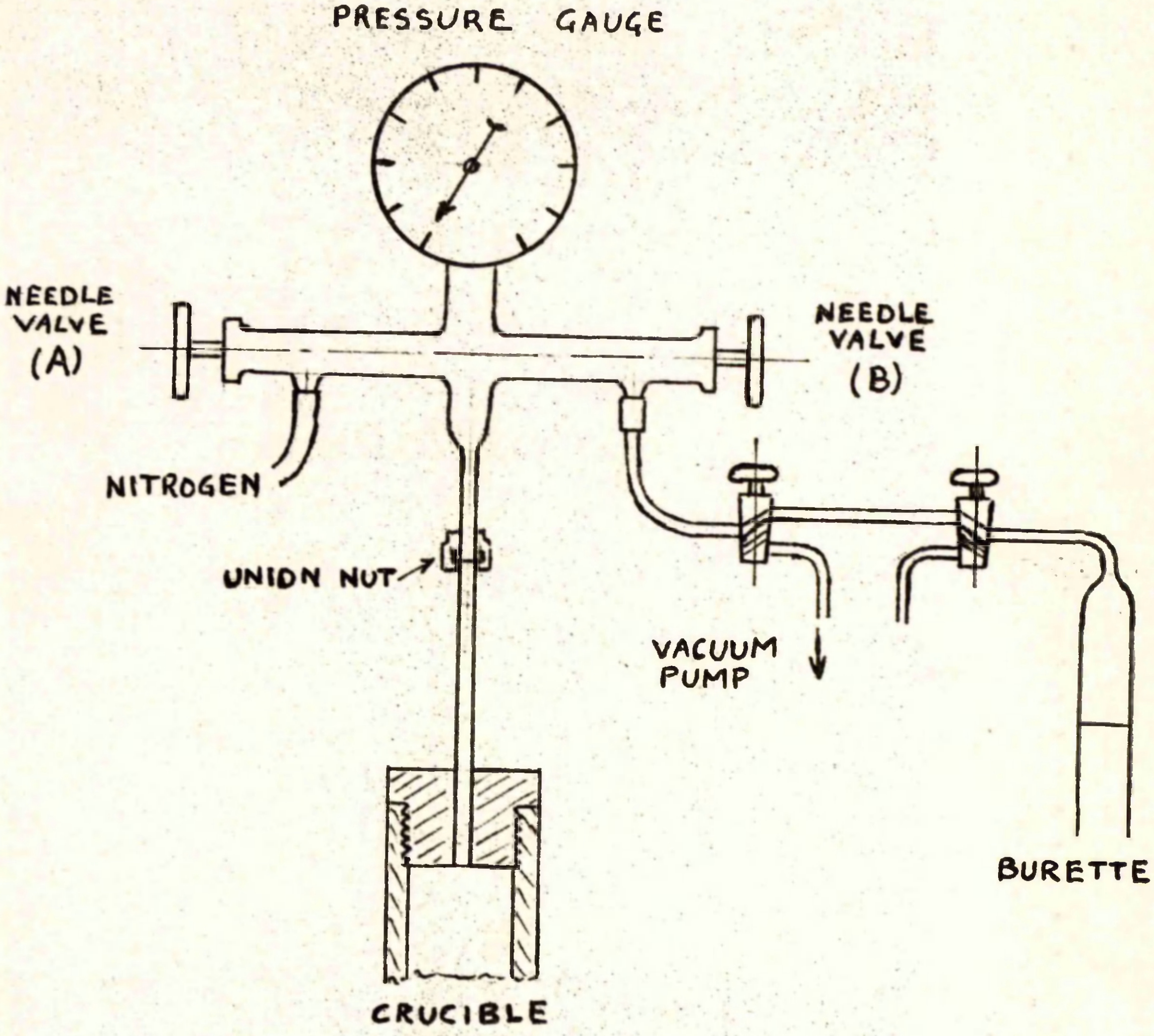

PRESSURE GAUGE
NEEDLE VALVE (A)
NEEDLE VALVE (B)
NITROGEN
UNIDN NUT
VACUUM PUMP
BURETTE
CRUCIBLE

FIG. 17

pressure in the system was kept constant throughout the test by allowing the gases produced to escape through the needle valve (B) to the gas burette, readings of the increase in volume with temperature being taken as in the determinations carried out at atmospheric pressure.

Since the metal pressure gauge and valve system tended to be heated by conduction during the test and since the volume of these connections was considerable, it was considered that the effect of the temperature gradient in the connections could not be considered negligible, as in the method of calculation used previously. Blank runs, in which no coal was used, were therefore carried out at each pressure and the rate of evolution of volatiles taken as the difference between the rate of volume increase in the experimental test and that obtained in the blank run.

The results of tests on the Hartley and Backworth coals using a heating rate of 2.5°C/min. are shown in Table 9, and it can be seen that there is no significant variation in the rate of evolution obtained in any of the tests from that found at atmospheric pressure.

TABLE 9.

Test No.	Absolute Pressure (at)	Total Volume Increase	Blank	R (15 gm) cc/NTP min.	
HV -	1.0	-	-	20.0	*
HVP 1	2.36	14.55	4.65	19.8	
HVP 2	2.36	14.65	4.65	20.0	
BV -	1.0	-	-	25.9	*
BVP 1	2.36	17.66	4.65	26.0	
- 2	3.04	18.55	5.55	26.0	
- 3	4.06	19.70	6.90	25.6	
- 4	4.40	20.30	7.40	25.8	
- 5	4.74	21.00	7.90	26.2	

* Average value of runs at atmospheric pressure.

Rate of Loss of Weight.

In order that a comparison could be made between the rate of evolution of volatiles as determined above and the rate of evolution on a weight basis, a series of tests was carried out in which the loss of weight during heating was determined, a continuousweighing technique similar to that of Audibert(47) being used. 0.75 gm. of - 36 + 72 mesh coal were placed in an open aluminium crucible which was suspended by a platinum wire from one arm of the chainomatic balance in a small vertical resistance furnace. The furnace tube was closed with stoppers at both ends; the lower stopper was provided with a tube through which nitrogen was passed during heating, the gas escaping via a small central hole in the upper bung through which the suspension wire passed. Since the attachment of a thermocouple to the crucible might have interfered with the accurate weighing of the crucible, the thermocouple junction was located in a small hole hored in an aluminium block supported in the hot zone of the furnace tube just below the suspended crucible.

The procedure used was similar to that of the volume rate determinations; the crucible was heated at a constant rate and readings of temperature and weight were taken at alternate minute intervals during the test. The loss of weight was then plotted against temperature and the rate of evolution determined from the gradient of the curve obtained. The results of tests, at a heating rate of 2·5°C/min., on the various coals used in the previous experiments are summarised in Table 10, the values shown being the average figures of two or more tests.

Table 10.

Coal	Temp. °C.*	Average Evolution Rate gm/min. (0.75 gm.)
Easton	428	0.0034
Kingshill	420	0.0032
Hartley Dross	438	0.0029
Backworth	422	0.0040
Sacristan	446	0.0027
Cwymtillery	438	0.0025

* Temperature at which gradient of evolution curve becomes approximately linear.

The general shape of the weight evolution curves was found to be very similar to that of the volume evolution rate curves, as can be seen from the comparison shown in Fig.18. The variation in the rate of loss of weight values for different coals was however considerably greater than that found in the volume evolution figures. Further reference will be made to this in the general discussion of the volatile evolution results, which follows.

Discussion of Results.

The primary consideration with regard to the results of the volume rate determinations was whether the values obtained did actually represent the total volume of thermal decomposition products as produced from the coal, since any condensation or decomposition of the vapours evolve in the crucible would lead to erroneous results. No signs of condensation were observed in the exit tube from the crucible in the actual tests but there is, of course, no direct evidence as to the conditions within the crucible. If, however, condensation or cracking of the higher molecular weight products occurred this would have been expected to lead to a variation in the evolution rate in duplicate determinations since it is unlikely that such effects would occur to the same extent in successive tests. Thus the degree of reproducibility shown by the experimental results, all the duplicate values obtained agreeing to within ± 2% of the mean (Table 8), is taken to be evidence that breakdown of the vapours produced from the coal does not take place to any marked extent and that the results may be considered to represent the total volume rate of volatile evolution during heating. This view is supported by the fact that the evolution rate is independent of the pressure at which the test is carried out, since this variable would be expected to have a considerable effect on the results if condensation did tend to occur.

The evolution curves obtained by measuring the loss in weigh on heating are very similar to the corresponding volume graphs. This is shown in Fig.18 in which curves for the Backworth coal are compared, the scales having been adjusted to give the same gradient over the linear portion of the graph. It will be noted that the general shape of curves is similar and that a linear rate of evolution is obtained over a considerable temperature range in both cases. The temperature at which the evolution rate becomes linear (points T_W and T_V, Fig.18) is also found to agree closely.

A typical swelling curve for the Backworth coal is also shown on a comparable scale in Fig.18. It will be noted that the temperature at which the gradient of the swelling graph becomes linear (T_S) is approximately 10°C lower than that obtained in the volatile evolution tests. A similar difference was found in all the coals tested, the swelling and gas evolution temperatures being shown in Table II.

This difference is probably due to the position of the thermocouple used to measure the temperature of the coal sample in the swelling and volatile evolution experiments. In the swelling tests the thermocoupl is located in a silica sheath in the centre of the coal charge. Since dielectric heating is employed the thermocouple is being heated by the

FIG. 18

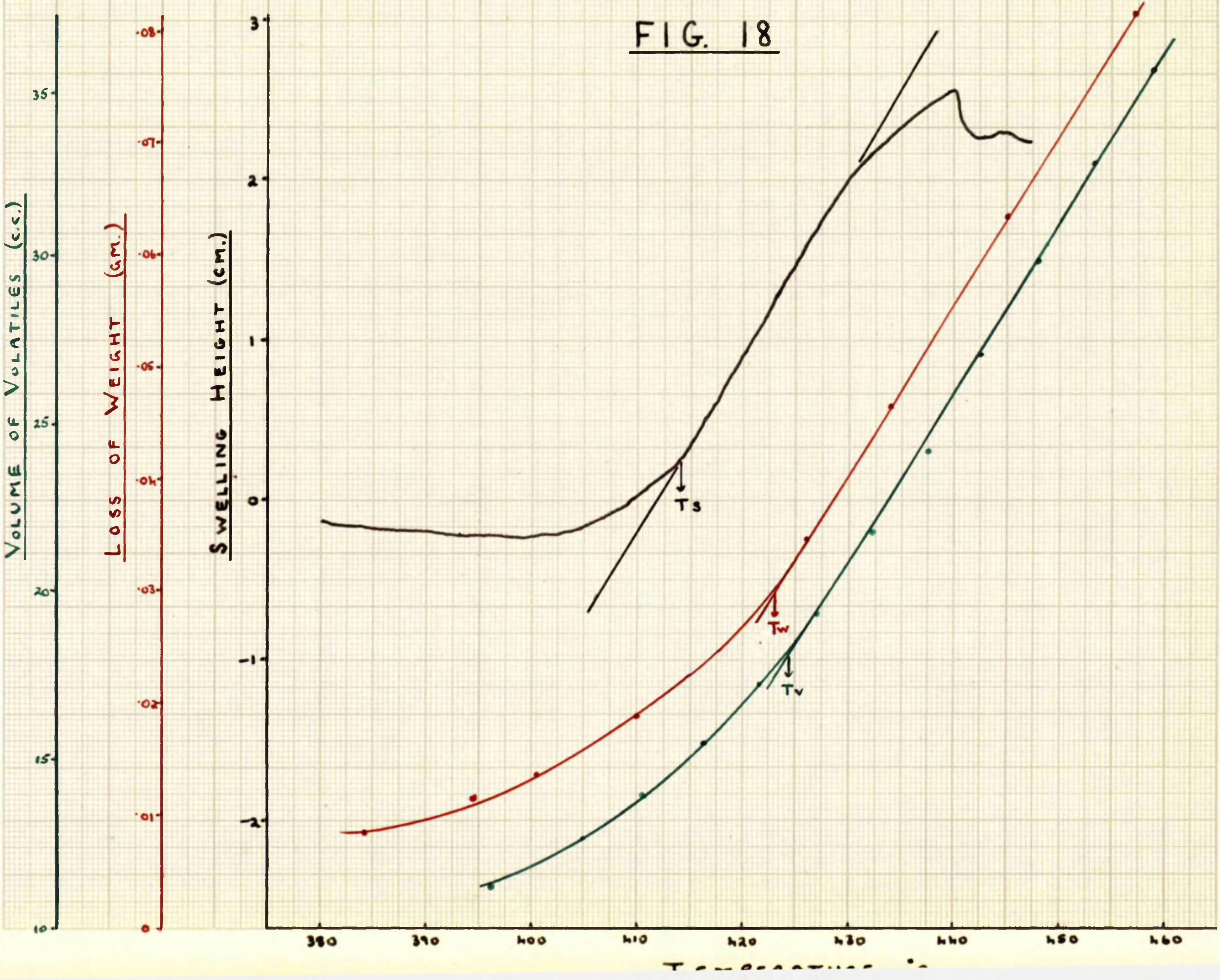

VOLUME OF VOLATILES (c.c.)
10
15
20
25
30
35
LOSS OF WEIGHT (GM.)
0
·01
·02
·03
·04
·05
·06
·07
·08
SWELLING HEIGHT (CM.)
-2
-1
0
1
2
3
380
390
400
410
420
430
440
450
460
Ts
Tw
Tv

Table 11.

Coal	I.S.T. °C.	Temperature at which linear gradient is found T°C Swelling Graph(T_s)	Volume Evolution(T_v)	Weight Evolution(T_w)
Backworth	404	414	424	422
Kingshill	409	412	422	420
Easton	417	422	428	428
Hartley Dross	427	433	440	438
Cwymtillery	428	438	441	440
Sacriston	435	438	448	446

surrounding coal and will therefore give a slightly lower temperature readings than that of the coal. In the volatile evolution experiments, however, heat transfer takes place from the crucible to the coal sample and the temperature registered will therefore be slightly higher than that of the coal sample throughout the test. Thus the additive effect of these errors could account for the discrepancy of several degrees found between the temperatures measured in the swelling and evolution tests.

Effect of Heating Rate.

The effect of heating rate on the volume rate of volatile evolution was investigated with the Hartley Dross and Backworth coals; the results of these tests were shown in Table 8. The evolution rate in cc at N.T.P. per minute was naturally found to increase at higher heating rates but the increase was not directly proportional to the rate of heating, the volume of volatiles being less than doubled by a twofold increase in the rate of temperature rise. This trend may be shown by expressing the evolution rate figures on a basis of cc at N.T.P. per °C, as in Table 12 from which it is evident that the rate of evolution is relatively lower at higher heating rates. Shimmura and Nomura(52), have noted that a decrease in the rate of gas production per °C was found with increasing heating rate in tests on Japanese coals. Their results are not, of course, strictly comparable with the evolution rates determined above since the volume of permanent gases only was measured in their experiments.

It was found that volatile evolution occurred at lower temperature when lower heating rates were used, the variation being similar to that found in the initial swelling temperatures of the coal samples in the coking tests with different rates of heating.

Volatile Evolution and Coal Rank.

The results of the various weight and volume evolution rate experiments carried out at a heating rate of 2.5°C/min. are summarised in Table 13. There appears to be no direct correlation between the actual volume evolution figures obtained and the rank or volatile content of the coals studied. Previous investigators (50), have attempted to relate the rate of gas production obtained during the swelling range in Gray-King assay tests with coal rank and swelling properties. No relationship was found however, and Mott(50) noted that similar rates of gas evolution were obtained for widely different coals, a finding which is in line with the volatile evolution rates obtained in the present work. The fact that there is no simple correlation between the swelling

TABLE 12.

Coal	Rate of Volatile Evolution. cc NTP/°C.			
	1.75°C/min.	2.5°C/min.	3.75°C/min.	5.0°C/min.
Hartley Dross.	8.40	8.00	-	-
Backworth.	10.95	10.35	10.08	9.86

TABLE 13.

Coal	Volatile Matter % (dry basis)	Volume Rate cc/min. (15 gm.)	Loss in Weight gm/min. (15 gm.)	Average Molecular Weight.
Backworth	37.8	25.9	0.80	69.2
Kingshill	34.2	25.6	0.64	56.4
Easton	32.1	24.6	0.68	61.8
Hartley	30.9	20.0	0.58	65.0
Cwymtillery	28.8	23.2	0.50	48.3
Sacristan	28.5	24.4	0.54	49.5

characteristics and the rate of generation of volatiles in no way detracts from the importance of this factor in the swelling process, since it is the combined effect of generation of volatiles and the resistance to gas escape or permeability of the plastic mass which determines the swelling properties of any given coal.

The temperatures of volatile evolution show a definite variation with volatile content, lower evolution temperatures being found with higher volatile matter coals, (see Table 11). This is in general agreement with the work of Holroyd and Wheeler(48), who noted that lower decomposition temperatures were observed in lower rank coals. The initial swelling temperatures of the coals tested also show this trend.

Although the volume evolution figures are not related to coal rank, the rate of loss of weight is found to increase with higher volatile content, as is shown in Table 13. From the evolution rates determined on a weight and volume basis, the average molecular weight of the gases and vapours evolved during the swelling range may be calculated. Molecular weights of between 50 and 70 were obtained for the series of coals tested, the individual values being shown in Table 13, from which it can be seen that the average molecular weight tends to increase with lower rank coals.

By measuring the contraction due to condensation on cooling the crucible after the volatile matter estimation, it was estimated that about 20% of the total volatiles evolved during swelling consisted of tars and condensible vapours. An average molecular weight of about 25 for the permanent gases produced, i.e., the remaining 80% of the volatiles, may be calculated from representative gas analyses given by Holroyd and Wheeler(48) Since the average molecular weight of all the constituents is between 50 and 70, it follows that the condensible vapours and tars produced have an average molecular weight of about 200, which appears to be a reasonable figure. There is, however, no data with which this value could be compared.

The main conclusions drawn from the results of this section, which are of particular interest with regard to the swelling investigations, are as follows:

The method used has been shown to give reliable values for the volume rate of generation of volatile matter from coal samples. The rate of evolution has been found to be practically linear over the swelling ranges of the coals tested; it is independent of pressure, but the evolution rate is relatively lower at higher heating rates.

CHAPTER VII.

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

Before entering upon a discussion of the results obtained from the point of view of an explanation of the swelling of coking coals based on the rate of gas escape from, and hence the permeability of, plastic coal, it is proposed to consider certain observations made on the characteristic temperatures of the plastic ranges of the coals tested.

The Initial Swelling Temperature.

It has been noted(11) that the initial swelling temperature (I.S.T.) of an aggregate of coal particles is the most reproducible of the various "critical temperatures" of the plastic range and that it remains constant over a wide range of applied pressure. This is borne out by the results obtained in the present work, the initial swelling temperatures shown in Tables 3 - 6, being reproducible to within a few degrees centigrade in all the tests on a given coal at any fixed heating rate. In fact, as has been mentioned earlier, any marked alteration in the initial swelling temperature was an indication that deterioration of the coal had occurred.

As stated in Chapter IV, it was found that, if pressure was applied to the coal sample under test before the plastic range was reached, the initial swelling temperature was somewhat lower than that obtained if pressure was not applied till swelling started. This fact may be explained by a consideration of the primary stages of swelling. Mott(53) showed that the primary swelling temperature of individual coal particles was coincident with the temperature of initial contraction of an aggregate of coal particles under load. Thus in the interval between the initial contraction and initial swelling temperatures of the aggregate coal sample "softening" and swelling of the individual particles is occurring, resulting in a gradual reduction of the voids present and the production of a homogeneous mass of softened coal. It would be expected that the application of pressure during this period would result in greater homogeneity and lower permeability being attained, so that, with increase in the rate of gas evolution, swelling would be expected to occur at a lower temperature than if pressure was not applied till swelling commenced.

Slightly lower initial swelling temperatures were obtained at lower heating rates, the figures for the Backworth coal being 414, **404** and 396°C for heating rates of 3·75, 2·5 and 1·75°C per minute respectively This is in agreement with the observations made by various authors including Audibert(47) and Mott(23).

A further conclusion which can be drawn from the results is that the initial swelling temperatures tend to increase with higher rank coals, as can be seen from the figures shown in Table 14.

Table 14.

Coal	Kingshill	Easton	Backworth	Hartley Dross	Cwymtillery	Sacristan
%C (Parr)	84.8	85.7	86.2	86.7	89.2	89.5
I.S.T.°C	409	417	404	427	428	435

It will be noted that the three Scottish coals (Kingshill, Easton and Hartley Dross) show rather higher swelling temperatures, in relation to the others than would be expected from their carbon contents, a fact remarked upon by Davidson(54). Holroyd and Wheeler(55) investigating the thermal decomposition of coal found that the temperature at which active decomposition of the coal material occurred also increased with rank, which tends to support the view that the swelling of coal is closely connected with the temperature at which decomposition, accompanied by marked gas evolution, occurs.

Length of the Swelling Range.

The maximum swelling temperatures (M.S.T.) of the individual tests carried out were noted in Tables 3 - 6 (Chapter V). It is apparent that these temperatures show greater variation with applied pressure and heating rate than the initial swellingtemperatures, resulting in a variation of the swelling range, i.e., the temperature interval between the initial and maximum swelling temperatures, in different tests.

The swelling intervals obtained in the various test series are summarised in Table 15.

The swelling ranges obtained in the tests on the Easton coal are not included since, due to the variation in heating rate from test to test, referred to earlier, the maximum swelling temperatures lose much of their significance.

TABLE 15.

Kingshill		Hartley Dross			Backworth		
$P_{(d)}$at.	2·5°/min.	$P_{(d)}$at.	1·75°/min.	2·5°/min	$P_{(d)}$at.	1·75°/min	2·5°/min.
	Swelling Range		Swelling Range			Swelling Range	
0·08	23°C	0·68	-	16	0·34	32	37
0·42	25	1.02	15	26	1.02	-	36
1.50	25	1.7	21	31	1.70	31	45
2.57	30	2.04	-	30	2.72	38	46
3.40	32	2.38	24	26	3.72	38	-
4.25	28	2.72	-	28	4.83	41	-
		3.06	25	31	5.51	39	-
		3.40	-	27	6.08	31	-
		3.74	28	-			
		4.08	-	29			
		4.25	24	-			
		4.83	18	28			
		5.40	18	28			

- Indicates test in which M.S.T. was not obtained.

From the results shown for the Hartley Dross and Backworth coals it is evident that when lower heating rates are employed the swelling range of the coal is shorter at any given pressure. Such an observation is considered to be in accord with the general dependence of the swelling properties on rate of heating .

Hirst(24) has postulated that the softening of coking coals is due to the less complex molecular units of the coal micelle which, on heating, attain a certain degree of mobility and act as "boundary lubricants' leading to plasticity and cohesion of the coal micelles. At a higher temperature however the structure again becomes rigid due to thermal decomposition and evaporation of these lubricants. Irrespective of whether the above view is held or whether the older theory of certain fluid constituents of the coal material causing cohesion of the coal particles is retained, it is obvious that the length of the plastic range must depend on the rate at which decomposition of these fluid constituents or boundary lubricants occurs.

In the results on the determination of the rate of gas evolution (Chapter VI), it was shown that with lower heating rates the rate of generation of volatile products, expressed in cc/°C, increased, which indicates that at any stage of the swelling range decomposition is more complete, the lower the heating rate. Such an effect would be expected to lead to a shortening of the range of temperature over which the above mentioned fluid constituents or plasticising molecules can induce plasticity and swelling as the heating rate is reduced.

Taylor(26) pointed out that the maximum swelling temperature for the Kingshill coal tended to increase with pressure. This effect is reflected in the swelling intervals shown in Table 15 for this coal. It will be noted, however, that a slightly lower swelling range is obtained under the highest pressure used. If the results obtained for the Hartley Dross and Backworth coals, heated at 1.75°C/min. are considered, it will be seen that with increasing pressure the swelling intervals show a definite maximum. This effect is also apparent, though not so marked, in the 2.5°C/min. Hartley Dross tests. In the corresponding Backworth series the swelling range could not be determined over the whole pressure range due to a tendency for escape to occur at high pressures towards the end of the experimental tests, but an initial increase in swelling range with pressure is obtained.

It is significant that the maximum swelling range is found at approximately the same pressure, namely about 3·75 atmospheres for the Hartley Dross and 4.75 atmospheres for the Backworth coal, as the maximum obtained in the swelling rate - pressure curves shown in Figs.12 and 13 (Chapter V). Since the swelling rate ($\frac{dv}{dt}$) expressed in cc. at N.T.P. is equivalent to the rate at which gas is entrapped in the plastic coal mass and since the rate of gas escape is given by ($R - \frac{dv}{dt}$) it follows that the swelling range increases with a decrease in the rate of gas escape from the plastic mass. This is considered to result from the same type of mechanism as that discussed above in connection with the variation of swelling range with heating rate, a decrease in the rate of gas escape having the effect of reducing the rate of loss of the fluidising constituents or plasticising molecules by diffusion and evaporation through the plastic coal and hence increasing the temperature range over which swelling occurs.

It may be noted here that the average swelling interval for the Backworth coal was considerably greater than the others. The average values of the swelling ranges were 27, 27, 28 and 41°C for the Easton, Kingshill, Hartley Dross and Backworth coals respectively. The range of coals studied is, however, considered too limited for any conclusion to be reached on the significance of this fact.

The Swelling of Plastic Coal.

Considering the natural heterogeneity of coal, the results of the swelling rate determinations show a considerable degree of reproducibility and confirm the view that the rate of swelling of coal samples under pressure, as measured in the present work, is of fundamental importance in the behaviour of coking coals during the plastic state.

The fact that the swelling of coking coal during the carburization process is due to the entrapment of the volatile products of decomposition in the plastic mass of coal material has been stated by several workers, including Foxwell(31) and Davies and Mott(11). Audibert(47) showed experimentally that all the volume increase during swelling was attributable to entrapped gas, there being no expansion of the coal material itself. He concluded that variation in the swelling of coal must be due to variation in the ease with which the products of decomposition could escape from the plastic coal mass. It has also been shown (30,56) that poorly swelling coals show superior coking powers when high heating rates are employed, due to more rapid gas evolution offsetting high inherent permeability and resulting in the production of sufficient internal pressure to produce coking and swelling.

On this basis the swelling of a plastic coal mass would appear to be governed by two main considerations, namely (1) the rate of generation of volatile decomposition products (R), and (2) the permeability of the material, which for a given value of the former will determine the extent of swelling. This view was taken by Taylor(26) who expressed the swelling mechanism by the equation :-

$$(R - \frac{dv}{dt}) = P(d). S \qquad \text{.......................} \qquad (1)$$

$(\frac{dv}{dt})$ being the volume rate of swelling in cc. at NTP/min. under a constant applied pressure $P_{(d)}$ atmospheres and S being the permeability of the coal in cc.NTP/at./min.

Taylor postulated, as has already been described in Chapter II, that the permeability of the coal material decreased with increase of applied pressure, due to closing of pores in the material by plastic coal, until a constant "S" value was reached. If this is the case and if the above equation is satisfied, then on plotting the rate of swelling $(\frac{dv}{dt})$ against pressure the graph should show an inflexion, corresponding to the point at which the constant permeability value is attained, and become linear and of negative gradient at high pressures. Also, on extrapolating this linear portion of the graph back to zero applied pressure, the value of R, the rate of evolution of volatile products, should be obtained. The experimental results of Taylor, which are shown in Chapter V, supported an interpretation of this type. It must be pointed out, however, that the number of results obtained was insufficient to confirm a strictly linear relationship between $(\frac{dv}{dt})$ and $P_{(d)}$ at high pressures, as required by the above equation.

In the present work data has been obtained on three further coals, namely Easton, Hartley Dross and Backworth. It is significant that the trend of results for all three coals is similar to that obtained by Taylor for the Kingshill coal. In the case of the Hartley Dross and Backworth coals a definite inflexion is found in the plot of swelling rate against applied pressure while for the Easton coal, although there is no break in the curve at the highest pressure used, there is an indication that a maximum is being approached. The similarity in the behaviour of all four coals becomes more apparent when the relationship between the permeability (S) and applied pressure is studied. As can be seen in Figs.11 and 14 (Chapter V), a minimum permeability value is approached in each case.

Two points, however, arise from this preliminary consideration of the results. The definite linear relationship between $(\frac{dv}{dt})$ and $P_{(d)}$, postulated by Taylor, cannot be said to have been established from the results obtained, since the constant permeability condition is reached only at pressures approaching the maximum possible with the apparatus, thus restricting the range of pressure over which the relationship can be studied. It was also found that if a straight line relationship is assumed, the extrapolation of the graph to zero pressure gives a lower value of R than that determined experimentally, as described in Chapter VI. In the case of the Backworth coal, for heating rates of 2.5 and 1.75°C/min. the extrapolation leads to values of 20 and 14 c.c. at NTP/min. for R, while the corresponding figures obtained experimentally are 25.9 and 19.5 c.c. per min. respectively. A decrease in the actual rate of generation of volatiles at high pressure would account for a discrepancy of this nature, and for this reason experimental determinations of the evolution rate under pressure were carried out, (see Chapter VI). The results however, showed no significant variation over the range of pressure used.

In view of these facts it was considered that further theoretical consideration of the swelling mechanism would be advisable with a view to determining whether the simple interpretation given above is justified. It will, in fact be shown later that the permeability (S) is a function of the "effective thickness" of the coal sample and that the swelling equation given above requires to be modified to take this factor into account.

Theoretical Consideration of the Swelling Mechanism.

In general the swelling mechanism may be regarded as being described by the equation:

Volume of gas generated = Volume of gas retained in coal + Volume of gas escaping.

It has been shown, in the experimental work described earlier, that both the rate of swelling and the rate of evolution of volatile matter remain constant over a considerable temperature range during heating through the plastic state. Since the rate of swelling is equivalent to the rate of increase in the volume of gas trapped in the coal, it follows that the rate of escape of gas from the coal is also constant, and this figure will be a function of the permeability of the coal material and the applied pressure. In order to express the loss of gas in terms of these quantities the mechanism by which gas escape occurs must be considered and this will obviously be dependent on the structure of the coal mass.

Initially there are a large number of voids present in the granular mass of coal particles. On heating to the plastic range, softening of the coal material occurs and the original voidage of the sample decreases due to the applied pressure causing flow of the softened coal material. The rate at which voids are eliminated will depend on the pressure causing flow and will also be connected with the fluidity of the softened coal and the wettability of the infusible particles present in the mass. The greater the applied pressure the greater will be the tendency for the existing pores to be reduced and it would be expected that at high pressures a limiting condition would be reached at which all the small pores present are closed by a continuous film of plastic material.

The mechanism of gas escape from the coal sample would therefore be expected to alter, with increasing pressure, from flow through pores and voids at the lowest applied pressures to flow through a network of increasingly fine pores and micro-pores and eventually to escape of gas through a continuous plastic coal membrane, which must occur by some diffusion mechanism. Diffusion of this type should show some similarity to the flow of gases through elastic membranes of highly polymerised organic substances such as rubber. (The micellar theory of solids has been extended to include both coals(24) and rubbers(57) and the effect of high oxygen contents on the caking properties of coals has been attributed to a cross linking of the coal micelle nuclei in a manner analagous to the vulcanisation of rubber by sulphur(24)).

Barrer(57) has discussed the flow of gases and vapours in organic solids. When macro pores are present it is probable that Poiseuille or streamline flow occurs, the gas escape being expressed as $V = \frac{\pi(P_1+P_2)(P_1-P_2)}{2.\ell}$ where V is the quantity of gas passing per unit time measured as the product of volume and pressure in atmospheres, $(P_1 - P_2)$ is the pressure difference causing flow, $(\frac{P_1 + P_2}{2})$ is the mean pressure and π is the permeability coefficient, l being the thickness of material through which the gas passes . With very fine pore systems, however, molecular streaming or Knudsen flow is found, according to the equation

$$V = \frac{\pi . P(d)}{l}, \; P_{(d)} \text{ being the pressure difference.}$$

In the case of diffusion through continuous membranes the rate of diffusion is found to be proportional to the pressure difference and inversely proportional to the thickness of membrane, although with vapours slight deviations from this law may occur. The equation for diffusion may therefore be expressed as $V = \frac{\pi . P(d).A.t.}{l}$ where V is the volume in cc at N.T.P. passing in t seconds through a membrane of thickness l mm. and area A cm.^{2} under a pressure difference of P cm of mercury. It will be noted that this expression is similar mathematically to that for molecular streaming and that there can, in fact, be no strict distinction in the mechanism of flow through very fine micro pores and diffusion through pores of molecular dimensions or intermicellar voids.

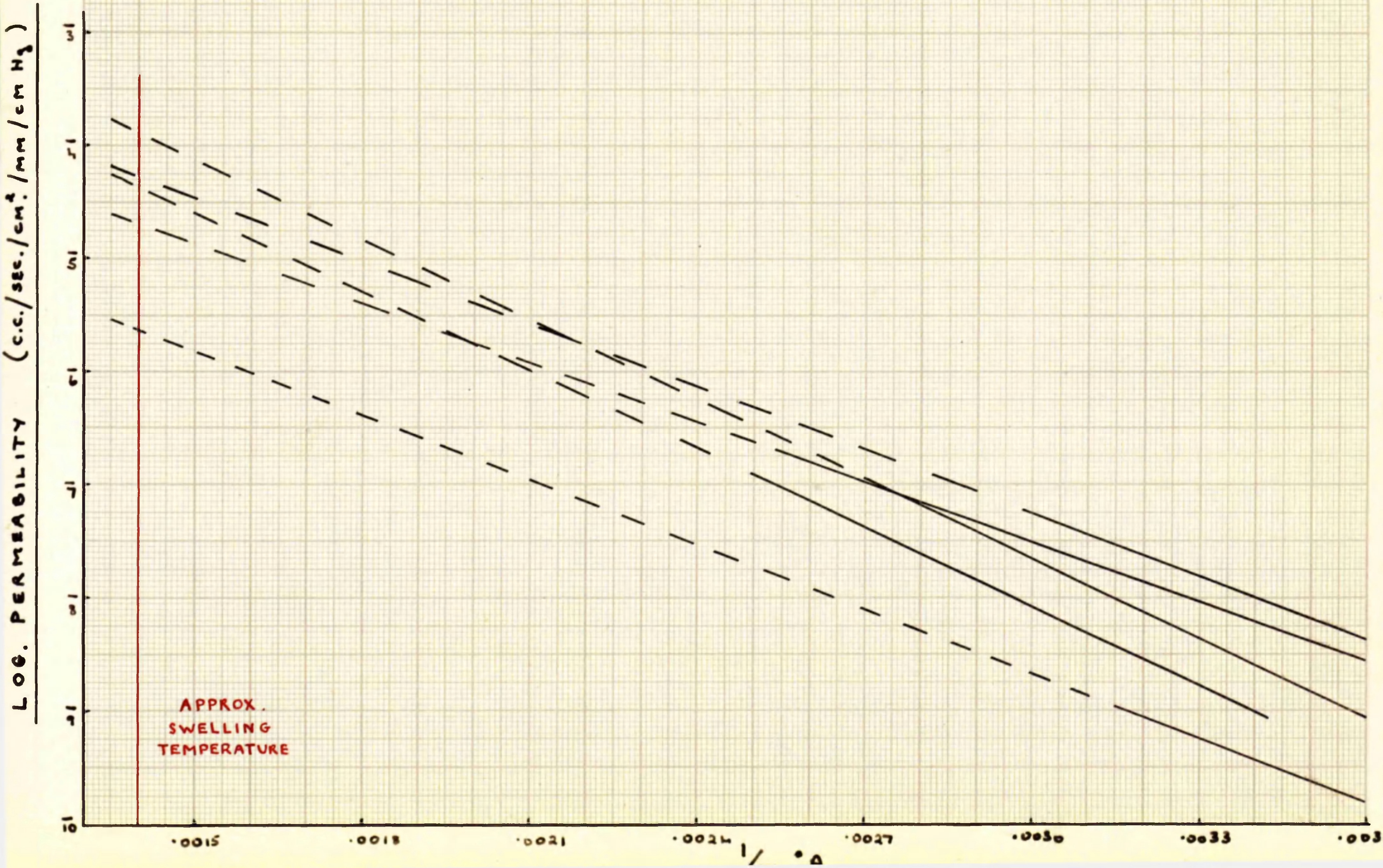
The minimum S value obtained experimentally for the Backworth coal is 2.90 cc at N.T.P. per atmosphere per minute which, on conversion to the above units, gives

$$\pi = \frac{2.90 \times 0.5}{76 \times 20 \times 60} = 1.60 \times 10^{-5} \text{ cc/sec/cm}^2\text{/cmHg/mm thick}$$

(The manner in which the value of l, i.e., the thickness of the coal, is determined is discussed below.) Barrer(57) has given data illustrating an exponential relationship between the permeability constant and temperature for several elastic membranes of the rubber type. By extrapolation of his results, as shown in Fig.19, to temperatures corresponding to the plastic range of the coal it is found that permeability coefficients of between 10^{-5} and 10^{-4} are obtained. While the validity of such an extrapolation over a wide temperature range may be questioned, the fact that the permeability of the coal falls between the above values is considered to support the view that gas escape occurs by some type of diffusion mechanism at high pressures. At lower pressures higher permeability values are obtained, but the permeability coefficients of the various coals at an applied pressure of 1 atmosphere are still of the order of 10^{-4}. From data given by Barrer(57), the probable mechanism of flow in materials with permeabilities of this order is molecular streaming or Knudsen flow the mathematical treatment of which is similar to that of diffusion as has been pointed out above. Thus the mechanism of flow over the range of pressure used in the experimental tests, with the possible exception of tests under very low applied pressure, may be represented by an equation of the type given above for diffusion flow.

The swelling process may be treated mathematically in the following manner. Since the rate of gas escape from the coal sample, and hence the permeability of the sample, remains constant during the period in which swelling takes place, it follows that the permeability constant depends not upon the total thickness of the swollen coal, but on the actual thickness of coal material, which can be calculated from the weight and specific gravity of the coal sample. During the plastic range part of the gas evolved causes swelling while the remainder escapes through

FIG. 19


LOG. PERMEABILITY (c.c./sec./cm.²/mm/cm Hg)
$\bar{3}$
$\bar{4}$
$\bar{5}$
$\bar{6}$
$\bar{7}$
$\bar{8}$
$\bar{9}$
$\bar{10}$
APPROX. SWELLING TEMPERATURE
·0015
·0018
·0021
·0024
·0027
·0030
·0033
·0036
1/ °A

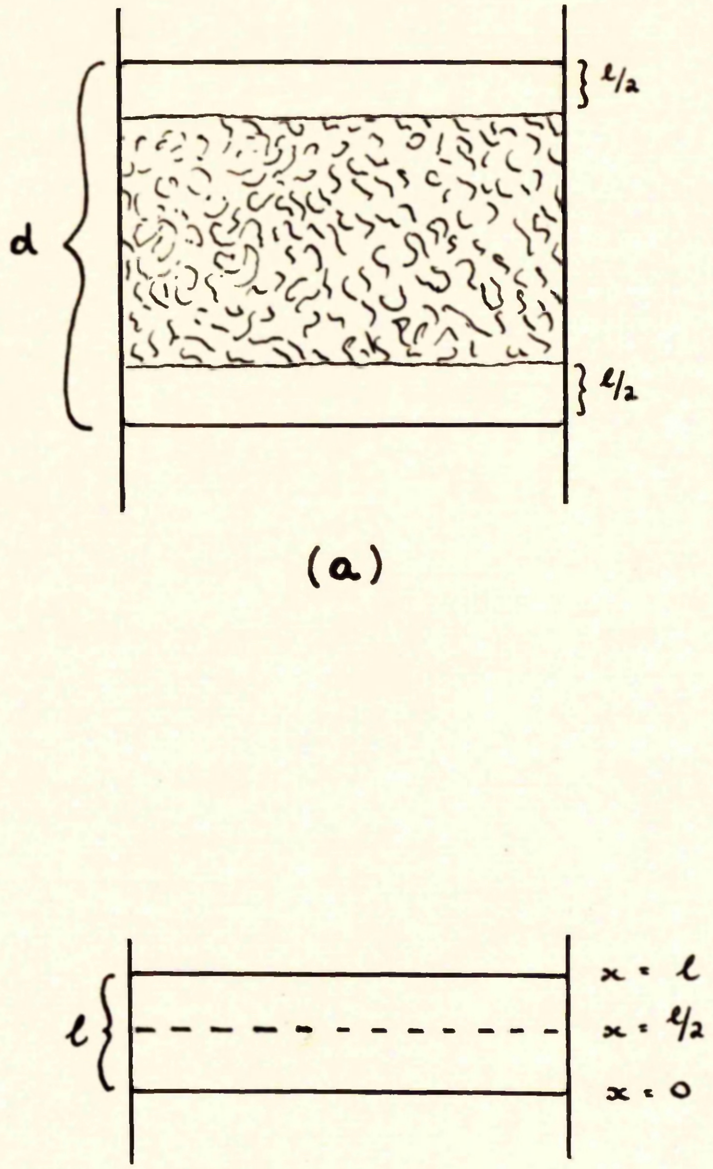
the plastic mass. Thus the coal sample may be regarded as consisting of three zones, as shown in Fig.20(a). All the gas evolved in the central zone is retained within the plastic coal and causes swelling, while all the gas generated in the upper and lower zones is considered to be lost by diffusion. If the total thickness of coal material is taken as d_1 then the fraction of coal material, ℓ, which supplies the gas which escapes will be given by the ratio of the gas escaping to the total gas evolution, i.e., $\ell = \frac{(R - \frac{dv}{dt})}{R}$ d and the effective thickness of the upper and lower zones referred to above will be $\ell/2$.

Thus, from the point of view of diffusion of gas, the coal sample may be regarded as a layer of thickness ℓ in which gas is generated uniformly and lost by diffusion at the surfaces $x = 0$ and $x = \ell$, as shown in Fig.20(b). This problem is similar mathematically to the conduction of heat in a rod, length ℓ , in which heat is generated uniformly, there being no heat loss at the sides, and whose ends are kept at zero temperature. Carslaw and Jaeger(58) show that for such a system the solution for steady temperature conditions, i.e., for the case in which all the heat generated is lost, is

$$T = \frac{Ao\ x(\ell - x)}{2K} \quad \text{where T is the temperature}$$

K is the conductivity and Ao is the heat produced per unit volume per unit time.

Applying this to the case of gas diffusion, at the centre of the coal layer $x = \ell/2$, T the temperature difference causing heat flow is equivalent to the applied pressure P(d) causing diffusion, and the



(a)

(b)

FIG. 20

permeability π corresponds to the conductivity K, while Ao is the volume of gas generated per unit volume of coal material per unit time and is given by $\frac{(R - \frac{dv}{dt})}{\text{area} \times \ell}$.

The equation for diffusion flow therefore becomes

$$P(d) = \frac{(R - \frac{dv}{dt}) \times \ell/2 \times \ell/2}{\text{area} \times \ell \times 2\pi}$$

hence, since the area of the crucible used is 20 sq.cm. the permeability

$$\pi = \frac{(R - \frac{dv}{dt}).\ \ell}{160.\ P(d)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

π being in cc at N.T.P./atmosphere/cm^2/min/mm thickness.

Since ℓ is equal to $\frac{(R - \frac{dv}{dt}).\ d}{R}$, it follows from the above expression that, when π reaches a constant value $(R - \frac{dv}{dt})^2 \propto P(d)$ and hence the graphical relationship between $\frac{dv}{dt}$ and $P(d)$ at high pressures is parabolic and concave upwards. An accurate extrapolation of the curve could not be made from the number of results obtained, as will be appreciated from Figs.12 and 13, (Chapter V). Such a relationship, however, explains why a linear extrapolation of the curve, referred to earlier, leads to a lower value of R than that determined experimentally.

The Permeability of Plastic Coal.

It is now proposed to discuss the results shown in Chapter V, with particular reference to the view of the swelling mechanism derived above. The experimental values of permeability (π) obtained for the various coals tested, including the Kingshill coal investigated by Taylor(26), were given in Tables 3 - 6 (Chapter V), while the graphical relationships between the permeability and applied pressure are shown in Figs.21 - 23.

FIG. 21

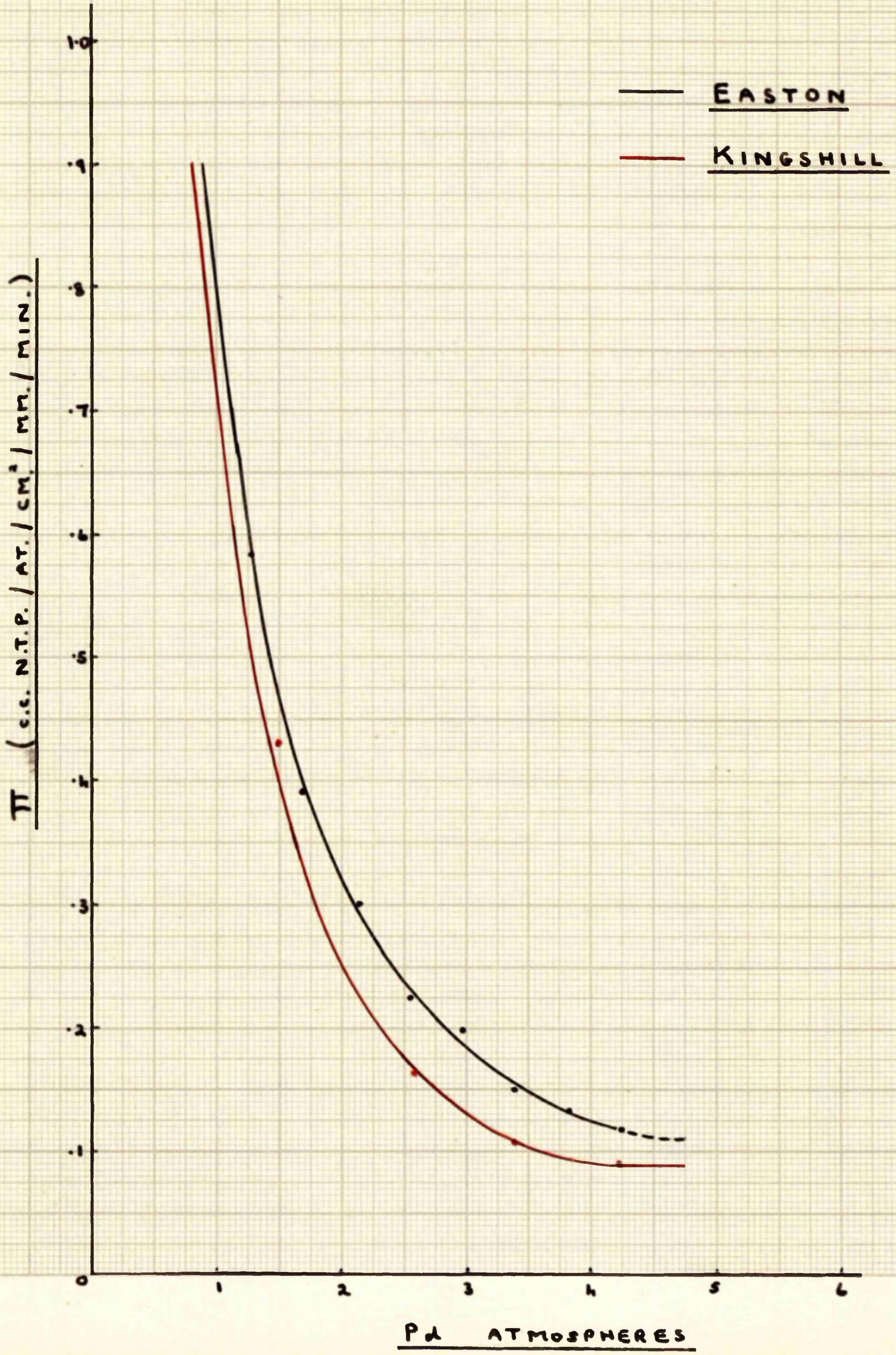

EASTON
KINGSHILL
Π (c.c. N.T.P. / AT. / CM.² / MM. / MIN.)
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
1
2
3
4
5
6
Pd ATMOSPHERES

FIG. 22

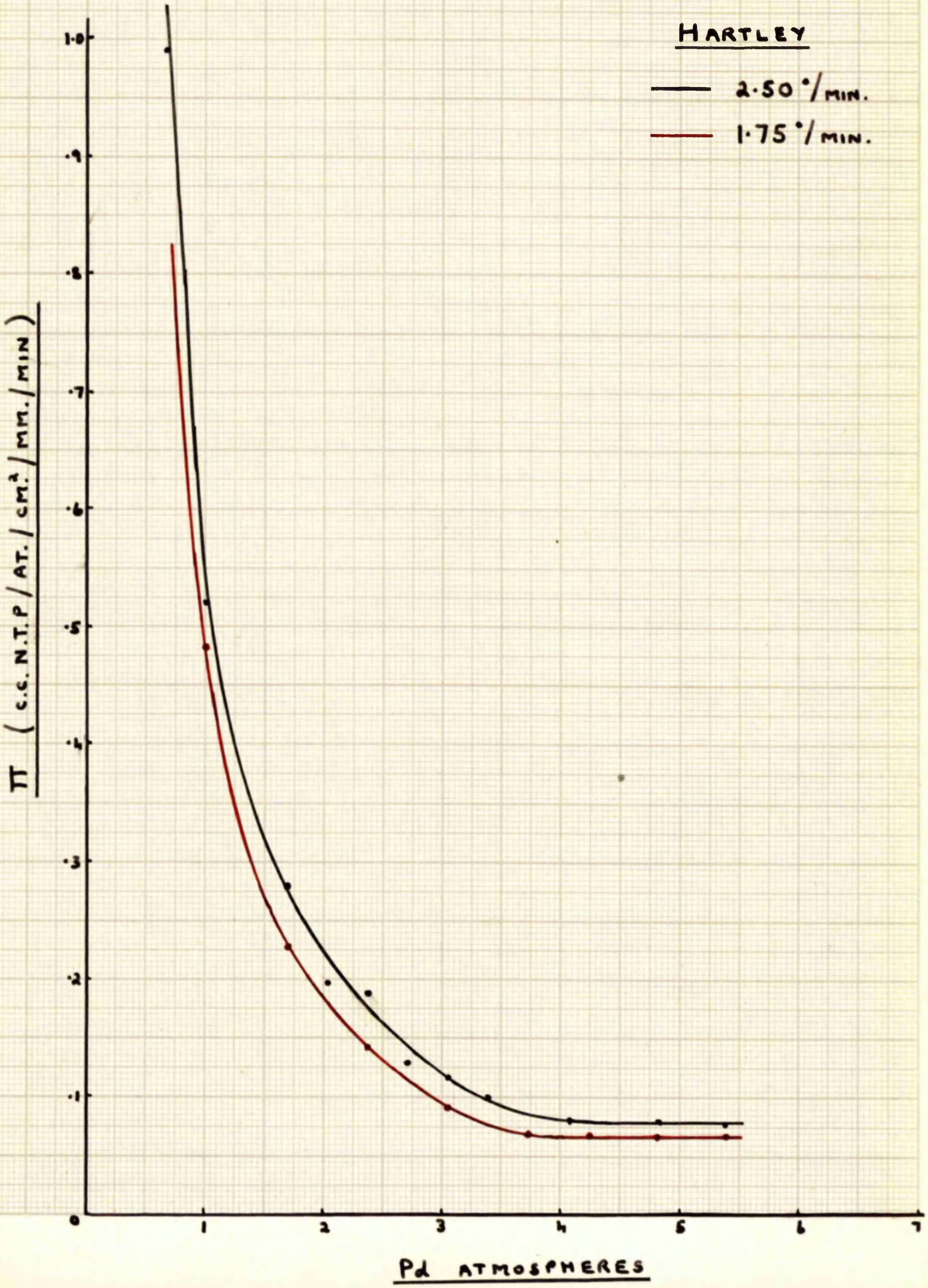
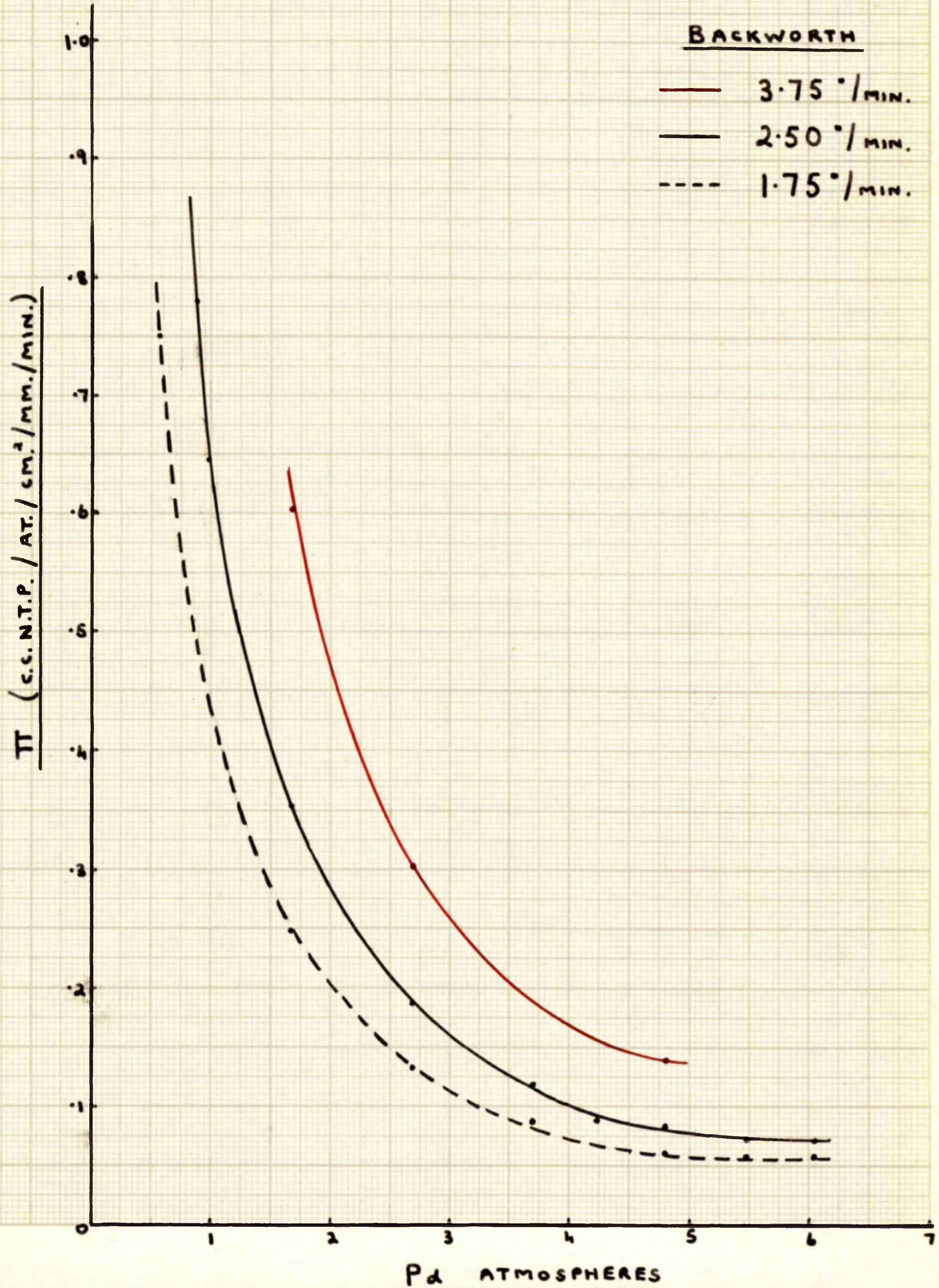

HARTLEY
2·50°/MIN.
1·75°/MIN.
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
1
2
3
4
5
6
7
π (c.c. N.T.P / AT. / CM.² / MM. / MIN)
Pd ATMOSPHERES

FIG. 23


BACKWORTH
3·75 °/MIN.
2·50 °/MIN.
1·75 °/MIN.
π (C.C. N.T.P. / AT. / CM.² / MM. / MIN.)
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
1
2
3
4
5
6
7
Pd ATMOSPHERES

It should be emphasised that, apart from the units in which it is expressed, the permeability coefficient (π) differs from the "permeability", (S), values referred to earlier in that the former takes the effective thickness of the coal sample into account. The general variation of π with pressure is very similar to that of S, as will be apparent from a comparison of the graphs referred to above and those showing the relationship between S and applied pressure (Figs.11 and 14 Chapter V). From the results given for the Backworth and Hartley Dross coals in Tables 6 and 5, however, it may be seen that whilst at high pressures the value of π for these coals becomes constant, the S values still show a slight decrease. This is due to an increase in the effective thickness (ℓ) of the coal sample at high pressures which is not taken into account in the latter permeability value.

Although the results obtained for the Hartley Dross and Backworth coals show that a constant permeability value is obtained at high pressure, as postulated by Taylor (26), the constant permeability condition is not so clearly established in the case of the Kingshill and Easton coals. In view of the inflexion found in the swelling rate - pressure curve (Fig.10 Chapter V) for the Kingshill coal, however, it is reasonable to assume that constant permeability has, in fact, been reached and the value of π obtained at the highest pressure used has been taken as the minimum value for this coal. Although no break was obtained in the corresponding swelling rate curve for the Easton coal (Fig.10), the results indicate that a maximum value is being approached. A slight extrapolation of the permeability curve for this coal has therefore been made, as shown in

Fig.21, in order to obtain a minimum permeability value comparable with those for the other coals.

Effect of Particle Size.

The results of a number of experiments in which the particle size and packing density were varied are shown in Table 16. These tests were carried out on the Backworth coal and the method of preparation of the samples was referred to previously (Chapter V). From the results obtained it is clear that, within the range of particle size used in the present work, the rate of swelling is practically independent of particle size and packing density, any variation being within the limits of experimental error. Such a finding supports the view that the swelling rate of a given mass of coal is determined solely by the rate of generation of gas, the applied pressure and the permeability of the mass at that pressure.

TABLE 16.

Backworth Coal 15 gm. samples.			Heating Rate 2.5°C/min.		
Test No.	Particle Size	P(d)at.	I.S.T.°C	Measured $\frac{dv}{dt}$ cc/min.	$\frac{dv}{dt}$ cc NTP/min.
B 28	-36 + 100 BSS	1.70	399	5.12	5.48
B 29	-3/32" + 1/16"	1.70	395	4.97	5.30
B 30	-36 + 100 BSS	2.72	403	4.70	6.91
B 31	-3/32" + 1/16"	2.72	398	4.55	6.71
B 32	65% -3/32"+1/16" 35% -36+100 BSS	2.72	398	4.68	6.89

It should be emphasised that the above statement, that the swelling rate is independent of the packing density or voidage does not conflict with the observations made on the effect of bulk density in various reports (35) on investigations of the coking process in experimental test ovens. In the latter case both the extent to which the plastic layer is free to swell, and hence the swelling pressure developed, are related to the voidage of the uncoked coal in the oven; bulk density would therefore be expected to be an important variable in such tests.

Variation of Permeability with Pressure.

The rapid fall which occurs in the permeability of the coal mass with initial increase of applied pressure is shown clearly in Figs. 21-23. Such a variation cannot be considered to be due to a change in the permeability of the actual plastic coal, since pressures of a few pounds per square inch could not be deemed sufficient to bring about any pronounced alteration in the structure of the coal material due to compression. It has in fact been shown(22) that pressures of three tons per square inch had relatively little effect on the internal surface of plastic coals as determined by heats of wetting.

It is considered therefore that the effect of pressure on the permeability must be due to the type of mechanism postulated above in the discussion of the escape of gas from the plastic mass, namely the gradual reduction and elimination of small pores by the application of increasing pressures with a consequent increase in the resistance of the mass to gas escape.

The swelling curves obtained in the experimental tests show a definite linear gradient over a considerable range of temperature. In view of this and the linear rate of generation of volatiles, discussed in Chapter VI, it follows that the permeability of the sample remains reasonably constant during the swelling period until, at higher temperatures loss of plasticity due to decomposition of fluid constituents or plasticising molecules and the gradual formation of a rigid semi-coke structure lead to an increase in permeability. The effect of pressure in reducing the permeability as described above must therefore reach an equilibrium with the effect of gas escape in preventing further closing of pores in the material, so that a certain constant permeability is maintained during swelling at any given pressure.

With the application of sufficiently high pressures it is found that a minimum permeability value is reached which is unaffected by further increase in applied pressure. This condition is considered to correspond to the stage at which all the micro pores in the coal mass are effectively sealed and gas escape occurs by a diffusion mechanism through the homogeneous plastic mass. The minimum value reached is therefore a measure of the permeability of the actual plastic coal material and is related to its diffusion constant. The diffusion constant is a fundamental property and has been used to derive information on the molecular structure of highly polymerised organic materials(59). This aspect of the present work could repay further study.

Variation of Permeability with Coal Rank.

The minimum permeability values obtained in the various series of tests carried out are shown in Table 17.

TABLE 17.

Coal	Minimum Permeability π 2·5°C/min.	Ultimate Analyses(Parr Basis)		
		C%	O_2%	H_2%
Easton	110×10^{-3}	85.70	7.63	5.23
Kingshill	90×10^{-3}	84.84	8.01	5.42
Hartley Dross	77×10^{-3}	86.70	5.73	5.25
Backworth	72×10^{-3}	86.20	6.38	5.52

The variation in the constant permeability figures obtained wit a heating rate of 2.5°C/min. for the four coals tested is considered to be significant. The full proximate and ultimate analyses of these coals were given in Table 2 (Chapter V); for ease of reference the more important details are also recorded in Table 17.

Hirst(21) and his co-workers have shown by determination of the heats of wetting of coals in methanol, that coking coals have a low internal surface area, synonymous with a low porosity or permeability. It was found that the heat of wetting varied with coal rank, a minimum being obtained at a carbon content of about 90%. It was also noted that the heat of wetting decreased with a decrease in the oxygen content of the coal. This work is supported by the evidence of Dunningham(60) who determined the porosity of coals from their inherent moisture content and obtained a very similar relationship between rank and porosity to that obtained by Hirst.

It would be expected therefore that the permeability figures obtained in the present work would show a decrease with increasing rank. It will be noted, however, that although the lower rank, higher oxygen Easton and Kingshill coals have higher permeabilities than the higher rank, lower oxygen Hartley and Backworth coals, the Kingshill and Backworth coal have lower respective permeabilities than the Easton and Hartley samples. It is considered, however, that this apparent discrepancy in the permeability - rank relationship can be attributed to the higher hydrogen contents of the Kingshill and Backworth coals; Mott(29) has stressed the importance of this latter factor in determining the swelling behaviour of coals. The higher permeability of the Easton coal may also be due in some measure to its markedly higher ash content, 7.7% compared with 4.1% in the Kingshill coal.

From a study of the swelling properties of a large number of coals, as determined by Sheffield Laboratory coking test, Mott(29) derived an empirical relationship between the swelling power of coals and their ultimate carbon and hydrogen contents, expressed by the equation

$$S^2 - (33 - 1{\cdot}5\,C)\,S + 0{\cdot}55C^2 + 6.25C + 105H - 155.5 = 0$$

$$\text{where} \quad S = \frac{\text{swelling }\%}{50} \qquad C = C\% - 80\% \text{ and } \quad H = H\% - 4\%$$

The swelling percentages of the above four coals, calculated according to this formula, are given in Table 18. It will be noted that the swelling percentage values obtained show a progressive increase with decreasing permeability. Since the swelling percentage figure is based on both the ultimate carbon and hydrogen contents of the coal,

TABLE 18.

Coal	Swelling Percentage (calculated)	B.S.S. No.	π
Easton	57.5%	3	110
Kingshill	75.0%	4	90
Hartley Dross	100.0%	$7\frac{1}{2}$	77
Backworth.	152.5%	$7\frac{1}{2}$	72

the relationship found is considered to support the above statement that the effect of hydrogen content accounts for the lower permeabilities of the Kingshill and Backworth coals in relation to their rank.

Thus, while data on a much wider range of coals would be required before any definite conclusions could be drawn as to the variation of permeability with coal rank, the results obtained are considered to support the view that the permeability of plastic coal as determined in the present work does have a degree of fundamental significance in relation to the composition and behaviour of coking coals.

The British Standard Swelling Numbers of the coals tested, given in Table 18, also show a certain degree of correlation with the permeability values. This criterion, however, does not distinguish so clearly the differences shown by either the calculated swelling percentages or the permeabilities of the coals.

There is comparatively little variation in the pressure at which the minimum permeability condition is obtained in the various test series. The values for Easton, Kingshill and Hartley samples are approximately $4\frac{1}{2}$, $4\frac{1}{4}$ and 4 atmospheres respectively. The Backworth coal, however, has the rather higher value of about $5\frac{1}{2}$ atmos. applied pressure. It would be expected from the view taken of the effect of pressure in reducing permeability, that a more fluid coal would attain a constant permeability under a lower applied pressure than a more viscous one, due to the great ease with which a homogeneous plastic mass would be obtained. Full data on the fluidity of the coals studied is not available. The results of Gieseler plastometer tests on the Easton and Hartley coals were, however, obtained from an independent source; the actual figures showed a maximum fluidity of 70 divisions per minute at 440°C for the former and 285 divisions per minute at 445°C for the latter coal. Thus the Hartley coal has an appreciably higher fluidity than the Easton, which is in accord with the lower pressure of 4 atmospheres at which minimum permeability was obtained with Hartley Dross samples. It is surprising to find, however, that the Backworth coal, which appeared to become very fluid during the swelling tests, attains minimum permeability at a higher pressure than any of the other coals.

Variation of Permeability with Heating Rate.

The effect of heating rate on the swelling behaviour has been studied with the Hartley Dross and Backworth coals. From a comparison of the permeability curves for these coals (Figs.22 and 23), and also from the minimum values which are shown in Table 19, it will be seen that both coals give lower permeability figures with lower heating rates, the difference between a rate of 2.5°C/min. and 1.75°C/min. being quite marked. This variation is confirmed by the results obtained for the Backworth coal at 3.75°C/min., though this series of tests was incomplete and the constant value shown in Table 19 was estimated by an extrapolation of the data available.

TABLE 19.

Coal	Minimum Permeability 3.75°/min.	2.5°/min.	1.75°/min.
Hartley Dross	-	77×10^{-3}	68×10^{-3}
Backworth	130×10^{-3}	72×10^{-3}	59×10^{-3}

The reason for such a variation of permeability with heating rate is not readily apparent, since an "a priori" consideration of the swelling mechanism leads to the view that the permeability would be independent of heating rate. Several workers, including Audibert(47) and Macura(61) have noted the effect of more rapid heating in reducing the viscosity of plastic coal. Such a variation in fluidity might be expected to reduce the permeability of the plastic mass leading to the opposite effect to that found above, namely a decrease in permeability with heating rate.

An explanation of the observed effect of heating rate based on the effect of pressure on the permeability was considered. It was noted previously that pressure is considered to reduce the permeability of the coal mass by causing flow of the plastic coal round the non fusible constituents present. If this process is dependent on the time for which pressure is applied as well as the actual magnitude of the pressure, the lower permeability obtained at lower heating rates might be due to the greater length of time for which the pressure is applied. Such an explanation was rejected however, since, while it could explain a relatively lower permeability at a given pressure with lower heating rate, the same constant value should ultimately be attained at higher pressures when the permeability measured is that of the actual homogeneous plastic mass. The view that pressure produces a decrease of permeability throughout the swelling range is also considered to be erroneous since the linear nature of the swelling curves obtained in the experimental tests over a considerable time and temperature range indicates that the permeability remains relatively constant.

It appears therefore that the reduction of permeability with lower heating rates must be due to some variation in the properties of the plastic coal which is not fully appreciated. It is thought, however, that this effect may be related to the variation of permeability with sample weight, which is discussed subsequently, and further reference will be made to the effect of heating rate at that stage.

Effect of Sample Weight.

The effect of using different sample weights in the experimental tests was the last variable to be studied in the present work. It had been expected that the result of varying sample size could be predicted from a consideration of the effect of the depth of coal sample

on the conditions for gas escape. Since, if the sample size is doubled, there is twice the volume of gas generated and the thickness of coal through which the gas has to pass is also increased, it was thought that the rate of swelling observed with the larger sample would be approximate: four times that obtained with half the sample weight and that the permeability calculated from $\pi = \frac{(R - \frac{dv}{dt})\,\ell}{P(d).160}$ ....(2)
would be substantially unaltered. (A factor of four for the expected increase in swelling is not strictly correct, as the relative values of R and $\frac{dv}{dt}$ must be taken into account, and the effective thickness of coal, ℓ, decreases with increase in the swelling rate).

The experimental results, however, do not agree with this hypothesis. It was found that on using twice the weight of coal sample the rate of swelling was scarcely doubled, which leads to a permeability value, for the larger sample, approximately four times greater than that calculated for the normal sample weight. The actual results obtained are summarised in Table 20.

TABLE 20.

Backworth Coal				Heating Rate 2.5°C/min.		
Test	Sample Wt. gm.	R cc/min. NTP	Applied Pres. P(d) at.	Actual $\frac{dv}{dt}$	$\frac{dv}{dt}$ NTP	$\pi = \frac{R-\frac{dv}{dt} \times \ell/6}{P(d)\text{-Area}}$
B33	15.0	25.90	0.34	5.41	2.81	2.19)
B34	10.0	17.27	0.34	3.42	1.79	0.98 }
B35	7.5	12.95	0.34	2.95	1.54	0.54)
B36	30.0	51.80	3.40	5.55	9.89	0.72)
B37	15.0	25.90	3.40	3.07	5.40	0.17)
B38	30.0	51.80	4.83	5.31	12.40	0.45)
B39	15.0	25.90	4.83	2.89	6.60	0.11)

Owing to the fact that this unexpected effect of sample weight was encountered in the final stages of the experimental work, when the time available was limited, the data obtained are by no means as full as might be desired. The variable has only been studied with the Backworth coal and the results although consistent within themselves are not strictly comparable with the main set of results obtained with this coal, since a slight reduction in swelling power had occurred before the tests on the effect of sample size were made. Nevertheless the results clearly indicate that both at high and low applied pressures and with larger and smaller than normal sample weights, the observed swelling rate shows less variation than would be expected, and in fact, the calculated permeability of the plastic coal increases with increasing sample size.

Reference may be made here to the results obtained by Taylor(26) using 7.5 gm. samples of Sacriston coal. A constant volume technique was used in most of the work on this coal. However, some data was obtained on the swelling under constant pressure and these results are shown in Table 21.

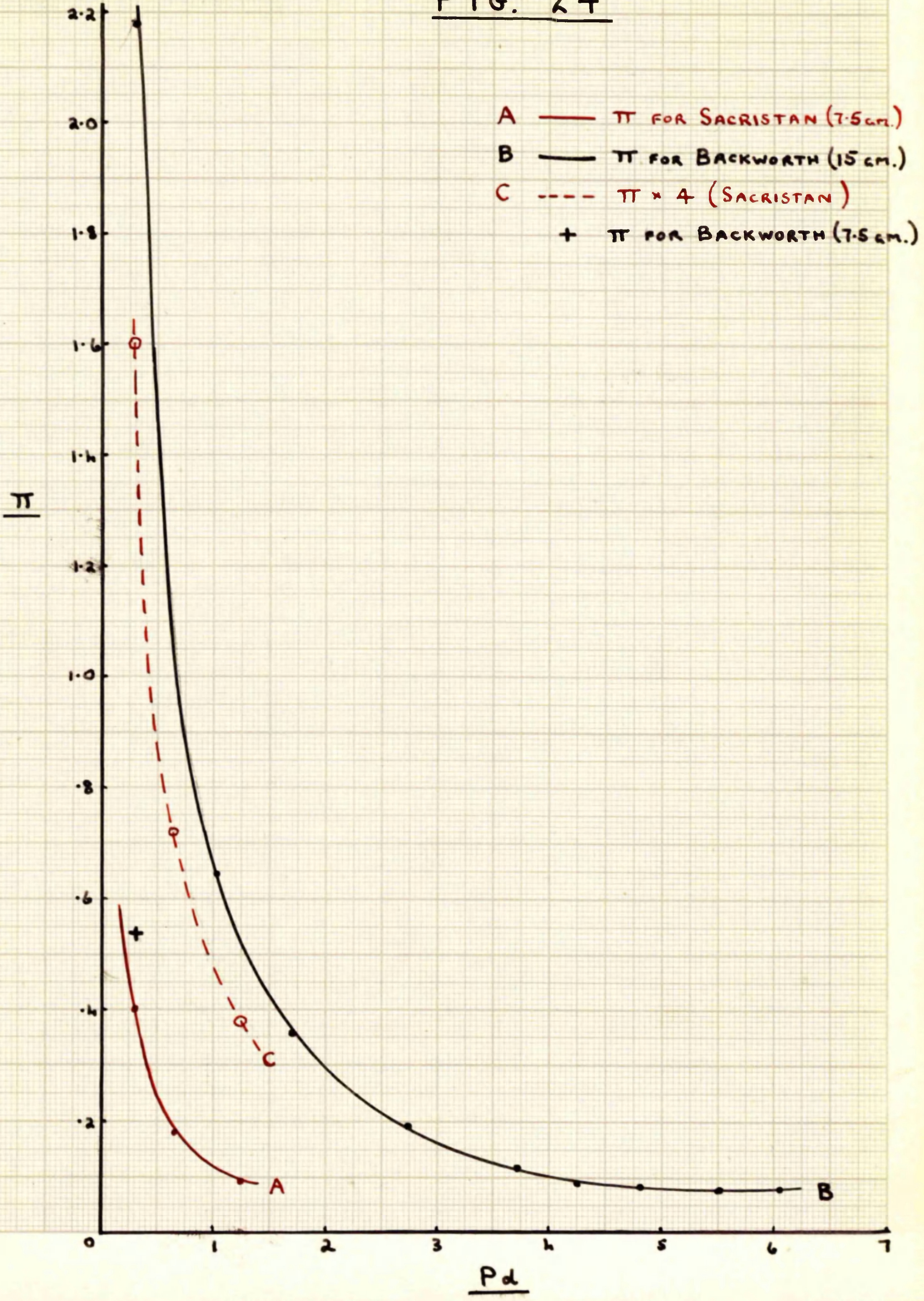
TABLE 21.

Sacristan Coal 7.5 gm. samples. R = 12.2 cc NTP/min. 2.5°C/min.

Test No.	Applied Pres. P(d) at.	$\frac{dv}{dt}$ cc NTP/min.	$\pi = \frac{(R - \frac{dv}{dt}) . \ell}{P(d) . 160}$	4π
S1	0.08	2.35	1.77	7.08
S2	0.32	2.80	0.40	1.60
S3	0.64	3.28	0.18	0.72
S4	1.27	3.15	0.094	0.38

The permeability values of the 7.5 gm. Sacriston samples are compared in Fig.24, curve A, with those obtained in the series of tests at 2.5°C/min. on 15 gm. Backworth samples (curve B). On the assumption that the permeability is not affected by sample weight the Sacriston permeabilities appear to be extremely low compared with the Backworth figures. If, however, the former values are multiplied by four, which is the approximate factor found for the variation in permeability of the Backworth coal with double the sample size, the values of 4π , shown in Fig.24 (curve C), give a graph very similar to that for the 15 gm. Backworth samples but lying somewhat below it. A lower permeability for the Sacristan coal is in agreement with the fact that it is the lowest volatile, lowest oxygen coal of those tested. Also, the swelling percentage figure, calculated from the ultimate analysis according to Mott's formula (29), which was found to place the coals tested in order of decreasing permeability, is found to be 275% compared with 152% for the Backworth coal. Only one result is available for a 7.5 gm. Backwort sample but as can be seen from Fig.24 this result is slightly higher than the corresponding 7.5 gm. Sacristan value. Thus, although there are no actual results on the effect of sample size for the Sacristan coal, it appears that the same type of relationship between permeability and sample size might be obtained with it. Possible explanations for the effect of sample weight on the permeability coefficient obtained for the Backworth coal are considered below.

FIG. 24


A —— π for Sacristan (7·5 cm.)
B —— π for Backworth (15 cm.)
C - - - π × 4 (Sacristan)
+ π for Backworth (7·5 cm.)
π
2·2
2·0
1·8
1·6
1·4
1·2
1·0
·8
·6
·4
·2
0
1
2
3
4
5
6
7
Pd
A
B
C

If the results are due to a failure of the experimental technique, the most probable cause would be non-uniform volume heating of the coal sample. It is true that in a few of the experimental tests carried out this difficulty had been encountered, especially at high heating rates and in some cases with large samples. It was found, however, that when this occurred a poor swelling curve was obtained and the resulting semi-coke showed definite signs of uneven heating, part of the sample still showing the original particulate natureof the coal and part having a greyish overheated appearance. This was also accompanied by difficulty in maintaining even operation of the high frequency generator, the supply current rising rapidly and fluctuating continually. In the tests under discussion none of these characteristic features was observed, and the fact that both smaller (7.5 gm.) and larger (30 gm.) samples behaved in a similar manner does not support any explanation based on a falling off of the volume heating efficiency with large sample sizes.

Any tendency for the upper and lower surfaces of the coal sample to be chilled by the refractory discs and electrodes should have a relatively smaller effect the larger the sample size and would lead to higher swelling rates with large samples. These considerations tend to discount the view that isothermal conditions were not obtained.

The other feature of the experimental technique which might be thought to affect the swelling characteristics is the effect of the asbestos discs used to prevent escape of the plastic coal from the crucible. If, however, the permeability of the discs controlled the rate of gas escape it would be expected that the amount of gas escaping would have remained constant with increasing sample size, whereas it actually increased. Tests were also carried out on the asbestos paper before and after use, and its permeability was found to be much greater than the permeabilities calculated for any of the coals studied. It is considered therefore, that the results obtained cannot be attributed to factors arising from the experimental method employed.

It can be shown from the results given in Table 20 that, for tests carried out under the same applied pressure, the proportion of the total volatile matter escaping [i.e., $\frac{R - \frac{dv}{dt}}{R}$] from different weights of coal sample is approximately constant, the results of tests B33, 34 and 35 on 15, 10 and 7.5 gm. samples showing a loss of 89, 89 and 88% of the total volatiles respectively. This could be interpreted as evidence that only certain constituents of the volatile products are able to escape from the plastic mass. Thus the condensible vapours produced might be able to escape by a solution and diffusion process through the plastic coal membrane, which, however, remains impermeable to the remainder of the gaseous products. Alternatively a type of selective diffusion might be considered to operate allowing escape of the constituents of lower molecular weight while the larger molecules are entrapped. The extent of swelling would then be controlled by the volume of decomposition products unable to escape, which would be proportional to the sample size, thus explaining the observed variation in swelling rate.

This is, to some extent, in accord with the view taken by Berkowitz(25) that coking coal had an inherent pore structure which acts as a "molecular sieve", the swelling power being governed both by the amount of volatile matter generated within the coal particle and the "size and shape" of the escaping molecules. Such a hypothesis, while explaining the effect of sample size, does not account for the general relationship found, in the main series of experimental tests, between the rate of swelling and applied pressure.

The fact that, under increasing applied pressure, the calculate permeability values decrease until a constant minimum is reached points to pressure causing a progressive reduction in the ease withwhich the thermal decomposition products can escape, presumably due to flow of the softened coal under pressure resulting in a gradual sealing of pores in the coal mass. If this is the case increase in the sample depth must be expected to reduce the rate of loss of gas, irrespective of its composition. The experimental results, however, show that an increase in sample size is accompanied by an increase in the rate of gas escape. Since this is a function of the permeability and the internal gas pressure, it would appear that the results must be due to either an increa in the permeability of the coal material or an increase in the pressure causing gas escape, with larger samples.

In the following paragraphs these two possibilities are discussed with a view to determining whether such variations are likely to occur.

The assumption has been made, so far, that the internal pressure developed in the plastic coal sample during swelling is equal to the external applied pressure, that is to say the force required to overcome the resistance to flow of the plastic mass has been considered to be negligible. Such an assumption, however, may not be justified and it is possible that a certain excess pressure must be developed within the plastic coal to cause movement of the viscous mass in the crucible. This pressure could be considered to be analagous to the pressure drop which occurs during flow of a fluid along a cylindrical pipe, which is stated mathematically in the form $P = \frac{32 \eta L v}{D^2 g}$ in c.g.s. units where P is the pressure drop, η the viscosity of the fluid, L the length of pipe, D its diameter, v the flow rate and g the gravitational constant.

Applying this to the movement of the plastic coal during swelling, it can be seen that, although the values of L and v are very small, the pressure P required to cause flow could be substantial due to the high viscosity of the coal mass. Also, since L and v increase with increasing sample size it would be expected that higher excess internal pressures would be developed with larger coal samples, leading to higher rates of gas escape.

The above expression for the pressure drop may be put in the form $P_E = kLv$, where P_E is the pressure producing swelling, L is the effective length of the coal sample and v is the swelling rate, k being a constant dependent on the viscosity of the plastic coal. Since the rate of gas escape from the coal sample and the amount of gas entrapped in the swelling coal depends on the total internal pressure, the swelling mechanism derived in equation (2) above may then be expressed in the form

$$\pi = \frac{[R - (\frac{dv}{dt})''. (Pd + kLv + 1)]. \ell}{160. (Pd + kLv)}$$

where the term $(\frac{dv}{dt})''(Pd + kLv + 1)$ represents the volume of gas entrapped in the coal, $(\frac{dv}{dt})''$ being the measured swelling rate corrected to standard temperature and $(Pd + kLv + 1)$ being the absolute pressure.

If π is assumed to be independent of sample weight the value of K, and hence the excess pressure required to account for the observed increase in gas escape, may be calculated from the results of two tests carried out with different sample sizes under the same applied pressure, by eliminating π between the two equations and solving the resulting quadratic equation for k.

If tests B38 and B39 (see Table 20) are considered, the calculated excess pressure is found to be approximately 2.2 atmos. and 8.0 atmospheres for the 15 and 30 gm. samples respectively, which corresponds to a value of 10^9 poises for the viscosity of the coal mass.

While a considerable amount of work has been done on the viscosity of plastic coal in various types of viscometers and plastometers there is little data available in which the results obtained are expressed in absolute units. Macura(61) determined the viscosity of several German coals by using a modified type of Giesler rotational plastometer which was calibrated by means of standard pitches of known absolute viscosity. He reported minimum viscosities during the plastic range of between 10^6 and 10^7 poises for strongly swelling coals. Soth and Russell(62) using a similar technique, quoted viscosities of from

10^3 to 10^6 poises for a series of coals of varying rank. It would appea therefore that the viscosity of 10^9 poises calculated above is considerably higher than would be expected, which leads to the conclusion that, if there is any excess internal pressure required to cause swelling, it is too small to account for the results obtained in the swelling tests.

Another obvious objection to the above explanation is that, while it would apply to higher applied pressures at which the minimum permeability is reached, at low applied pressures the higher excess pressure developed in a large sample would be expected to cause a large reduction in the permeability of the coal mass as will be appreciated from the permeability - pressure curves shown in Figs.21-23. The experimental results, however, show that the relative effect of sample weight on the swelling rate and permeability is the same at both high and low pressures.

The obvious alternative to all the views discussed above is that the "permeability" of the coal mass actually increases with sample size. It was noted earlier, when the diffusion of gases through membranes was discussed, that although in general the volume of gas passing was proportional to the pressure difference and inversely proportional to the membrane thickness, deviation from this law did take place. It has been shown(57) that when dealing with gases some deviation from the linear relationship between rate of diffusion and pressure difference may occur at pressures of several atmospheres. In the case of vapours, much larger deviations occur and the linear relationship may break down at pressures of considerably less than one atmosphere. In general, increases in the permeation rate "constant" of organic membranes are found(63) with increasing vapour pressure difference and the permeability "constant" has also been shown to increase with greater thickness of membrane, this tendency being more pronounced at high vapour pressures.

It would appear, therefore, that the increase in the calculate permeability of the Backworth coal with larger sample weights might be expected to be due to the effect of increasing membrane thickness mentioned above. It is impossible to estimate the actual increase in permeability which might occur due to this effect, since the degree of departure from ideal behaviour in the organic polymer-gas systems referred to above is dependent on both the membrane and the diffusing gases and vapours, diffusion of the latter being closely connected with the extent to which the vapour is absorbed by the membrane. The data given by Barrer(63), however, shows that variations in permeability due to such an effect are relatively small and it is considered impossible that the large increase in permeability obtained in the tests under discussion, by doublin the size of coal sample, can be attributed solely to this phenomenon.

In his paper on the viscosity of coal, Macura(61) reported that the viscosity values he obtained were dependent on the rate of shear used in the experimental tests. He found that if higher loads were applied to the stirring shaft of the plastometer, resulting in an increased rate of rotation, the viscosity of the coal increased. That is to say the relative resistance to shear increased with increasing rate of shear. Such an effect cannot be due to fictional losses in the rotation mechanism since this would lead to a relative increase in the speed of rotation with larger loads.

Rheological systems which exhibit increasing resistance to shear with increasing rate of shear are termed dilatant. This phenomenon has been encountered in various types of particle-vehicle suspensions, and is attributed(64) to a condition of minimum voidage in the suspension which is disrupted by any force or shearing action resulting in a dilation of the voids and a partial hardening or drying of the material with a consequent increase in resistance to shear. Such an effect would also be accompanied by an increase in permeability. Lee and Markevich(65) have reported that certain asphalt mixtures show dilatant behaviour, an expansion being observed under shear.

It is suggested, therefore, that the viscosity data of Macura(61) implies that plastic coal, which may be regarded as a type of colloidal dispersion, is capable of showing dilatent properties and such behaviour could account for the variation of permeability with sample size observed in the present investigation. Swelling of a plastic coal mass is equivalent to a continuous shearing of the coal material. The increase in permeability obtained with larger coal samples would therefore be due to their higher swelling rates, since, if coal exhibits dilatent properties, it would be expected that higher rates of swelling would produce greater resistance to shear and a consequent increase in permeability due to some type of void dilation mechanism.

It was noted earlier, when the effect of rate heating on permeability was discussed that lower heating rates gave lower values of permeability and it was pointed out that the greater fluidity of coals at higher heating rates might have been expected to lead to the opposite effect. In view of the above observations, however, the variation may be explained by the lower swelling rates obtained at lower heating rates resulting in lower permeability. From the π values obtained it would appear that, as a first approximation, the permeability decreases in proportion to the swelling rate. The fact that permeability shows a greater dependence on swelling rate in the sample size experiments (increasing roughly as the square of the expansion rate) may be interpreted as an indication that the "true" permeability does decrease with increased heating rate, as might be expected due to greater fluidity(47,61) but that this effect is reversed due to the higher expansion rates at higher heating rate. Thus a mechanism of the type postulated above could account for both the effect of heating rate and sample size on the calculated permeability of the plastic coal.

If such a view is taken, the rate of swelling under steady pressure for any given size of coal sample will be determined by a rather complex dynamic equilibrium between the rate of gas evolution, the permeability of the plastic coal and the rate of swelling. A given rate of gas evolution together with a certain inherent permeability of the coal material will tend to produce a certain rate of swelling. The higher the rate of swelling, however, the greater will be the resistance of the coal to shear and the increase in permeability due to dilation. Both these effects will tend to reduce the rate of swelling, which in turn will lower the resistance to shear and reduce the permeability, leading to a further compensating increase in the rate of swelling and so on. It would appear therefore, that the permeability values obtained are probably functions of the swelling rate, which is itself a function of the permeability and rate of gas evolution. The interdependence of these variables means that the relationship between permeability and coal properties is not so simple as hitherto thought and that the experimental permeability values cannot be considered to be independent of the experimental conditions as was postulated by Taylor(26).

The above effect of sample size does not invalidate the general conclusions reached previously on the variation of permeability values of the range of coals studied. Since these results were all obtained with 15 gm. samples, the permeability values should be comparable as they represent the properties of a given thickness of plastic coal alyer. In so far as the π values are modified by the rate of expansion this will tend to accentuate the variation in the permeability of the different coals, since, as shown in Table 17, the higher the swelling power of the coal the lower is its measured permeability. Thus if the swelling rates were taken into account this would lead to still lower relative "true" permeability values for the low measured permeability coals.

Further investigation of the effect of sample size on the swelling behaviour would be highly desirable in order to clarify the position and determine whether the interpretation of the results suggested above is borne out by more complete data, or whether the view taken of the mechanism of swelling and gas escape from the plastic mass requires further modification.

Independent measurements of the permeability of the coal samples would be of considerable value in reaching more definite conclusions. Such measurements could be attempted during swelling of the coal sample, by the application of some type of gas flow method, such as that used by Foxwell (66). Alternatively, using the present technique, samples could be heated to various temperatures in the plastic range under varying conditions and then cooled. Independent measurements of the gas permeability of such samples could then be made and it would be interesting to determine the variation of such permeability figures with sample weight.

If the rate of swelling is an important factor in determining the permeability, the effect of this variable might be eliminated by calculati permeability figures from the rate of increase of pressure in constant volume tests, since this value can also be employed to determine the rate of gas escape from the plastic mass. Such calculations have in fact been made from data obtained by Taylor(26) on the swelling behaviour of the Sacristan coal, referred to previously, in constant volume tests. The basis for comparison with the constant pressure values, given in Table 21, is not very sound, since the pressure increase results were obtained from tests on coal-sand mixtures. Within these limitations, however, the constant volume results are consistent with the view that movement of the plastic coal leads to higher permeability values.

Coke Oven Conditions.

Finally it is proposed to discuss the coking process in commercial ovens with reference to the development of "coking pressures" within the plastic layer and the role which may be played by coal permeability in this connection.

In industrial coking plants, carbonization takes place by transfer of heat from the coke oven walls inwards through the coal charge. Thus the layers of coal adjacent to the oven walls are the first to pass through the plastic range and thereafter the two plastic layers move slowly inwards from the opposite walls of the oven until they finally coalesce at the centre of the charge.

After the initial formation of a thin layer of coke at the oven walls, a type of dynamic equilibrium is set up within the oven, the degree to which the plastic coal layer is free to expand being dependent on several factors, namely the packing or bulk density of the uncoked coal, the extent of the pre-swelling contraction and post swelling collapse of the plastic mass, and the subsequent shrinkage of the rigid semi-coke already formed. Since the latter contraction is relatively small, the extent to which expansion is possible will be determined mainly by the other factors, which remain practically constant during the coking period, so that the plastic mass swells under approximately "constant expansion" conditions.

As carbonisation proceeds the temperature gradient within the charge decreases. There is a consequent proportional decrease in the rate of temperature rise in the swelling layer. But at the same time the thickness of this layer and also of the contracting layers on either side increases in inverse proportion. The rate of contraction, under the same pressure, therefore, remains constant. During carbonisation it is necessary to consider a plastic layer, which tends to swell at the same rate but the rate of heating and thickness vary inversely with one another. The pressure built up within the plastic layer and the variation of this pressure during coking will depend on the altering permeability of the plastic coal layer under these conditions. Since the rate of swelling of the plastic coal is relatively constant and cannot affect the permeability markedly, the main variable to be considered is the alteration of permeability with heating rate, as discussed below.

Due to the fact that the heating rate and thickness of plastic layer vary inversely, the total amount of volatile matter generated within the plastic layer per unit time will remain approximately constant during the coking period. Actually, as shown in Chapter VI, a slight increase in the rate of volatile evolution might be expected with decreasing heating rate. Depending on the manner in which permeability varies with heating rate, there are three main possibilities for the variation of expansion pressure during coking. If the permeability of the plastic coal material remains unaltered by a decrease in the rate of heating, the rate of gas escape from the plastic mass will gradually decrease due to the increasing thickness of the plastic layer and, since an increase in the rate of expansion is prevented, this will lead to an increase in the pressure within the plastic layer as carbonization progresses. If, on the other hand, the permeability increases proportionately as the heating rate decreases, these two effects will tend to balance one another, so that the pressure in the plastic layer could remain relatively constant during the coking period. Thirdly, a rapid increase in permeability with lower rates of temperature rise would result in a decrease in the expansion pressure as the plastic layer moves inwards and this could result in poor or incomplete coking towards the centre of the oven.

All the above conditions can occur in industrial coking practice. The first effect, namely increasing pressure during carbonization, corresponds to the behaviour of "dangerous" coals, which may develop sufficient pressure to cause damage to the coke oven walls, while the third case may be encountered with poor quality coking coals. Investigations of expansion pressure in moveable wall test ovens(35) indicate that many coals and blends have relatively constant expansion pressures throughout the greater part of the coking period which, as described abov could be explained by a proportionate increase in permeability with decreasing heating rate. In such cases, however, a rapid increase in expansion pressure is generally found when the two plastic layers coalesce at the centre of the oven (34,35). The development of a "peak" pressure at this stage follows logically from the mechanism postulated above, since the thickness of the plastic layer has suddenly been doubled without any compensating decrease in heating rate, and since the swelling is no longer partially accommodated in the voidage of the uncoked coal.

The above consideration of the probable role of permeability in the coking process is only tentative and is much simplified since the relationship between the variables involved is more complex than has been assumed. Nevertheless, it has been shown that it is possible to explain the development and variation of coking pressures on the basis of the permeability mechanism derived for the swelling process.

As already discussed, the most important variable with respect to the coke oven conditions is the effect of heating rate on permeability Unfortunately the present work has afforded little information on this particular problem, since the permeability figures obtained at varying heating rates are not comparable, due to the effect of swelling rate on permeability, evidenced by the tests carried out with different weights of coal sample. Thus although the permeability of the Backworth coal appears to be lower at reduced heating rates, the effect of swelling rate is more than sufficient to account for this trend and, suggests that there is actually a decrease in the "true" permeability of the coal with increase in heating rate. Experimental tests, under both constant pressure and constant volume conditions, in which sample weight and heating rate are varied inversely, would be of particular interest in assessing the validity of the above arguments and in indicating the probable variation of expansion pressure during the coking of different coals and blends.

CONCLUSION.

The significant points of the preceding work may be summarised as follows:-

The results obtained in the swelling and volatile evolution tests carried out on various coking coals confirm the general view that the swelling of plastic coal is directly related to the "permeability" of the plastic mass and the rate at which volatile decomposition products are formed within it. It has been shown, however, that the relationship between these factors is not so simple as at first supposed.

The development of a direct experimental method allowing of an accurate evaluation of the volume rate of volatile evolution has been of considerable value in deriving permeability values for the coals studied, and the minimum permeabilities attained by these coals under pressure have been found to show a significant variation with coal rank.

The variation in permeability found with increasing sample weight i.e., sample thickness, has proved to be one of the most interesting features disclosed by the present work. An increase in the thickness of the plastic layer was expected to result in a decrease in the rate of gas escape from the plastic mass, whereas the rate of gas loss was actually found to increase. This behaviour is attributed to the plastic coal exhibiting dilatant properties, an increased rate of swelling resulting in an increase in the permeability of the material.

Due to the dependence of permeability on the swelling rate, the inter-relationship of rate of gas evolution, permeability, swelling rate and heating rate during the swelling process is extremely complex and cannot be said to have been fully elucidated by the present investigation. Further investigations of the effect of sample thickness and heating rate in the light of the results already obtained would allow more definite conclusions to be drawn on the interdependence of the above variables.

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