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

THESIS
presented by
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PART I.

INTRODUCTION.

The significance of blast furnace coke properties, relative to efficient operation of that smelting unit, has long been appreciated but difficulty is still experienced (1,2,) in evaluating the relative importance of the several properties concerned. Initially, when the theoretical basis of the reduction process was being evolved, discussion centred around the property of chemical reactivity, (3,4,5) but investigations both from a theoretical (6,7,) and a practical standpoint (8,9,10), indicated that the combustion process, at the operative temperatures in a blast furnace hearth, was controlled mainly by the physical and not by the chemical properties of the coke. Specifically interest now centres on such properties as size and size distribution, coke strength, and bulk density which all control, directly or indirectly, the ease with which air can be introduced to the stock and also the resulting gas-solid contact; investigation, (8,9,10) adequately substantiates the importance of these factors in affecting the overall reduction efficiency. The importance of such additional properties as apparent and real specific gravity, reactivity, etc., is of a more speculative nature and their effects are undoubtedly overshadowed by those of the former properties.

Having mentioned, by way of introduction the importance of coke properties on blast furnace efficiency, it is now proposed to discuss and emphasize, the close interrelationship /

relationship of these properties and the physical factors operative while the coking coal or blend is passing through the so called "plastic" range. It is now fully appreciated that this transient, low temperature stage is of considerably greater moment, as regards final coke properties, than the subsequent one when the semi-coke is raised to the final carbonising temperature; during the latter stage, it is true, much of the coke strength is developed (11) but there is evidence (12,13), to suggest that the effects of this latter heat treatment are reasonably the same with all semi-cokes so treated.

This "plastic" stage shown by all coking coals or blends to a greater or less degree, on heating in the range 330-500°C, would appear to be sine qua non of coke making. During this stage, the particulate nature of the original coal charge is lost by the softening and subsequent swelling of certain of the coal constituents; this swelling is induced by the entrapment of the volatile decomposition products from the break down of the organic material. Similar thermal effects continuing to a higher temperature, result in the subsequent loss of "plasticity" owing to the disappearance of certain essential "plasticising" molecules; the resulting semi-coke is quite rigid and, although fissured, is considerably larger in average size than the original coal charge. It will be appreciated that such a description is grossly oversimplified, but for the sake of a lucid argument, a detailed /

detailed discussion of the more accurate theories of the "plastic" state is omitted till a later stage (Part VI). Differences in the coking behaviour of different coals are now generally attributed primarily to differences in degree and extent of the "plasticity" attained by the several coals. Such differences in "plasticity" arise on account of the following factors which are variables in different coals:-

(a) Chemical composition as given by the ultimate coal analysis. Mott and Spooner (13) showed the effect of increased percentage of fixed carbon and also of increased percentage of hydrogen, in increasing the degree of swelling in the Sheffield Laboratory Coking Test. It is now generally recognised that the best coking coals are those with a fixed carbon content in the 90% range. The effect of increased carbon and hydrogen contents appear to be that they increase the dispersibility or "solubility" of the non fluid portion of the "plastic" coal, in the "plasticising" molecules; it would appear that the oxygen content of these non fluid portions is the critical factor, and that the lower oxygen content of high rank coals accounts, in some degree, for their better coking properties. These points will be elaborated at a later stage.

(b) The micellar size and method of aggregation. Attention has recently been drawn (14) to this aspect of coal structure and it has been shown that the best coking coals are those which /

which have a low internal surface area; differences in micellar size are also indicated from similar measurements. Hence if surface wetting has any influence on "plasticity", as suggested by Mott (15) this newly noted variable may also have an effect on coking.

(c) Petrological composition. The sofetning and swelling characteristics are confined almost entirely to the constituents vitrain and clarain. Durain has been shown to possess very limited powers of swelling (16), i.e., about 8% volume change as compared to 103% for a vitrain under similar experimental conditions, while fusain is quite inert from this point of view. Differences in petrological composition result in wide variations of the physical properties of the "plastic" coal, and this effect is rendered more complex, not only by the fact that it is difficult to obtain an accurate petrographic analysis of a coal, but variations in the swelling powers of vitrain and clarain also occur with rank. The aim of the coal technologist was therefore to devise tests which would measure the several physical constants of the "plastic" coal, the ultimate goal being the direct correlation of one, or some, of these constants and the resulting coke properties. In view of the significance now attached to the size and strength factors of coke, the correlation has usually been made with one of the latter properties. Such correlations will be discussed in the following paragraph while a more detailed discussion of some of the tests used therein will be presented in Part II.

Marshall & Bird (17) using a modified agglutinating test showed that for a number of American coals of different rank, an increase in the relative strengths of the cokes produced therefrom, was accompanied by a corresponding increase in the agglutinating value. They also showed that there was a general relationship between this value and the chemical nature of the coal; the agglutinating value fell as the oxygen content of the coal increased and increased with increased carbon/oxygen and hydrogen/oxygen ratios, in a similar way to the coking value of the coals. Perhaps the most interesting correlation of the physical properties of the "plastic" coal and coke properties was that shown by Mott (18) using a dilatometric method. He demonstrated conclusively the close inter-relationship of the percent swelling with final coke properties; his graph of Volume Change % - Fixed Carbon %, shows a marked increase in the gradient of the relationship at a fixed carbon content of 85 - 86%, which corresponds to the superior nature of cokes given by coals with fixed carbon contents above this value, e.g., Durham and Welsh coals. His work also indicated that the characteristic temperatures of the "plastic" range, e.g., the initial contraction and the initial expansion temperatures, were less reliable guides to the coking properties of the different coals. In a subsequent paper, (13) he presented a graphical relationship between the amount of swelling of a coal and its ultimate carbon and hydrogen contents, which was an excellent guide to /

to the coking behaviour of different coals. The American approach to this problem has been along somewhat different lines, and the general outcome of their investigations was less satisfactory than that of Mott. They have attempted to correlate coking behaviour with the characteristic temperatures of the "plastic" stage, and also with certain rheological properties of the "plastic" coal, e.g. its so called "fluidity" as measured in the Davis or Giesler plastometer . Fieldner (19) states that there is no precise relationship between "plastic" properties and physical properties of the coke. It was found (20) that coke strength generally increased with increased length of the "plastic" state, and it is interesting to note that this is in contrast to the findings of Brewer & Atkinson (21). Lowry & Junge (20), however, in an investigation of such a relationship, showed that for a series of coals, of limited range of fixed carbon content, there was a statistical relationship between the ($1\frac{1}{2}$") shatter index and certain of the characteristic temperatures of the "plastic" stage. In this respect the temperature found to be of greatest significance with relation to the ($1\frac{1}{2}$") shatter index was that of maximum resistance in the Davis plastometer. This latter observation may be of value when the theories of fissure formation in coke are considered critically. Mott's theory (22) of residual volatile matter after the "plastic" stage, receives little support from a study of several tables of residual volatile matter contents for different coals, and it may well be that a theory based on the idea of a certain amount of residual "plasticity" in the coal, after the final expansion temperature is attained will fit the experimental facts more satisfactorily.

Finally it is proposed to discuss the possible importance of the pressure built up within the "plastic" layer as a factor of importance in the coking process. The enhanced coking properties of a variety of carbonaceous materials, heated under increased pressure, have been adequately demonstrated by the results of a number of workers, (23, 24, 25) while the particular significance of this factor in the making of high grade coke is emphasized by Foxwell (26) and also by Blayden, Gibson & Riley (11). The latter authors clearly showed that, for a series of poor or weakly coking coals pressures of the order of 20 lbs/sq.in. were most effective in improving the micro-strength of the cokes and that this effect arose as a result of the pressure being applied during the time the coal was "plastic". The effect of such pressures built up within the "plastic" coal, must arise from the greater homogeneity which they will induce in the mass; the "fluid" constituents will be forced onto the surfaces of any non fluid material, e.g. fusain, durain, shale, etc., and may even penetrate the internal structure of these constituents. This low temperature bond is the precursor of the high temperature bonding stage, i.e., 650-1000°C, when the stable co-valent bonds are formed and the more thorough the former physical /

physical process is, the greater will be the possibilities of the latter. It will be appreciated that a measurement of the pressure developed within the "plastic" coal layer will depend, essentially, on the same properties of this layer as does Mott's Sheffield Laboratory Coking Test ; Mott, in fact (27) actually measured the pressure required to prevent the expansion of the "plastic" coal and this is a direct measure of the pressure within the "plastic" layer, provided the entire coal sample is in the same "plastic" state at the one time. Furthermore, it seems possible that a study of this pressure phenomenon may throw some light on the rheological properties of the "plastic" coal which are of importance in the coking process; any such measurements, e.g., by Foxwell's gas flow method, by the Davis or Giesler plastometer, have failed to show any distinct relationship between the property measured and the coking value of the coal.

In view of the significance of the pressure developed within the "plastic" layer, during the making of metallurgical coke, and of the possibility of such a measurement yielding further useful information regarding the mechanism of that process, the aims of this investigation were drawn up as follows:-

(a) To develop and perfect a method of accurately measuring the pressure built up within a coal layer when in the "plastic" state and to study the variation of this pressure with temperature.

(b) To study the pressure-volume relationships for a number of coking coals of different rank.

(c) To carry out a simultaneous study of the coking mechanism with the aim of appreciating the results obtained in sections (a) and (b).

PART II.

SWELLING PRESSURE MEASUREMENTS

and

THE THEORY OF DI-ELECTRIC HEATING.

Introduction.

Previous measurements of the swelling pressure or "Treibdruck" as defined by Damm (28) of the "plastic" coal fall, from the point of view of the present discussion, into the following two classes:-

(a) Measurements of swelling pressure as a destructive agent to coke oven walls, either directly, or indirectly by the formation of the so-called "sticker" of coke oven parlance.

(b) Measurements of swelling pressure as one of the physical manifestations of the "plastic" state of coking coals, and thereby a significant factor in the coking mechanism.

The two classes of measurements differ in that while (b) is a study of a single, discrete, stage, at least from an ideal point of view, of the coking process, class (a) is a study of the joint effects of swelling pressure and of contraction of the semi-coke on further heating. The difficulty of isolating completely the "plastic" stage from the complicating effects of others, e.g., the semi-coke to coke stage, has militated against the extensive study of this stage by measurements of a class (b) type; hence as much as ninety five per cent of all measurements of swelling pressure are made by methods belonging to class (a)., see Brewer (29). Logically a study of the mode of action of "dangerous" coking coals would entail a simultaneous investigation of the individual and discrete stages which form the entire coking process, e.g., the /

the "plastic" stage, the semi-coke to coke stage, etc.; such detailed investigations have only proved possible to a limited extent so far, and this explains the paucity of measurements of type (b) and the superfluity of those of type (a). The development of a method of study permitting of, initially, a detailed and accurate measurement of the swelling pressure, and finally, a study of the other stages of the coking process in complete isolation of one another, would be highly desirable.

Swelling Pressure Measurements.

Perhaps the earliest study of the swelling pressure of coal, per se , was that made by Taylor (30) in connection with the formation of "spongy" coke. He realised the limitations of the methods devised previously by Damm, Hofmeister, Korten, etc., and the desirability of obtaining true swelling pressures. The method used to achieve a uniform "plastic" stage consisted in using a small coal sample, i.e., 3 grs., spread over an area of 8.5 sq. cm. giving a coal thickness of about 2 m.m. The coal sample, heated in an electric furnace, was restrained from swelling by applying loads to a suitable piston; for a series of strongly agglutinating coals, of unspecified composition, he recorded swelling pressures of 30-60 Kg., i.e. equivalent to pressures of 50 — 110 lbs/sq.in. These values were considerably higher than any previously recorded and they were correlated directly with the degree of sponge formation. It is interesting to note Taylor's observations on the effect of pressure on the coke texture and its possible effect /

effect on the degree of fissuring. It would appear now that these values are rather low possibly as a result of oxidation (i) during drying of the fine coal at 105°C and (ii) during heating to the softening temperature. Nevertheless, these results are some of the few reliable measurements made up to this time.

A second paper on the swelling pressure of the "plastic" coal was presented by Foxwell (26) who, like Taylor, appreciated the value of swelling pressure as an agency in coke formation. Foxwell apparently realised the difficulties of measuring such a value directly, and he applied a rather novel technique, based on an earlier observation that the yield of gas, and particularly tar, was retarded when the coal was "plastic". The principle of his thesis was that (a) if a coal sample was free to expand greatly, and (b) if it were confined to give zero expansion, the rate of evolution of volatile matter would be considerably greater in (a) than in (b); a measurement of any such difference could be utilised to give a measure of the swelling pressure of the "plastic" coal at different stages therein. Basically, such a principle is sound, provided the results are interpreted with due caution. Thus it is surprising to find a durain even from a Durham coal, with a swelling pressure of 25 Atms., when it is recalled that this petrographic constituent is normally non swelling or but weakly so. Furthermore the effect of bulk density on the swelling pressure of the Derbyshire coal seems /

seems of an unduly critical nature and indeed it is surprising that this method shows bulk density to have an effect on the swelling pressure as the swelling pressure calculated is presumably for zero expansion of the coal particles; this would be expected to be quite independent of bulk density. Such anomalous effects can only be attributed to limitations of the experimental method. The experimental measurements made using a relatively large coal sample (2" x 1" D.) are undoubtedly in error due to the presence in the sample of considerable temperature gradients, which cause the measured gas volumes to be average results instead of isothermal ones considered to exist in the ideal state. This error, common to all attempts to study discrete stages of the coking process undoubtedly influences the final results, unless the rate of temperature loss of volatile matter is constant over a considerably wide temperature range. Nevertheless, this treatment probably gives a good indication of the order of magnitude of swelling pressures and suggests how it will vary with temperature. In this respect it was observed that the swelling pressures calculated by Foxwell were considerably greater than any of those measured by Taylor, even allowing for the fact that the former values were for zero expansion of the coal while the latter were measured after the coal had expanded to fill the voids of the original aggregate mixture.

Mott (27) while trying to study the effect of pressure on the "plasticity" of the semi-fluid coal, recorded some interesting results relevant to this discussion. Using a modification of the newly standardised Sheffield Laboratory Coking Test, in which the coal sample was heated at 1°C/minute in the form of a 0.4" D rod or column he attained conditions which could be considered as being very nearly isothermal. The data recorded included a list of the pressures required over the entire "plastic" range, to maintain the coal sample at its original volume, i.e., the swelling pressures. The shape of the plot of these pressures against temperature was generally similar to that found by Foxwell, viz., a steady rise to a sharp maximum followed by a sharp fall and subsequent rise, or alternatively by a flat and continued maximum. The respective maximum values for a number of different coals were as follows:-

Table I.

Coal.	Carbon Content % D.A.F.	Maximum Pressure Lbs./sq.in.
Silkstone	86	290
Parkgate	85	600
Burty	88	800
Brockwell	88	800
Two Foot Nine	89	800

These results compare with those of Foxwell, e.g., for a Durham coal, of unspecified carbon content, at 1°C/min. the maximum pressure was 19 Atms. ≡ 280 lbs/sq.in. Thus the two methods check as regards order of magnitude of the results /

results and it is unfortunate that Mott's results had not been of a more extensive nature, as they probably represent the best experimental method so far used in measuring pure swelling pressures.

These three investigations represent a very substantial portion of the total work done in this field of swelling pressure measurements; their fewness in number and the meagre information they contain on this important aspect reflect the difficulties encountered in any such study and demand that such difficulties be surmounted in every way possible. A similar conclusion can be drawn from even a cursory examination of the results from the other class of measurements of swelling pressure, i.e., those concerned with "dangerous" coking coals.

The aim, at least of the laboratory tests, of this class of measurements has been to devise a test capable of indicating what coals are liable to develop excessive pressures on coke oven battery walls; this implies a correlation of experimental determinations with practical experience of several coals used in a full sized oven enabling any other coals or blends to be suitably assessed if their effects were in any doubt. A survey of the literature clearly indicates that such a correlation has not been easy or particularly accurate, and one cannot feel satisfied with the manipulations of experimental technique required to improve such a correlation, (32). Mott (32) concluded that the /

the factor of greater importance in determining whether a coal was "dangerous" was not the swelling pressure of the "plastic" coal, but the after contraction of the semi-coke on further heating; a low after-shrinkage, by failure to accommodate the swelling pressure, resulted in a "dangerous" coal. This conclusion is undoubtedly related to his theory (22) that after-shrinkage of the semi-coke is directly proportional to the residual volatile matter, "dangerous" coals being invariably of low volatile matter, i.e., below 25%, their semi-cokes will likewise be low in volatile matter and their after-shrinkage proportionately smaller. This conclusion is directly opposed by the findings of Auvil, Davis and McCartney (33) who measured the after-shrinkage of granulated semi-coke on heating to 900°C and found it to be reasonably constant at 23.8 - 28.3% for coals of a very wide range of rank. In addition Franklin (12) has shown that the variation of true density with temperature, is largely independent of coal rank between 500 to 900°C; from the published data, the change in specific volume of semi-coke on heating to 900°C is about 25%, i.e., a very close figure to the average of Auvil, Davis and McCartney. Finally, one worker (34) has indicated that, above 600°C at least, there is no direct relationship between shrinkage and gas evolution; he suggested that shrinkage was controlled by the petrographic constitution of the coal, the ash content and its distribution, etc. These investigations cast considerable doubt on Mott's conclusions, and on the basis of these arguments, it could just be as easily concluded that the "dangerous" nature of some coals, is directly related to the swelling pressure, i.e., quite the contrary of Mott's conclusion. This ambiguity is a further reflection of the need for methods of investigation which allow of the study of the individual stages of the coking process. The theoretical basis of a method conceivably able to allow such a study, will now be given prior to its application to a detailed investigation of the "plastic" stage and swelling pressure.

The Theory of Di-Electric Heating.

Previous attempts to study the "plastic" range have been handicapped by the impossibility of obtaining truly isothermal heating, and the results of most measurements can be taken only as the average value of the several stages passed through in the entire "plastic" range. The more conventional types of heating cannot fail to introduce temperature gradients in the coal sample, due to the low thermal conductivity of the coal substance. Such gradients and the results they produce, render an already complex phenomenon more so, in view of the critical dependence of the physical properties of the "plastic" coal on temperature. Di-electric heating methods appeared to offer a possible way of eliminating such differential thermal effects, provided that coal had the requisite electrical properties and that a suitable experimental technique could be evolved.

A /

A di-electric material, made the essential element of a capacitor, stores energy when a charging voltage is applied to the plates of the condenser. If that voltage is alternating, the condenser is alternately charged and discharged and a capacitive current is said to flow in the di-electric. In a so-called"perfect" di-electric, the passage of this current generates no heat; in many others, however, the di-electric material becomes very strongly heated, and in this case heating can be continued by the continued application of the high frequency alternating electric field. The generation of this heat has its origin in the phase difference between the electric field strength (F) and the displacement (D) which the former produces; qualitatively, the effect is synomymous with that of magnetic hysteresis where the magnetising current is out of phase with themagnetic flux produced, the magnitude of this phase difference determining the extent of the residual magnetism. For a di-electric in an alternating field the expression for the volume distribution of the power or heat generated is given thus:-

$$Pv - W.Ko.\varepsilon.\tan\delta.F^2. \qquad (1)$$

where Pv - Power generated/unit volume of material.
W - Angular frequency.
Ko - Capacativity of free space.
ε - Dielectric constant
δ - Angle of phase difference between (F)&(D).
F - Field strength.

It will be readily appreciated, from equation (1) that uniform volume heating can be achieved, for a given di-electric, only if the field strength, F, is uniform throughout the entire volume of the sample. Such a condition is /

is realised by suitable design of the electrodes and by suitable arrangement of electrodes and dielectric; the electrodes should be parallel and of equal area, while the dielectric block, fitting exactly between the electrodes, should be preferably of smaller area than the latter. When the electrodes are the same area as the specimen, there appears to be a slight distortion of the electric field at the periphery of the sample but this will probably be compensated for by the use of a convection-radiation furnace placed immediately around the electrodes and sample, for the purpose of correcting any such effect and of reducing peripheral heat loss. The relative ease with which any dielectric heats is governed solely by the value of (δ); when (δ) = 0, that particular di-electric is a "perfect" one and no heat is generated therein. Little published data exists regarding the appropriate electrical constants, i.e., (δ) and (ε) for coal, but from an a priori consideration of the possible molecular structures of coal it seemed very unlikely that much trouble would be encountered on that score. Thus the materials exhibiting di-electric heating most readily are often those with unsymmetrical or polar molecules which under the action of an applied electric field tend to become polarised due to the unbalanced electrical structure of the molecules. When the applied electric field is alternating at radio-frequencies, i.e., 1-1000 Mc/s, the highly damped nature of the continual reorientation occurring, causes the /

the molecular displacement to lag behind the driving force, and it is this lag which gives rise to the function (δ). It has been shown that for optimum conditions the relaxation time (T) of such a displacement, i.e., the time for the displacement to reach its steady value should be of the same order as the periodic time ($1/f$).

From these, and other qualitative considerations, it can be concluded that radio-frequency heating of coal to give uniform volume heating is possible under suitable experimental conditions.

PART III.

EXPERIMENTAL APPARATUS.

Introduction.

For the sake of clarity in the description of the several units comprising the experimental apparatus, a brief summary of the procedure will be given at this stage. Heating of the crushed coal sample, (about 10 gms. of material), is carried out in a 2" I.D. Morganite crucible fitted with suitable top and bottom refractory discs to confine the "plastic" coal. This crucible sits on a fixed bottom electrode while an upper moveable electrode rests on the top refractory disc, these two electrodes and the coal sample forming the condenser unit in which heat is generated by the radio frequency electric field. Surrounding this condenser unit is a normal resistor type furnace to compensate the heat loss at the periphery of the crucible; this will be referred to in the context as the heating chamber. The top moveable electrode records any movement of the coal sample and is in direct communication with (a) a volume indicator and (b) a pressure valve and pressure gauge; it is thus possible to measure either the swelling pressure at constant volume or the amount of swelling at any fixed swelling pressure, while the coal sample is "plastic". Photographs of the entire assembly are given in Figs. I and II; the lower rectangular cabinet contains the electrical generator, while resting immediately on this is the heavy base plate and framework supporting the pressure gauge and valve, the heating chamber, and volume indicator. Diagrammatic sketches of these several components, in their working positions, are given in Figs. III & IV.

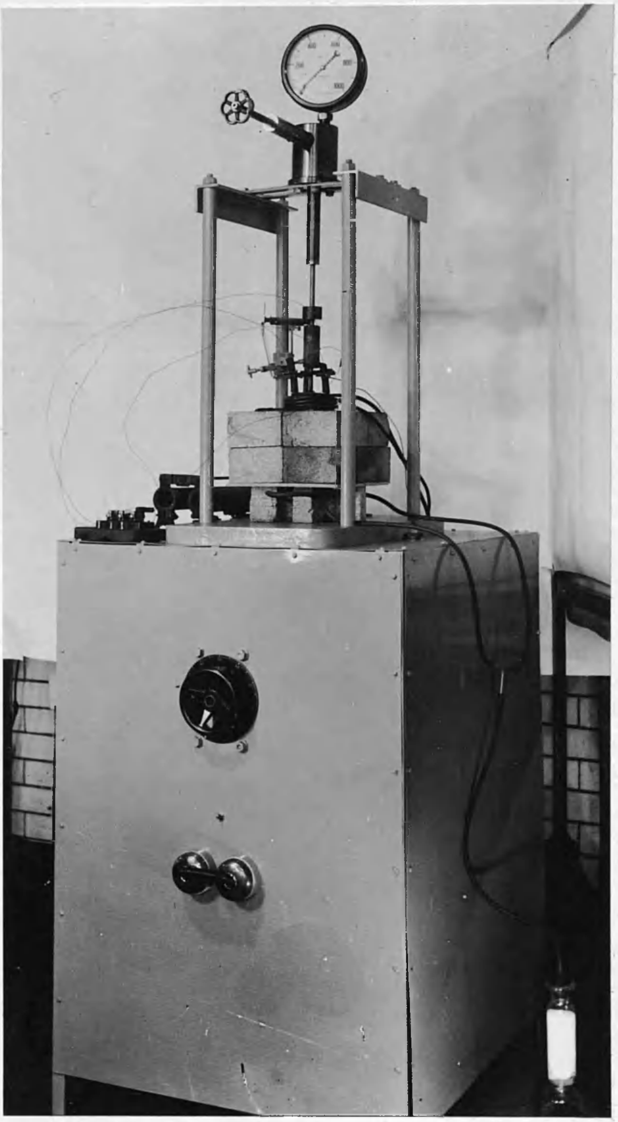


FIG. I

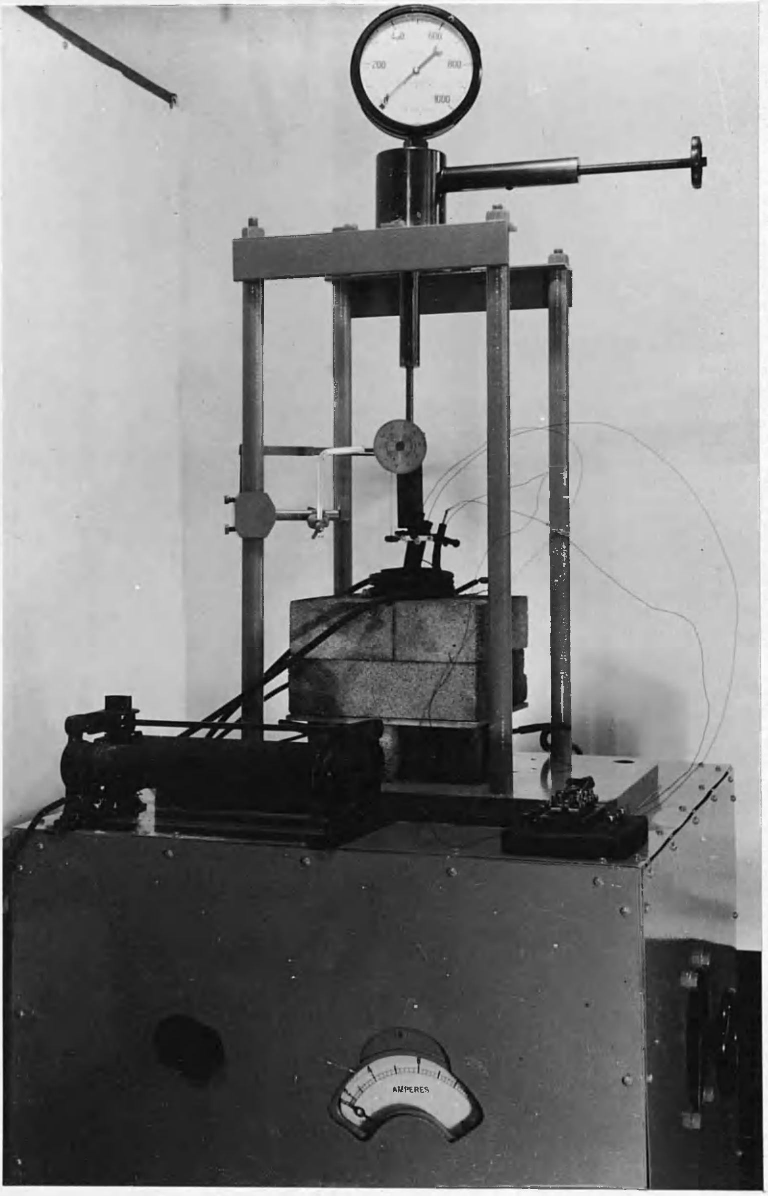


FIG. II

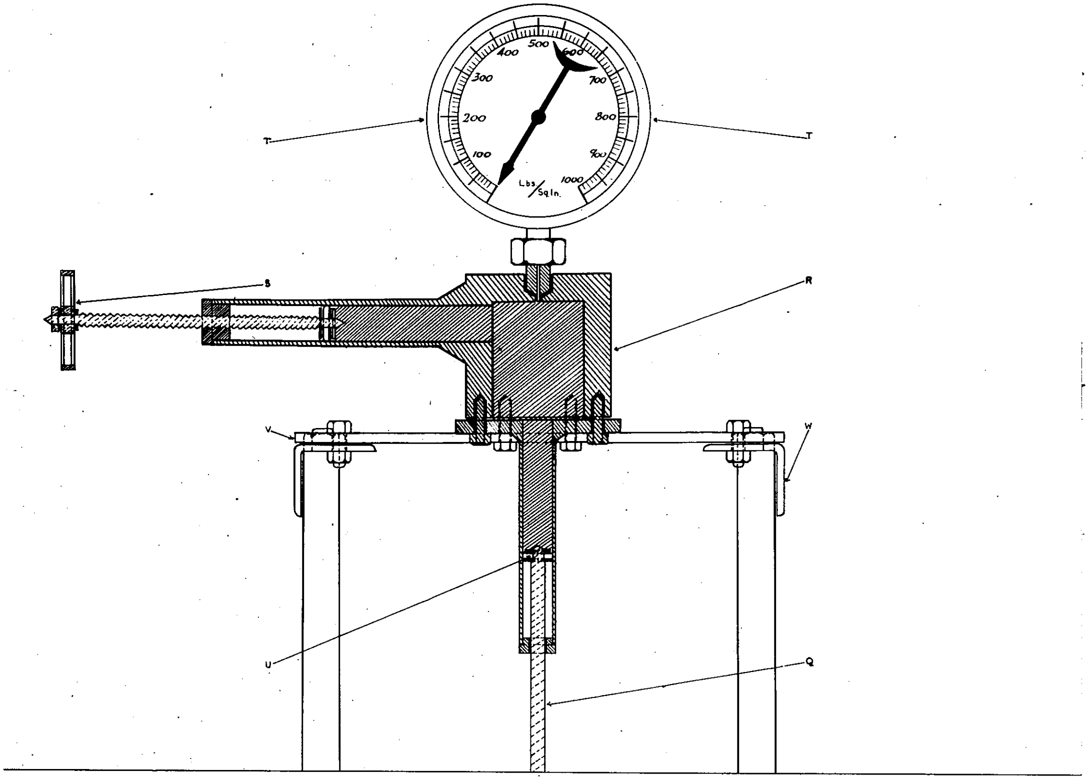
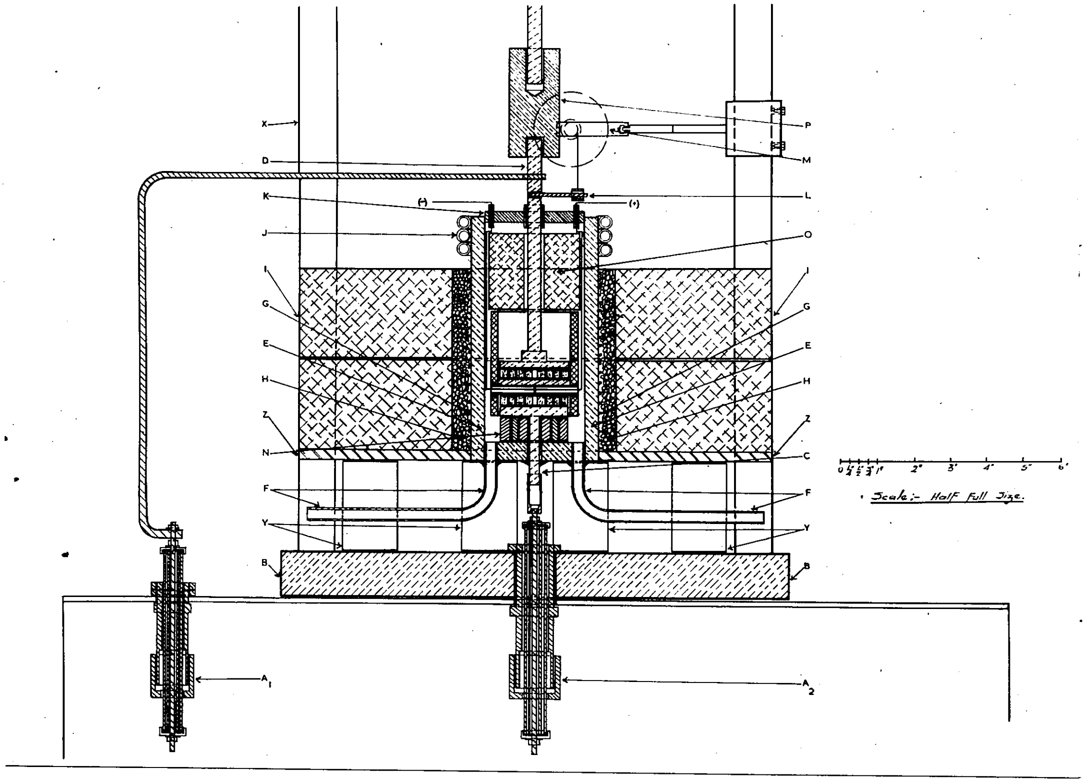


FIG. III



Scale:- Half Full Size.

FIG. IV

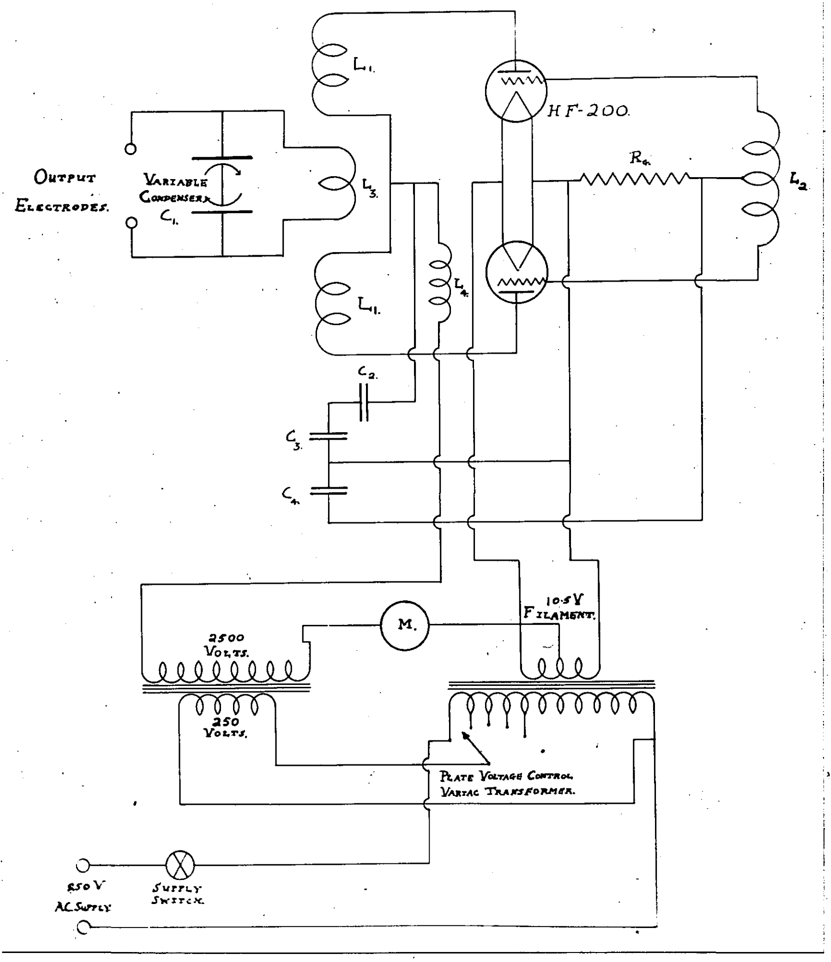

L₁.
HF-200.
R₄.
L₂.
Output Electrodes.
Variable Condenser C₁.
L₃.
L₄.
L₁.
C₂.
C₃.
C₄.
10·5V Filament.
M.
2500 Volts.
250 Volts.
Plate Voltage Control Variac Transformer.
250 V AC Supply
Supply Switch.

FIG. V

Thus the apparatus may be described as comprising these several units, viz:-

(a) Electrical Generator
(b) Crucible & Thermocouples.
(c) Heating Chamber & Electrodes.
(d) Volume Indicator.
(e) Pressure Gauge and Valve & Supporting Framework.

(a) Electrical Generator. This comprises a valve generator set with a working frequency of 35 Mc/S, and an output of some 200 W; the circuit diagram is shown in Fig.V, whence it can be seen that the generator is of the push-pull type. The power output, i.e., the heating rate in the condenser unit, is controlled (i) by the plate voltage control seen diagrammatically in Fig.V and actually in Fig.I, and (ii) by the variable condenser seen likewise in Figs. V and II respectively; a very fine control of heating rate can thus be excercised.

The output electrodes (A_1 & A_2 Fig.IV) pass through the containing cabinet at two points; the central lead (A_2) through the heavy base plate, (B), is that to which the bottom fixed electrode, (C) is attached while the offset lead (A_1) is directly attached to the upper moveable electrode, (D).

(b) Crucible & Thermocouples.

(i) Choice of crucible material was dictated by two quite distinct conditions, viz., (a) requisite strength to stand 60 lbs/sq.in. at a temperature of 500°C, and (b) requisite electrical properties which would allow heat to be generated in the coal sample and not preferentially in the crucible walls. As published data on the appropriate values of (ε) & (δ) for both coal and available ceramics was lacking, choice of crucible material had to be by trial and error methods. Thus two abortive attempts were made; one used slip-cast fireclay crucibles which frequently failed at pressures of the order of 30-40 lbs/sq.in. while the other used silica crucibles, of form similar to that finally adopted, which failed due to the preferential development of heat in the crucible walls. The material finally chosen was mullite in the form of a 2" I.D. cylinder, some 3" long, fitted, along a diameter 3/4" from one end, with a ¼" D silica sheath to accommodate a thermocouple at the centre of the coal charge. The final crucible design and the arrangement of the coal charge is best seen by reference to Figs VI and VII which are largely self explanatory. It must be stated that this, the final form of crucible, was modified in two stages from the original form; in the latter the alundum discs had no perforations and the basal disc was cemented into the Mullite cylinder by an alundum cement, while in an intermediate form the bottom disc was loosened entirely, as in the final form, and both discs were perforated by nine 3/32" D holes compared with the fifty-seven 1/16" D holes in the final form. These several crucible forms will be referred to in the subsequent section (Part IV) when an explanation of the modifications will be given. The asbestos discs, placed between the coal sample and the top and bottom refractory discs, were used in all tests and were essential to confine the "plastic" coal while under pressure. At one point it was questioned

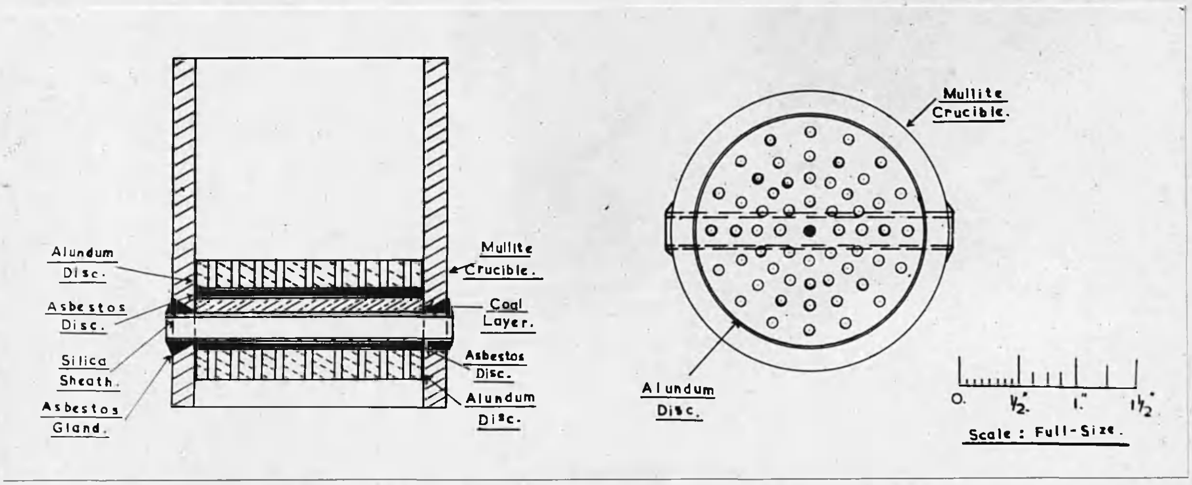


FIG. VI

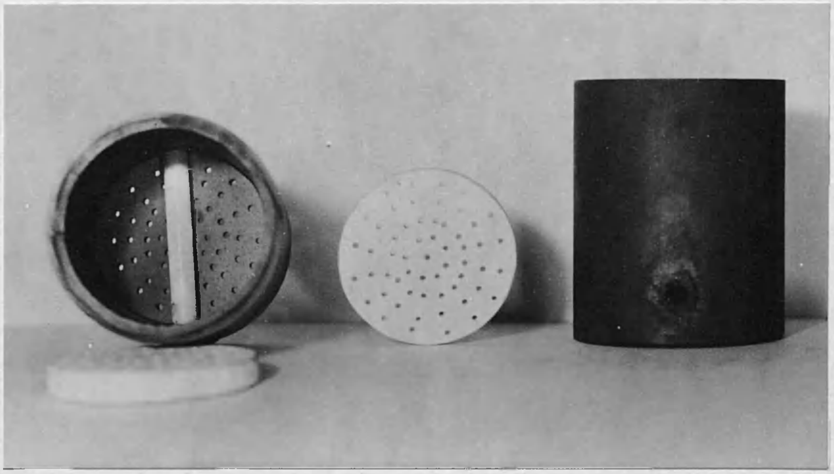


FIG. VII

whether they might not be contributing to the high swelling pressures recorded by hindering, unduly, the escape of volatile matter reaching the top or bottom of the coal sample; attempts to use 250 B.S.S. gauze instead were quite fruitless as the "plastic" coal, even under very small pressures, e.g. 1 lb/sq.in., readily penetrated this fine mesh.

(ii) Sample temperatures were recorded at two points the first at the centre of the silica sheath traversing the crucible and referred to in (i) above, the second at a point on the periphery of the crucible level with the first point but in a plane perpendicular to the plane of section of Fig.IV. The arrangement of the first couple can be seen in Fig. IV while the top of the peripheral couple may be seen in Fig. I & II. The transverse nature of the first couple ensured that the distortion of the field by the wire was at a minimum and thus the temperature recorded was a true value for the sample at that point; the milli-voltage set up and recorded was independent of whether the electric field was on or off. However, this couple did pick up very considerable high frequency currents, e.g., 150 m A, and a filter circuit had to be interposed in front of the potentiometer to prevent the latter being damaged ; 22 S.W.G. chromel-alumel couples were used in conjunction with a Cambridge portable potentiometer reading to 0.01 m V ≡ 0.25°C.

(c) Heating Chamber and Electrodes. The original heating chamber comprised a 3½" I.D. alundum cylinder, on which the compensating Nichrome winding was placed; this form of chamber was quickly replaced by the one described below as the former allowed considerable oxidation of the coal sample to occur due to its open nature. A scale drawing of the heating chamber and accessories finally used is shown in Fig. IV. The chamber itself (E, Fig. IV), consists of a cylindrical pot some 3" I.D. machined from steatite, hydrated magnesium silicate, thereby allowing the chamber to be made in a single piece; a previous attempt to use a composite one, consisting of silica cylinder with a recessed asbestos board base failed due to the differential expansion of the two materials. Two $\frac{1}{4}$" D copper tubes, (F), are let into the base of the pot, diametrically opposite one another, and serve for the introduction of the inert nitrogen atmosphere; the bottom fixed electrode, (C), passes out centrally from the base of the pot and is connected directly with the central electrical lead from the generator, (A_2). The joints between the base and the copper tubes, and the base and the electrode, are made gas tight with a cement of water-glass and alundum. The wall of the pot is occupied mainly by a winding of 22 S.W.G. Nichrome resistance wire (G) arranged so as to give a uniform hot zone 3" in length, on the inside of the pot wall, to a maximum temperature of 500°C; the variable resistor used to control this temperature is not shown in the diagram but may be seen in the photograph (Fig.II). Insulation for this winding is provided by the annulus of crushed insulating brick (H) and by the insulating bricks (I), surrounding this. Above the level of the winding and of the insulation, is a water cooling coil, (J) to keep the rubber bung, (K) reasonably cool. This bung serves to maintain the inert atmosphere in the chamber; it carries two small capillary exit tubes for the central thermocouple wires and the peripheral couple is also let into it at one side, all of these exit tubes being effectively gas tight. The top moveable electrode, (D) passes out through the centre of this bung and a small silica sleeve is provided to permit perfectly free movement; the clearance between this sleeve and the electrode shaft, i.e., about 1/32" is the sole means by which the nitrogen can escape and this ensures that the coal sample is entirely surrounded by inert gas. The top, (D) and bottom, (C), electrodes are of mild steel with the heads, 2" D, fitting neatly into the crucible as shown in Fig. IV; the shaft of the top electrode is considerably longer than that of the bottom one and it carries a small steel side arm, (L) which is attached to the volume indicator (M). The bottom electrode is raised about 1" from the base of the pot by the stool, (N) which facilitates maintaining an even peripheral hot zone about the crucible; excessive radiation of heat from the hot zone to the rubber bung is prevented by the insertion of the insulating block, (O). The entire chamber and insulating materials are supported from below by the blocks, (Y), via the asbestos board, (Z).

(d) Volume Indicator.

A diagrammatic sketch of the volume indicator is given in Fig. VIII & IV, while it can be seen in the photographs Figs. I & II. Fig. VIII is largely self explanatory; the top moveable electrode is in direct communication, via a small side arm, insulating sleeve, and iron cable, with a spring loaded coiling drum, which, in turn, is co-axial with a $2\frac{1}{2}$" D graduated dial, so that any small movement of the top electrode is immediately translated into an appreciable movement of the dial. The latter is calibrated into 100 divisions, and, as the small drum was 3/8" D, each division was equivalent to 0.012" of movement of the electrode; it is possible to read to ± 0.2 divisions, i.e., ± 0.0024" of movement of the electrode. An accuracy of this order is necessary on account of the critical inter-dependence of the pressure-volume relationships of the "plastic" coal when using fairly small samples. The advantage of this particular design, over any one based on a lever principle, is its virtually unlimited range and constant magnification ratio over that range.

The coiling drum, spring loaded shaft, and dial are carried on a light supporting framework attached to a clamp which slides on one of the uprights of the heavy framework; this arrangement facilitates adjusting to zero on the dial and allows the entire indicator to be swung to the side when not actually in use.

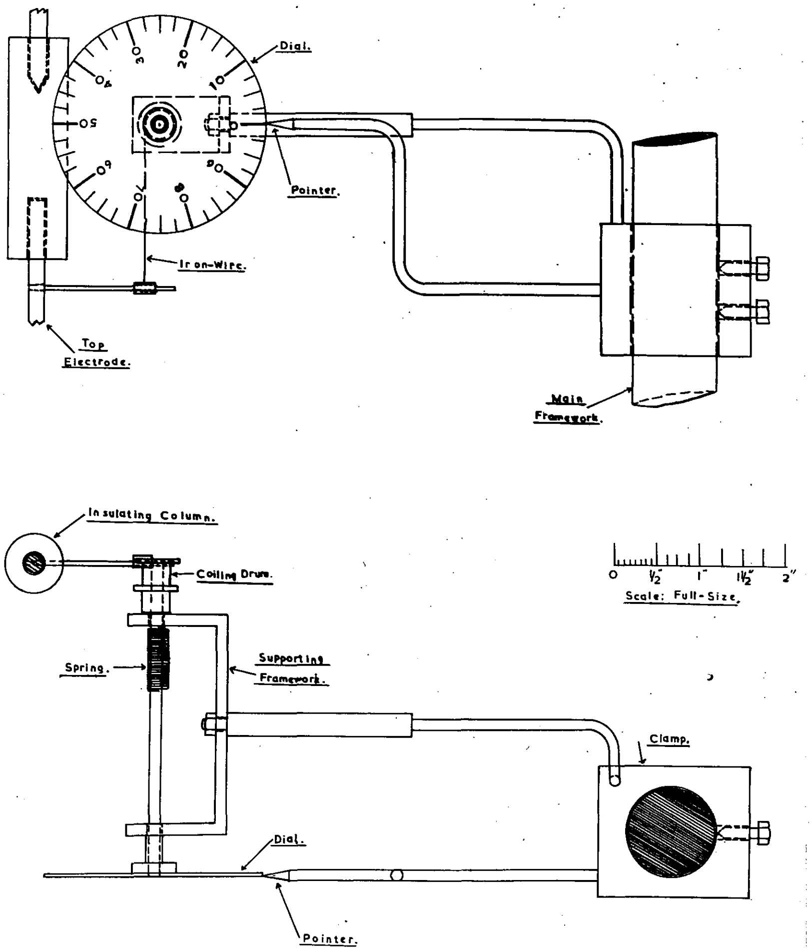

Dial.
10
20
30
40
50
60
70
80
90
Pointer.
Iron-Wire.
Top Electrode.
Main Framework.
Insulating Column.
Coiling Drum.
Spring.
Supporting Framework.
Clamp.
Dial.
Pointer.
0 ½" 1" 1½" 2"
Scale: Full-Size.

FIG. VIII

(e) Pressure Gauge and Valve; Supporting Framework.

The hydraulic pressure system is simple indeed, and can be seen in Figs. III, II & I. Pressure can be applied to the coal sample via the top moveable electrode, (D, Fig. IV), which communicates through an insulating block of steatite (P) with the steel piston rod, (Q). The pressure of the oil reservoir, (R, Fig.III), with which the latter piston is directly connected, is controlled by the hand operated screw-valve, (S), and measured by the pressure gauge, (T), which is of the Budenberg steel-tube type, having a range of 20-1000 lbs/sq.in. at increments of 20 lbs/sq.in. The pressure recorded on the gauge is actually 16 times the pressure developed in the "plastic" layer, owing to the relative areas of the crucible and the piston head (U).

The entire hydraulic system is supported centrally above the heating chamber by a suitable steel framework. The reservoir is bolted directly to two steel cross spars, (V), which in turn are attached, at either end, to 2" angle irons, (W), supported on four 1" D steel uprights, (X), rising from the heavy base plate, (B). This arrangement is very robust and has successfully withstood the strains involved in measuring pressures up to 1000 lbs/sq. in.

PART IV.

EXPERIMENTAL DEVELOPMENT.

Introduction.

The development work required to attain an experimental technique with the requisite degree of reproducibility of test results entailed considerably more than the mere application of the di-electric heating method. Thus the relationship between the swelling pressure and the sample volume, at which that pressure was measured, proved to be of an exceptionally critical nature especially at higher swelling pressures and lower sample volumes; an experimental method with a high degree of inherent accuracy was thus essential. Furthermore, the difficulty of measuring such arbitrary physical properties was enhanced by the fact that these properties were very critically affected by small alterations in experimental procedure. A preliminary survey of the several stages of the development work might suggest that this was carried out in a haphazard manner, but a closer study will reveal, in fact, that few of the problems encountered could have been tackled by methods yielding concrete and positive results. Thus the only available method, in circumventing such problems, was one of controlled experimentation followed by a deductive study of the results so obtained.

The problems encountered fell into three broad classes, viz:-

(i) Those having their origin in the extreme chemical reactivity of coal to oxygen; Oxidation Effects.

(ii) Those arising from the difficulty of measuring exactly any physical property of such a heterogeneous system as "plastic" coal; Crucible Effects.

(iii) Those having their origin in the inhomogeneous petrographic composition of coal; Petrographic Composition Effects.

In the following discussion it is proposed to treat each problem in its chronological order; such a treatment presents an erraticaccount of the effect of any one class of problems, but this is deemed preferable to a study of each class separately as, in the latter case, confusion would arise due to the several stages of each class not being comparable.

All development work was carried out using the one coal, i.e., Sacriston (Durham), details of which will be given later, (Part V); different bulk samples of this coal were used at different stages in the work and these will be referred to in the context.

Preliminary Development.

This stage was concerned with the choice of suitable experimental conditions, e.g., coal sample size and composition, crucible material and construction, heating rate and heating characteristics of the sample, etc. The first bulk coal sample comprised 1Kg. of the Sacriston coal which, subsequent to air drying at room temperature, was screened into the size fractions -½ + 3/8"; +¼"; + 1/8"; + 1/16"; +20; +40; +70; +100; -100 mesh B.S.S., the respective fractions being stored in separate containers for use; a 35 gm. sample of the following size analysis was used for individual tests:

- ½ + 3/8"	2.58%	+ 1/16"	24.35%	+ 70m.	4.02%
+ ¼"	14.60%	+ 20m.	13.18%	+ 100m.	1.43%
+ 1/8"	22.85%	+ 40m.	11.44%	- 100m.	5.73%

The crucible used in these tests was described elsewhere, (Part III), as the "original crucible form". The carefully mixed sample was added to this crucible, in such a way as to avoid size segregation, and the bulk sample volume, about 56 c.c.s., was measured; thereafter, the sample was covered by a layer of asbestos paper followed by the top moveable alundum disc. The crucible was then placed in the heating chamber, which at this stage comprised the alundum form described in Part III. It was considered undesirable, at this time, to complicate the experimental set up by the introduction of an apparatus capable of maintaining an inert atmosphere round the coal while it was heating; it was reasoned that any effects of oxidation would be fairly constant from test to test and that such effects, on account of the enclosed nature of the sample and the choice of a coal of high rank, i.e., low relative rate of oxidation, (35) should be of limited extent.

A heating rate of 2.5°C/min. was used as it was readily maintainable and also because it approximated the average heating rate in modern coke ovens, (36). A typical time and temperature plot of the readings of the two thermocouples is shown in Fig. IX, whence it can be appreciated that a very close approach to isothermal conditions is

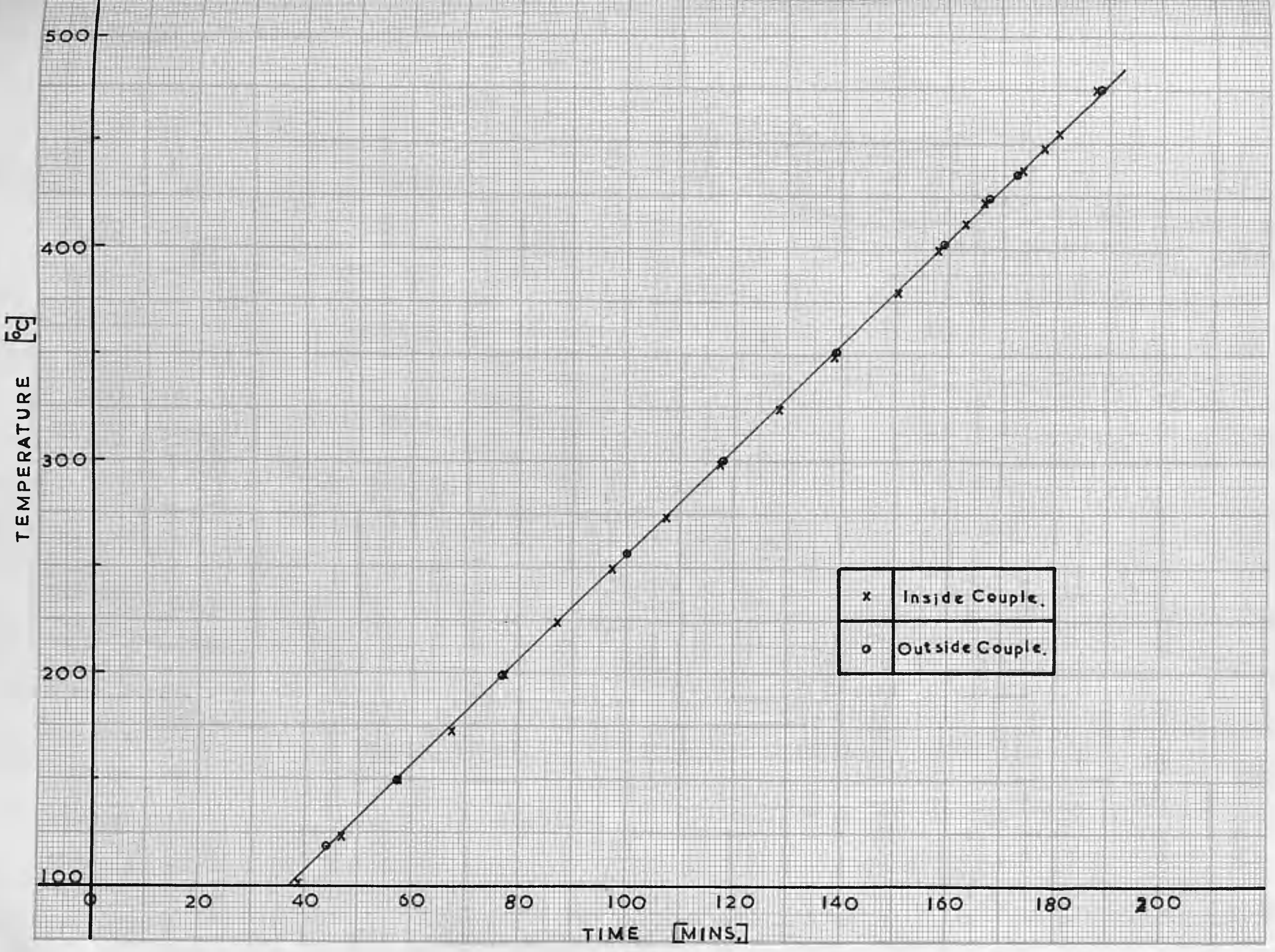

500
400
300
200
100
TEMPERATURE [°C]
0
20
40
60
80
100
120
140
160
180
200
TIME [MINS.]
x Inside Couple.
o Outside Couple.

FIG. IX

obtained and that the control of heating rate is fine.

Once the crucible was in position the procedure in these tests was as follows:-

The coal sample was heated continuously at 2.5°C/min. before, in, and through the "plastic" stage; temperatures were recorded in both couples at least every 25°C before the "plastic" stage and every 5-10°C during the latter. Once swelling had started it was allowed to proceed to a certain pre-determined value, expressed as a percentage of the initial bulk sample volume, when pressure was applied to the sample to maintain the volume constant at this value; a continuous record of this pressure was kept as it rose to a maximum and then fell to zero. In referring to the several test results obtained, it will be customary, for brevity, to quote only the maximum swelling pressure (M.S.P.), and the swelling volume, (S.V.) at which that pressure was obtained; a full description of the pressure and temperature curve will be found in the subsequent chapter (Part V.). The aim of the development work can be summarised as an attempt to obtain reproducible M.S.P. - S.V. values from consecutive tests.

Main Development.

The following are the main stages in the development work; each stage is referred to the three classes of problems mentioned in the Introduction and is numbered to indicate the order of occurrence of that stage in any one of these classes.

(i) Oxidation Effects: Stages I & II.

The first series of tests carried out using the above procedure and apparatus gave very erratic results; for a M.S.P. of 62.5 lbs/sq.in. the S.V. values ranged from 3.6 - 17.5% of initial bulk sample volume. Simultaneously, it was observed that certain characteristic temperatures, e.g., the initial swelling temperature, (I.S.T.) at which appreciable swelling commenced, and the temperature at which the maximum swelling occurred, (M.S.T.) etc., varied considerably from test to test contrary to the experience of earlier workers, (38); thus the I.S.T. and the M.S.T. varied over the range 375 - 400°C and 400 - 470°C respectively. In seeking the cause of these wide discrepancies, it was but natural that the possible effects of oxidation should be questioned and a test was thus designed to show the effect of any variation in the degree of such factors. The test procedure was identical save that a thin layer of fine semi-coke was placed around the base of the crucible to give conditions slightly less oxidising. This procedure resulted in considerably enhanced swelling properties, i.e., M.S.P. of 18.8 lbs./sq.in at a S.V. of 26.4%. That this procedure had but only reduced the oxidation effects slightly was confirmed when a test was run in which the crucible was entirely surrounded by crushed semi-coke; the figures now obtained were M.S.P. of 62.5 lbs./sq.in. at a S.V. of 55.0%. This result stressed the significance of oxidation of the pre-"plastic" coal as an agent in reducing swelling and also as a variable in the measurement of such swelling properties. The modified heating chamber, first of silica with an asbestos base, and finally of steatite (Part III) was the outcome, so permitting the heating of the sample in an atmosphere of oxygen-free nitrogen.

The results of the first three tests carried out in this modified apparatus are shown in Table II.

Table II.

Test No.	M.S.P. Lbs/sq.in.	S.V.(%)	I.S.T. (°C).	M.S.T. (°C).
1	62.5	68.5	377	455
2	40.0	69.0	382	475
3	62.0	66.5	377	455
4	62.5	91.0	376	460

The overall agreement in these three tests was considerably closer than in any previous set and represented a considerable step forward, even though improvement was still desirable.

The fourth result witnessed the discovery of a second stage in the effects of oxidation. This sample was being tested in the normal manner, but a power failure curtailed the heating cycle when the sample was at a temperature of 90°C; the sample was allowed to cool in a slow nitrogen stream and was left there till the test was resumed some 18 hours later. The result was as shown in Test No.4 in Table II. This initial heat treatment had apparently "desorbed" a considerable amount of oxygen held by the coal surface, with a consequent improvement of swelling; this result was in keeping with the known instability of the peroxygen complexes, considered to be formed at room temperature when coal is oxidised and which are said (39) to decompose rapidly in the range 70-120°C. The oxygen adsorbed by the bulk coal sample appeared to be sufficient to reduce the swelling of the coal, since its partial removal, by the above treatment in an inert gas stream, was capable of enhancing the swelling properties of the coal. As such an effect was likely to be aggravated by time of standing, steps were taken to procure a fresh bulk sample which, after drying, was stored in vacuo to reduce this second oxidation effect to a minimum.

The serious nature of this adsorbed oxygen was seen by comparing the swelling figures obtained with the new coal sample, i.e., M.S.P. of 62.5 lbs/sq.in. and a S.V. of 180%, with that of Test No.4, Table II. As a consequence of this pronounced increase in the degree of the swelling, the sample size was reduced from 35 gms. to 17.5 gms. to accommodate the swelling within the limits of the hot zone of the heating chamber.

(ii) Crucible Effects: Stage I.

Further attempts to duplicate the result quoted for the new coal sample failed the tests yielding in every case swelling figures considerably lower than that quoted, viz., 2.5 - 7.5 lbs/sq.in. in M.S.P. at S.V. of 180%. In each case this lower figure was associated with a characteristic appearance of the semi-coke which, till then, had had a very uniform sponge structure and a characteristically black appearance; in these low results the semi-coke was no longer uniform in structure and colour, a portion of the sample, to the extent of 30-40% by weight being markedly dense in structure and decidedly steel grey in appearance. This latter appearance suggested localised over heating, and it was subsequently observed that this densening of the residue always took place on the periphery of the crucible at a point where the bond, between the alundum basal disc and the morganite crucible wall, had ruptured suggesting that this localised overheating, might be caused by a disturbance of the electric field in this region. Whither such an explanation was indeed valid, it was found that, by substituting a fresh crucible with an intact basal seal, results of the desired order of magnitude were obtained, viz.,

Table III.

Test No.	M.S.P. Lbs/sq.in.	S.V.%	Remarks.
5	26.3	178	New Crucible used.
6	40.0	178	
7	48.5	182	
8	62.5	175	
9	62.5	178	
10	37.6	177	Crucible heated to 950° C before run No.10.

The degree of swelling rose progressively from Test No. 5 to Test No.9 while an appreciable drop was recorded in Test No.10, i.e., after the crucible had been heated to 950°C. The latter treatment would serve to detach any semi-coke which had penetrated the small fissures round the periphery of the basal alundum disc, and would thus tend to undo the progressive sealing of such fissures which apparently took place in Tests 5 to No.9. This effect, which was a direct result of the degree of "gas tightness" of the crucible, was finally confirmed by carrying out a test in a crucible, of exactly the same shape, size, and design as the morganite one, machined from steatite with a neatly fitting top disc; this crucible had a much better degree of "gas tightness" which was reflected in the values, M.S.P. 11.2 lbs/sq.in. at a S.V. of 228% .

Such results immediately posed the problem as to what arbitrary degree of "tightness" of crucible should be used in measuring swelling pressure. To simulate coke-oven conditions an arrangement was desirable which allowed the free escape of volatile matter at the top and bottom of the sample, the impermeable morganite walls acting as the experimental counterpart of the impermeable "plastic" layer above and below any point in the "plastic" layer in the coke-oven. The attainment of such an ideal, experimentally, was limited by the fact that the "plastic" mass had to be confined within the crucible while the various pressures, up to 62.8 lbs/sq.in. were applied. This latter consideration militated against the replacement of the asbestos paper discs, the permeability of which was doubted as a consequence of the above results, by the more permeable copper gauze referred to previously (Part III). However, an approach to the ideal arrangement was attempted by perforating both top and bottom alundum discs; simultaneously, it was deemed advisable to detach the bottom disc from the crucible walls and thus make it resemble its upper counterpart in all respects. These several modifications in crucible design were incorporated in the "intermediate crucible form" of Part III. That this venting procedure had had the desired effect, to some extent at least, was reflected in a comparison of the results obtained using the "original" and "intermediate" crucible forms, viz:-

Table IV.

Test No.	M.S.P. Lbs/sq.in.	S.V.(%).	Crucible Form.
9	62.5	178%	"Original"
11	39.0	143	"Intermed."

(iii) Oxidation Effects: Stage III.

Before the effects of these several modifications could be studied completely, a further ramification of the oxidation problem was discovered. Previously it had been customary to withdraw the required amounts of the individual size fractions from the vacuum as required by breaking that vacuum with air, the composite sample being assembled in the usual manner . Thus the total time of exposure of the sample to air, from the point when the vacuum was broken till the crucible was assembled in the heating chamber was never more than one hour, and any air entrapped in the sample, or heating chamber, was considered to be flushed out by the nitrogen which was passed for one hour prior to the sample being heated. In one instance the sample, assembled in the crucible, could not be tested immediately and so it was kept in vacuum till required, when the vacuum was broken in the customary manner with air. The results of this test and a confirmatory one are shown opposite Tests Nos.12 and 13, Table V and these may be compared with that from Test No.11 in which the assembled crucible was heated immediately without any intermediate evacuation; Test No.14 was carried out similarly to Nos.12 and 13, i.e., evacuation after the sample was assembled in the crucible, only the vacuum was finally broken with nitrogen instead of air.

<u>Table V.</u>

Test No.	M.S.P. Lbs/sq.in.	S.V.%	Remarks.
11	39.0	143	No intermediate evacuation.
12	62.5	150	(Intermediate evacuation
13	62.5	151	(Vacuum broken with air.
14	50.0	177	Intermediate evacuation Vacuum broken with nitrogen.

Thus the oxygen adsorbed on exposing the desorbed coal to air had reduced the swelling power by about 10%. Consequently, at all future stages, the vacuum was broken with nitrogen, and the assembled coal sample was evacuated for 18 hours prior to heating.

The cumulative effect of these modifications was reflected in the better agreement of the results from three consecutive tests, viz:-

Table VI.

Test No.	M.S.P. Lbs/sq.in.	S.V.%
14	50.0	177
15	62.5	178
16	62.5	188

A further reduction in the sample size was necessitated on account of the progressive increase in the degree of swelling, and this reduction from 17.5 to 12 gms. undoubtedly accentuated the effect of petrographic composition.

(iv) Petrographic Composition Effects.

Using a maximum particle size, in the composite sample of 3/8" it was quite possible to obtain an anomalous effect due to the segregation of the several coal constituents, e.g. vitrain, clarain, durain and also shale particles, in different samples, as only relatively few particles of the larger sizes were contained in a 12 gms. sample. Two tests were run in one of which the larger size fractions + 3/8"; + $\frac{1}{4}$"; + 1/8"; were made preponderately rich in "dull" particles, in the other of which these size fractions were correspondingly "bright"; the results were as follows, viz:-

Table VII.

Test No.	M.S.P. Lbs/sq.in.	S.V.%	Remarks.
17	32.4	185	"Dull" sample.
18	62.5	240	"Bright" sample.

To reduce the effects of such segregation the maximum particle size was reduced to $-1/8'' + 1/16''$; the size grading was simultaneously altered from the "as received" condition and placed on a more rational basis by incorporating the Rosin-Rammler distribution equation, viz:-

$$R = e^{(x/\bar{x})^n} \qquad (2)$$

where R - cumulative percent on screen size X ins.

$\bar{x}$ - a particle shape factor, constant for any material.

n - constant, related to the size distribution in an aggregate.

A mixture with an $n=1$ was chosen, i.e.,

- 1/8" + 1/16"	16.8%	- 36 + 72	29.3%
- 1/16 + 16 B.S.S.	15.2%	- 72 + 100	2.3%
- 16 + 36	30.0%	- 100	6.4%

A series of tests performed applying this new modified experimental technique yielded results in which the scatter of results was fairly small, this scatter nevertheless being considered to be outwith the experimental error of the tests; there was no obvious explanation for the fluctuations which occurred in the results listed in Table VIII.

Table VIII.

Test No.	M.S.P. Lbs/sq.in.	S.V.%	Test No.	M.S.P. Lbs/sq.in.	S.V.%
19	37.5	207	24	18.1	204
20	16.3	200	25	8.8	210
21	23.8	206	26	6.3	208
22	16.3	208	27	15.6	204
23	7.5	204	-	-	-

(v) Oxidation Effects: Stage IV.

In view of the critical effects of oxidation noted previously, it did seem possible that the cause of the fluctuations might be in the extent to which the finer size fractions of the bulk sample had oxidised in the earlier stages of storage when air, and not nitrogen was used to break the vacuum. It was decided therefore to carry out a number of tests in which the composite sample was made up of the several size fractions outlined above, these fractions being obtained by the progressive crushing and screening of 25 gms of+$\frac{1}{4}$" material which up till then had been stored in vacuo; in this way it was hoped that all the test samples would be devoid of any slight differences in the extent of oxidation of the several fractions contained therein. The results of four tests, carried out using this further modification, are reported in Table IX whence it can be seen that a fairly high degree of reproducibility had been attained.

Table IX.

Test No.	M.S.P. Lbs/sq.in.	S.V.%
28	45.0	224
29	48.8	226
30	47.5	227
31	43.8	228

Before starting the full investigation of the pressure-volume relationship of the "plastic" coal, it was deemed necessary to obtain a fresh bulk sample of + ¼" coal, as the existing sample was of limited amount and was suspected of being weathered to some extent. The introduction of this fresh coal sample resulted in a further increase in degree of swelling attained and a further reduction in the sample size used was necessitated. A reduction in the weight of coal used was essential but it was decided that the coal sample should be diluted with an inert constituent so as not to involve an excessive reduction in the weight of the coal sample. Tests indicated that a 15 gm. mixture of 50% crushed coal and 50% washed silica sand (- 52 + 72 B.S.S.) would be convenient. This further complication did not seriously affect the accuracy of the results obtained provided due care was taken in assembling the mixed sample.

(vi) Crucible Development : Stage II.

The final stage involved the study of the reproducibility attained using different crucibles of the same nominal design, as it had been customary in previous work to use the one crucible for the study of any particular problem and, in view of the results obtained therein it seemed unwise to assume that different crucibles would behave identically.

Preliminary tests had shown that considerable discrepancies could be obtained when using different crucibles of the same nominal size, e.g., results contained in Tables X and XI.

Table X.

Crucible	M.S.P. Lbs/sq.in.	S.V.%	Remarks.
"A"	38.7	276	-
"B" (1)	62.5	336	-
(2)	62.5	329	Same Alundum Discs as B(1)
(3)	62.5	280	Discs not as in B(1)
(4)	50.0	280	New Discs.
(5)	62.5	280	Discs as in B(4).

Table XI.

Crucible	Average Diam. (ins.)	Silica Sheath. Length."	Silica Sheath. Diam."
"A"	2.05	2.06	0.28
"B"	2.03	2.03	0.28
"C"	2.06	2.06	0.28

From Table X it can be seen that an alteration of the alundum discs was instrumental in effecting a change in the swelling characteristics of the sample. It was further noted, in B(4) and B(5) that the making of new discs which fitted the crucible very neatly (many of the morganite tubes were far from circular) did not result in increased swelling compared to B(1) and B(2); thus the clearance between the disc and crucible appeared not to be the important factor in causing such discrepancies and attention was therefore turned to the effective area of perforations offered by the different discs. This point was investigated using crucibles "B" and "C" of Table XI; two tests were carried out in the normal manner one in each crucible and an additional two in which the respective discs of the crucibles were intercharged. Table XII contains these results.

Table XII.

Test No.	M.S.P. Lbs/sq.in.	S.V.%	Remarks.
32	23.7	460	Crucible "C" & Discs "C"
33	10.0	464	Crucible "C" & Discs "B"
34	12.5	445	Crucible "B" & Discs "B"
35	32.5	468	Crucible "B" & Discs "C"

Thus tests using discs "C", regardless of the crucible, gave considerably higher test results than those using discs "B". By increasing the effective area of perforations it was considered that those effects should be largely overcome; the "final crucible form" referred to in Part III, had discs with 57 x 1/16" D holes. Results obtained from different crucibles were as follows, viz:-

Table XIII.

Crucible	M.S.P. Lbs/sq.in.	S.V.%
"B"	56.1	454
"C"	57.4	456
"C"	56.1	456

Summary and Conclusions:-

From the foregoing discourse it will be readily appreciated that attainment of the required accuracy of experimental results can be achieved only by a very careful supervision of the method of preparation of the coal sample and the final method may be summarised thus:

The bulk coal sample is stored in vacuo in the form of +¼" material; if this is not convenient then the largest possible size below this is used. Appropriate amounts of this bulk sample are carefully selected, so as to avoid the inclusion in any one sample of a preponderance of any single coal constituent; this sample is then progressively crushed, and screened and the composite coal sample with a fixed size distribution is made up. If inert material is being used, it is then added and the composite sample is carefully mixed and fed into the Morganite curcible which takes that form described as the "final" one in Part III. The coal sample volume is measured by measurements taken at eight points on the periphery of the crucible, the sample is covered by the top asbestos disc and finally by the top alundum disc; the sample weight is checked. Care is taken in assembly to expose the coal to air for the shortest possible time and thus the overall assembly time is rigidly standardised. The assembled crucible is evacuated for 18 hours prior to heating when the vacuum is broken with oxygen-free nitrogen; the crucible is placed in the heating chamber and the latter is flushed out with nitrogen for 10 mins. prior to starting the run. This procedure was the standard adopted and any deviation therefrom will be noted in the context.

The most striking result of the development work is the very serious role which oxygen plays in reducing the swelling pressure of the "plastic",coal. Similar experiences were encountered by Ball (40), who found that a method for measuring the expansion pressure of coal was very sensitive to oxidation, e.g., he found that a few tenths of a per cent of oxygen reduced this pressure to zero; Kucherenko, (41), measuring the swelling pressure at constant volume, likewise found that such measurements were very susceptible to the effects of oxidation. The difficulty of determining the small changes in oxygen content which cause these very appreciable changes in swelling properties has been emphasised (42), and it would thus appear that even a detailed chemical analysis of the coal prior to testing would have been of little avail in elucidating the many ramifications of this problem. The possible mechanism of action of such small quantities of oxygen in reducing swelling will be discussed in a later section, (Part VI).

PART V.

EXPERIMENTAL RESULTS.

Introduction.

Subsequent to the establishment of a suitable experimental technique, the second aim of this study was the investigation of the relationship of swelling pressure and swelling volume for a number of coking coals. The development work had shown adequately, at least for the Durham coal, that the direct measurement of what may be called the "absolute" swelling pressure, i.e., the pressure required to confine the coal sample at its original volume, would be quite impossible on account of the large pressure involved; even a limited extension of the existing pressure range, i.e., 0 - 62.5 lbs/sq.in. would not have been easy due:-

(i) to the difficulty of confining the "plastic" coal under higher pressures, and

(ii) to the need for reinforced asbestos discs which tended to burst at pressures of the order of 62.5 lbs/sq.in.

It was thus apparent that the relationship would have to be investigated at a minimum swelling volume considerably above the initial coal sample volume, and at this stage there was no indication which of two possible ways of establishing the desired relationship would be more instructive. Thus a constant pressure could be applied to the swelling coal and the maximum swelling volume determined, or the coal could be allowed to swell to a certain volume and the pressure required to maintain that volume, under rising temperature, recorded. As swelling in the "plastic" layer of a coke oven charge would most likely be under constant volume conditions, the latter procedure was the one first adopted. Thus the desired relationship was established for the Durham coal, under "constant volume" conditions and the results are presented in section (i) below. Thereafter a second coal, a Scottish one of lower rank than the Durham coal, was studied and the nature of the swelling characteristics of this coal demanded that it be studied under "constant pressure" conditions. Section (ii) contains these results.

To render a comparison of these two coals possible, a study of the Durham coal under "constant pressure" conditions was carried out and these results are presented in Section (iii) below.

Finally Section (iv) includes the results of an investigation of the mechanism of swelling at the start of the "plastic" stage.

Coals Tested.

In the course of the investigation three different coals were used and details of their respective origins, proximate analysis and swelling characteristics, as given by the British Standard Swelling Test, are contained in Table XIV.

Table XIV.

Coal		Proximate Analysis (Dry Basis)			Br.Standard.
Name	Origin	V.M.%	F.C.%	Ash %	Swelling No.
Sacriston	Durham	28.78	63.46	7.76	8
Kingshill No.1 Pearls.	Scottish	35.56	59.59	4.85	4
Auchengeich Gum	Scottish	31.34	56.70	11.96	2

Samples of these coals were selected by standard sampling practice from wagons of fresh coal arriving at an industrial coke oven battery; a point worthy of note was that these samples were screened so as to give the largest available size fractions, for reasons given in Part IV, and in that respect the samples tested may not have been truly representative of the particular coal seam. The fractions actually stored and tested were -3/8" + ¼"; -3/8" + ¼"; -¼" + 1/8" for the Sacriston, Kingshill and Auchengeich Gum, respectively.

Test Procedure and Specimen Test Sheet.

Subsequent to assembly in the heating chamber, the crucible was invariably heated at 2.5°C/minute to a final temperature in the range 450-475°C, i.e., beyond that at which maximum swelling had been attained; a continuous time-temperature record was kept of the readings of both thermocouples. Once swelling started, the procedure depended on whether the particular measurement was being made at constant pressure or constant volume, viz:-

(i) At constant volume. The coal sample was allowed to expand under a nominal pressure of 1.25lbs/sq.in. to a predetermined volume, when pressure was applied to maintain that volume, while temperature was still rising a continuous record of time-pressure readings was kept until the pressure had passed through its maximum value and dropped to its original 1.25 lbs/sq.in.

(ii) At constant pressure. As swelling started, pressure was gradually applied so as to maintain the sample at its original volume; once the desired swelling pressure had been built up, the coal was allowed to expand under the latter, which was constantly adjusted to keep it at the desired value. A continuous record of volume-time readings was maintained till the maximum swelling had taken place.

It was found experimentally expedient to record pressures or volumes as a function of time, rather than directly as a function of temperature since the latter procedure would have proved arduous on account of the number of adjustments necessitated during the swelling process. The cold crucible was weighed to determine the loss of volatile matter; the swelling volume was measured directly at this stage and in conjunction with the final reading of the volume indicator was used to determine the conversion ratio of dial readings to cubic centimetres of swelling.

A specimen test sheet is recorded in Table XV for a test carried out, under constant volume conditions, on a 15 gm sample of a 50-50 mixture of Sacriston coal and silica sand, as described elsewhere (Part IV). In Table XV, Section I records the sample thickness as measured at eight points on the crucible periphery, from depth measurements taken before and after the sample was charged; Section II records data for the vertical swelling of the sample as measured by the difference in depth of the top disc from the top of the crucible before and after the test. Section

Table XV.

No. of Point on Crucible Circumference	SECTION I.			SECTION II.		
	Cruc:ible Depth.	Depth to top of Sample.	Sample Thick:ness.	Depth to top of Disc before test.	Depth to top of Disc after test.	Vertical Expansion of Sample.
1	6.09cm.	5.31cm.	0.78cm.	4.43cm.	3.46cm.	0.97cm.
2	6.19	5.29	0.80	4.43	3.44	0.99
3	6.08	5.28	0.80	4.49	3.43	1.06
4	6.08	5.26	0.82	4.50	3.42	1.08
5	6.04	5.26	0.78	4.45	3.51	0.94
6	6.02	5.26	0.76	4.45	3.44	1.01
7	6.06	5.28	0.78	4.47	3.46	1.01
8	6.11	5.30	0.81	4.47	3.49	0.98
Average.			0.79cm.			1.01cm.

SECTION III.

Crucible Dimensions.

Crucible Diam. = 5.10 cm.
Crucible Area = 20.45 cm.
Sheath Diam. = 0.71 cm.
Sheath Length = 5.08 cm.
Vol. of Sheath = 2.00 c.c.

SECTION IV

Sample Thickness = 0.79 cm.

Volume(Bulk) of sample = Crucible Area x Sample Thickness - Sheath Volume.

= 20.45 x 0.79 - 2.00 = 14.2ccs.(a)

Specific Volume of Coal ($\delta = 1.25$gm/ccs.) = $7.5/_{1.25}$ = 5.94ccs.(b)

Specific Volume of Silica ($\delta = 2.6$gm/ccs) = $7.5/_{2.6}$ = 2.88ccs.(c)

Pore Volume of Sample = 14.2 - (5.94 + 2.88) = 5.38ccs. (d)

Recorded Swelling = $20.45 \times \frac{1.01}{0.287} \times \frac{0.300}{1}$ = 21.3ccs. (e).

Total Swelling Volume = Recorded Swelling + Pore Volume

= 21.3 + 5.38 = 26.7 ccs. (f).

Table XV.

SECTION V.

Wt. of initial sample = 15.09gm.

Wt. of semi-coke = 13.68gm.

% Loss in wt. = 1.41/7.5

= 18.8%

SECTION VI.

Temperature of outside Couple.	Temperature of inside Couple.	Time from Switching on	Volume Indicator Reading (Scale Divs.)	Applied Pr. (Lbs/sq.in.)	Time From Switching on.
- °C	51°C	20 mins.	1.0	1.25	80 mins.
-	85	36	1.8	1.25	145
142	-	36	2	1.25	156.40
200	182	75	3	1.25	157.10
255	245	96	4	1.25	157.55
290	280	101	5	1.25	158.45
370	357	143	10	1.25	161.35
381	377	149	20	1.25	163.45
395	387	153	30	1.25	164.50
409	402	156	30	10.0	165.45
-	415	163	"	16.9	166.45
-	428	167	"	21.9	169.30
455	445	175	"	30.0	170.20
			"	38.8	171.10
			"	43.9	172.25
			"	49.5	173.20
			"	26.6	174.45
			"	10.0	176.30
			"	2.5	179.10

28.7 Divs. on Cooling.

Table XVI.

Test No.	Swelling Volume		Maxm.Swelling Pressure. (Lbs/sq.in.)	I.S.T. (°C.)	M.S.T. (°C.)
	c.c.s.	% of Actual Coal Vol.			
S.1	70.8	1189	1.25	390	440
S.2	55.6	934	"	398	443
S.3	57.4	968	"	398	443
*S.4	42.4	712	6.25	400	448
S.5	43.2	728	12.50	393	443
S.6	42.7	719	12.80	390	455
S.7	36.9	621	15.0	388	443
*S.8	37.1	623	15.8	395	440
S.9	37.8	637	21.2	398	430
*S.10	31.0	523	28.7	388	448
S.11	30.5	513	30.9	393	443
S.12	30.1	507	36.9	395	448
*S.13	28.6	482	38.1	390	448
*S.14	26.7	450	49.2	395	443

Table XVII.

Test No.	Swelling Volume.		Maxm.Swelling Pressure (Lbs/sq.in.)	I.S.T. (°C.)	M.S.T. (°C.)
	c.c.s.	% of actual Coal Vol.			
S.15	58.7	987	1.25	400	-
S.16	58.2	979	3.75	398	432
S.17	49.0	827	18.8	398	437
S.18	42.2	711	24.4	390	440
S.19	30.9	520	25.0	398	448
S.20	31.8	536	37.5	395	443
S.21	32.1	540	35.0	398	440
S.22	31.2	525	41.0	400	440
S.23	28.0	472	47.3	400	443
S.24	27.9	470	48.0	393	446
S.25	27.4	461	53.8	393	443
S.26	24.8	417	56.1	395	437
S.27	24.8	417	62.5	398	437
S.28	25.2	424	62.5	400	448
S.29	25.2	424	62.5	398	440
S.30	25.2	424	62.5	393	445
S.31	23.9	402	62.5	398	-

Table XVIII.

Test No.	Swelling Volume. c.c.s.	% of actual Coal Vol.	Maxm.Swelling Pressure (Lbs/sq.in.)	I.S.T. (°C.)	M.S.T. (°C.)
K.1	30.6	255	1.25	387	415
K.2	30.2	251	1.75	384	415
K.3	34.5	287	62.5	389	423
K.4	39.5	329	62.5	387	425

III records relevant crucible dimensions which are utilised in Section IV to calculate the bulk sample volume, (a), the pore volume of the sample, (d), the recorded swelling as given by the volume indicator reading, (e), and finally the total swelling volume (f) which is the sum of (e) and (d). Appropriate recordings of temperature, swelling pressure and volume are recorded in Section VI; in this test the constant swelling volume was 30 scale divisions, i.e., total swelling volume of 26.7 ccs. A graph of the swelling pressure-temperature data for this sample is shown as Curve No.1 in Fig.X.

Section (i):- Pressure-Volume Relationship for Sacriston Coal by Constant Volume Method.

The sample used in these tests was the 15 gm.composite sample of coal and silica sand described earlier (Part IV), the heating rate being 2.5°C/minute.

A series (Series One) of tests was run in which the only variable from test to test was the swelling volume which the coal samples were allowed to attain before pressure was applied. Table XVI contains the results of this series of tests, the swelling pressure recorded being the maximum

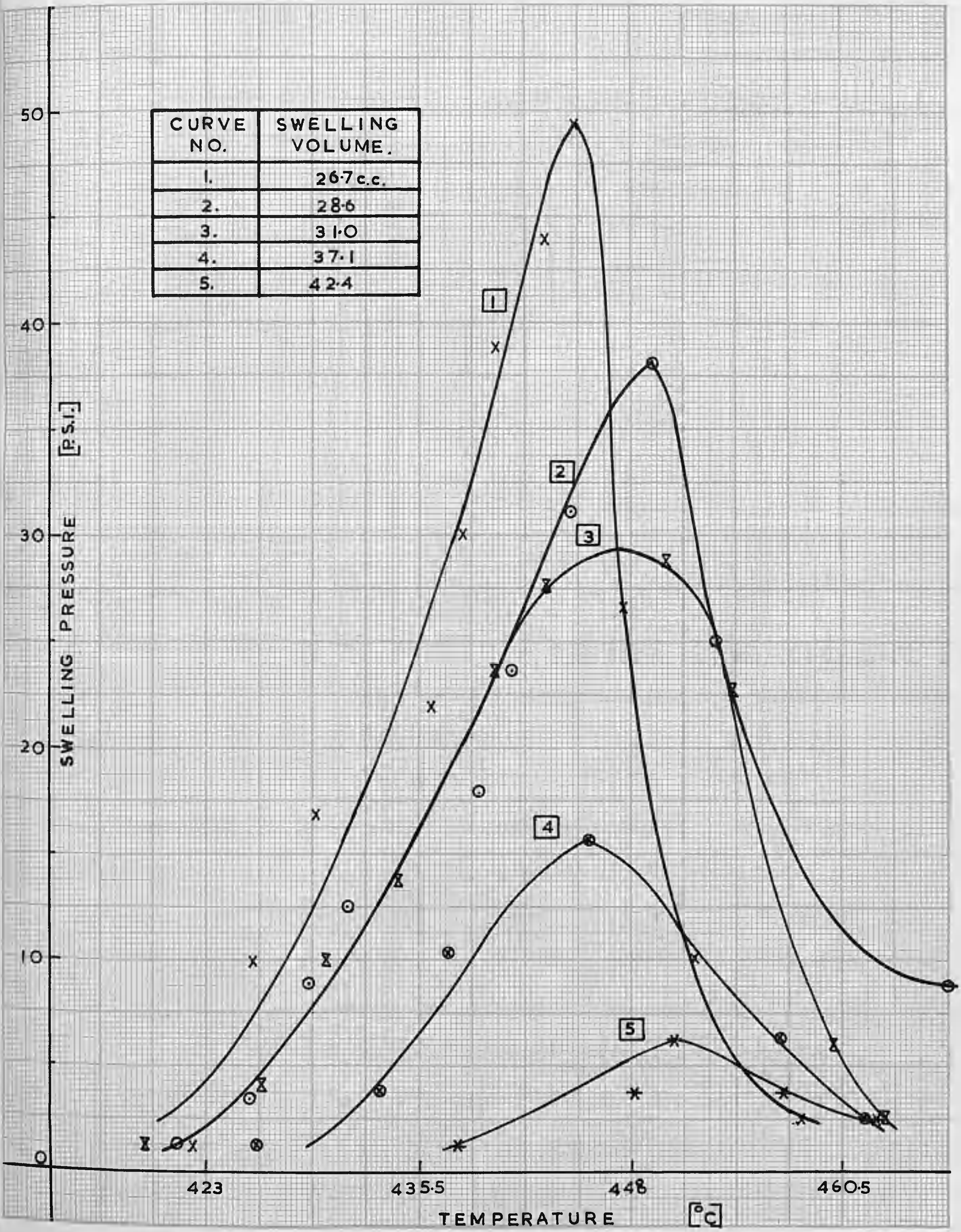

CURVE NO.
SWELLING VOLUME.
1. 26·7 c.c.
2. 28·6
3. 31·0
4. 37·1
5. 42·4
50
40
30
20
10
0
SWELLING PRESSURE [P.S.I.]
423
435·5
448
460·5
TEMPERATURE [°C]
1
2
3
4
5

FIG. X

value attained; the Initial Swelling temperature, (I.S.T.) was that at which swelling started when the sample was under 1.25lbs/sq.in. while the Temperature of Maximum Swelling, (M.S.T.) was that at which the swelling pressure attained its maximum value. The five tests marked in Table XVI with asterisks, have their pressure-temperature curves recorded in Fig.X; these show the general form of this curve over the entire swelling range. A noticeable feature about these curves was the rapid fall from the maximum swelling pressure, especially at higher pressures, and it was observed that the coal mass was still "plastic" at a temperature of, say, 460°C; at this temperature the mass could be readily compressed under low pressures without causing the residue to shatter as it would have done if "plasticity" had been lost entirely. Such a compressed sample would, on removal of the applied pressure, expand slightly and it was apparent that the drop from the maximum swelling pressure was not due to a complete loss of "plasticity" but rather to some fairly sudden alteration in the physical properties of the "plastic" material, e.g., greatly increased permeability. In this respect, the constant nature of the maximum swelling temperature, under a wide range of applied pressures, is considered significant.

The relationship between the maximum swelling pressure in lbs/sq.in. and the swelling volume in cubic centimetres is shown in Fig.XI and the points (Series One) are seen to fall quite closely to the parabolic curve; the same relationship is shown in Fig.XII with the maximum swelling pressure expressed

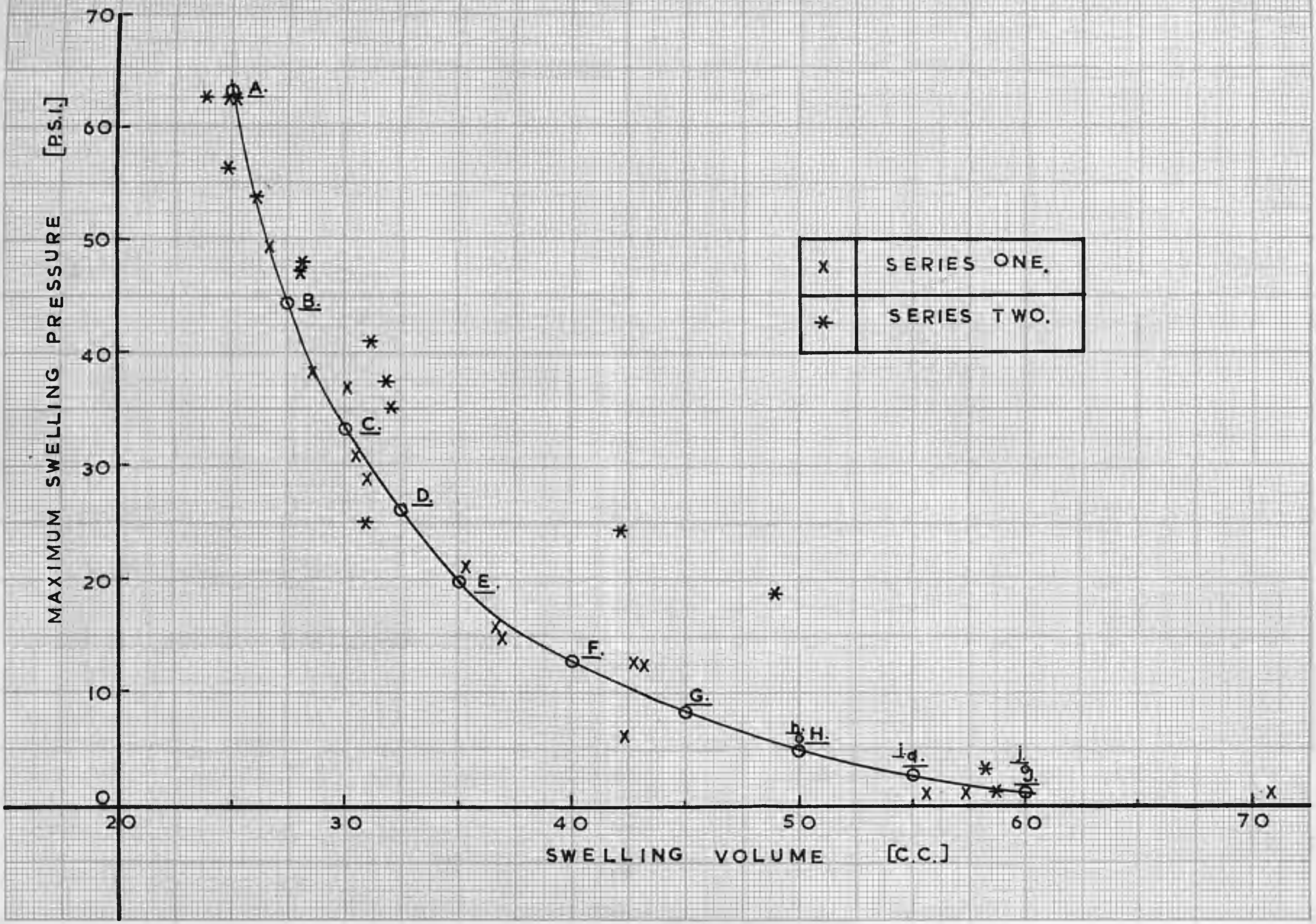

MAXIMUM SWELLING PRESSURE [P.S.I.]
SWELLING VOLUME [C.C.]
0
10
20
30
40
50
60
70
A.
B.
C.
D.
E.
F.
G.
h.
H.
i.
d.
j.
g.
X SERIES ONE.
✱ SERIES TWO.

FIG. XI

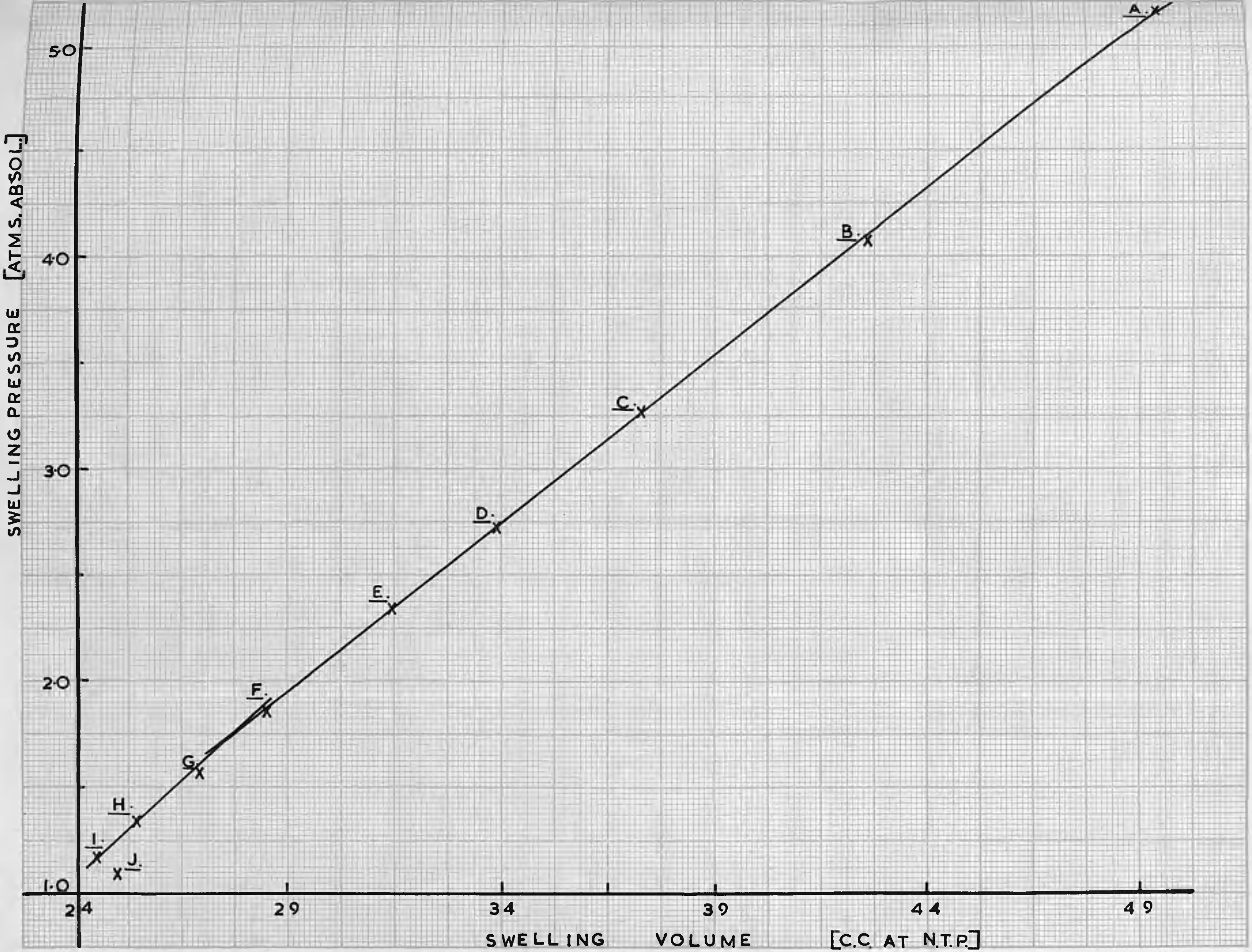

SWELLING PRESSURE [ATMS. ABSOL.]
5·0
4·0
3·0
2·0
1·0
24
29
34
39
44
49
SWELLING VOLUME [C.C. AT N.T.P.]
A.
B.
C.
D.
E.
F.
G.
H.
I.
J.

FIG. XII

as the absolute pressure in atmospheres and swelling volume corrected to cubic centimetres at N.T.P. The nature of this relationship will be discussed subsequently (Part VIII).

A second series of tests (Series Two) was carried out to confirm the above pressure-volume relationship and these results are presented in Table XVII and the maximum swelling pressure - swelling volume points are plotted in Fig. XI. The agreement of Series Two results with the curve drawn through those of Series One will be seen to be reasonable except for two intermediate values. It was considered inadvisable to draw a separate curve through the points of this second series and the view was taken that the results of Series Two offered reasonable confirmation as to the accuracy of the general swelling relationship. It was considered expedient, at this stage in the investigation, to proceed with the study of a second coal to determine whether the relationship observed was specific or general for different coking coals.

Section (ii): Pressure-Volume Relationship for Kingshill Coal by Constant Pressure Method.

The initial intention had been to carry out a series of runs under identical conditions to those pertaining in the above tests, except perhaps as regards the addition of inert silica sand and the size of coal sample used since, due to the lower rank, the swelling characteristics of this coal were expected to be less pronounced than in the previous case. Initial tests showed, in fact, that a 15 gm. sample of undiluted coal would be quite suitable; in all other experimental points the procedure was as carried out above.

The first two tests K.1 and K.2 were carried out under a constant pressure of 1.25 lbs/sq.in. corresponding to S.1 - S.3 of Table XVI; these results are reported in Table XVIII.(P. 55) In K.3 the intention had been to confine the swelling volume to 24 c.c. and to measure the maximum swelling pressure in the customary manner; swelling duly started, reached 24 c.c. when pressure was applied in the usual way. In the subsequent 15°C the pressure had risen from 1.25 to 62.5 lbs/sq.in. and swelling proceeded under the latter value to a final volume swelling of 34.5 cc. ≡ 287% i.e., 36% greater than when the swelling pressure was 1.25 lbs/sq.in. A fourth test, K.4., confirmed this anomalous effect of applied pressure increasing the degree of swelling.

The possibility of such an effect had been mentioned (43) by Brewer but no record of an actual case occurring had been discovered in the literature. It had been observed that the Kingshill coal was essentially "duller" than the Sacriston one and it was considered that under the effect of pressure the "fusible" constituents present would surround, permeate and wet the larger amounts of durain and other "non-fusible" materials, thereby rendering the entire mass less permeable to escape of volatile matter and so resulting in increased swelling It appeared unlikely that the latter effect was the result, solely, of the slight increase in the range of "plasticity" noted in Table XVIII. This effect was shown also by the Auchengeich Gum coal which was tested at this stage to confirm whether or not this new effect was reproducible in other less strongly swelling coals; tests A.1 and A.2 were run using a 15gm. sample of the undiluted coal as for the tests K.1 - K.4 and the results of these tests in Table XIX show that this effect is indeed present in this coal, but to a smaller extent due to the inferior swelling characteristics.

Table XIX.

Test No.	Maxm.Swelling Pressure (Lbs/sq.in.)	Swelling Volume (c.c.s.)
A.1	1.25	8.0
A.2	31.2	11.8
B.1	1.25	17.8
B.2	62.5	21.7

To test the hypothesis as to the cause of this effect, two tests were carried out using a synthetic mixture of 12 gm. of crushed and sized durain and 3 gm. of Sacriston coal (-36+72 B.S.S.), the experimental procedure being that described for all these tests. One test, B.1 was carried out under an applied pressure of 1.25 lbs/sq.in., the second, B.2., was carried out under an applied pressure of 62.5 lbs/sq.in., with the results given in Table XIX. These two tests suggest that the proposed hypothesis is basically correct and this will be more fully discussed later.

Consequently it was apparent that the swelling characteristics of this Kingshill coal could be studied only under constant pressure conditions, if the anomalous effect of applied pressure was to be elucidated.

The volume-temperature curves, for a first series of tests run under different constant applied pressures, are shown in Fig.XIII; Table XX contains the maximum swelling volumes attained under the different applied pressures, and also the characteristic temperatures of the "plastic" range, i.e., the Initial Swelling Temperature and Temperature of Maximum Swelling, Fig. XIV shows the plot of the swelling volume in cubic centimetres against the swelling pressure in lbs/sq.in. while in Fig. XV these are corrected respectively to cubic centimetres at N.T.P. and atmospheres (absolute) respectively. With reference to Fig.XIII, the remarkably linear nature of the volume-temperature curves will be noted and the constancy of the function ($^{dV}/_{dt}$) will be referred to subsequently. The effect of increasing pressure increasing the value of this co-efficient is at once apparent and the integrated effect of this is shown in Figs. XIV and XV where the degree of swelling increases progressively up to a certain applied pressure. With reference to Table XX, the constant nature of the initial swelling temperature is again noticeable; the temperature of maximum swelling tends to rise slightly as the applied pressure is raised. A notable point was the much lower value of this latter temperature compared with the corresponding Sacriston temperature, viz., 35-50°C lower, which resulted in a much shorter "plastic" range. A difference was also noted in the behaviour of the two coals near the end of the "plastic" stage. Compared to the Sacriston coal, the behaviour of which is described elsewhere, the Kingshill samples

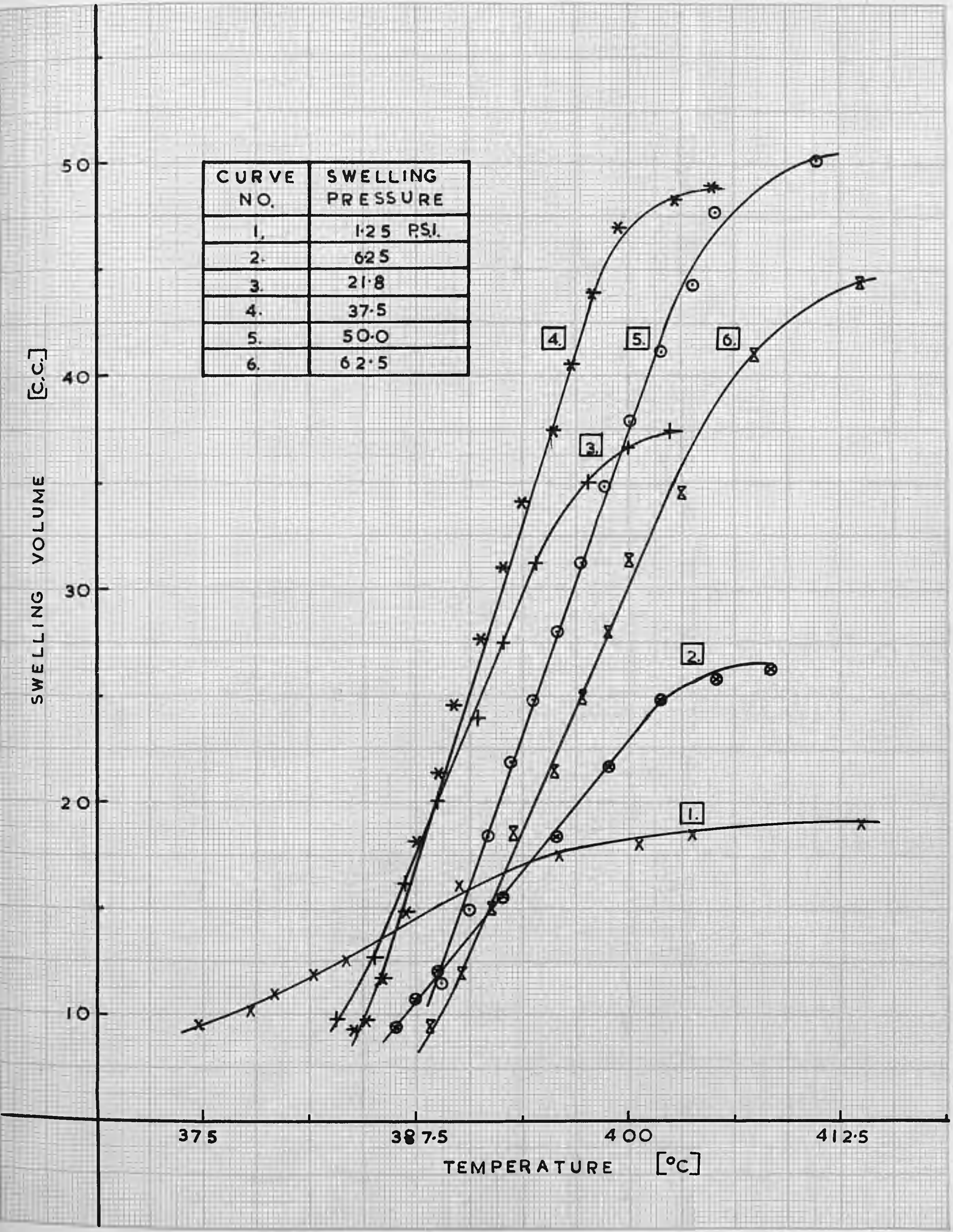

CURVE NO.
SWELLING PRESSURE
1. 1·25 P.S.I.
2. 6·25
3. 21·8
4. 37·5
5. 50·0
6. 62·5
1.
2.
3.
4.
5.
6.
SWELLING VOLUME [C.C.]
10
20
30
40
50
375
387·5
400
412·5
TEMPERATURE [°C]

FIG. XIII

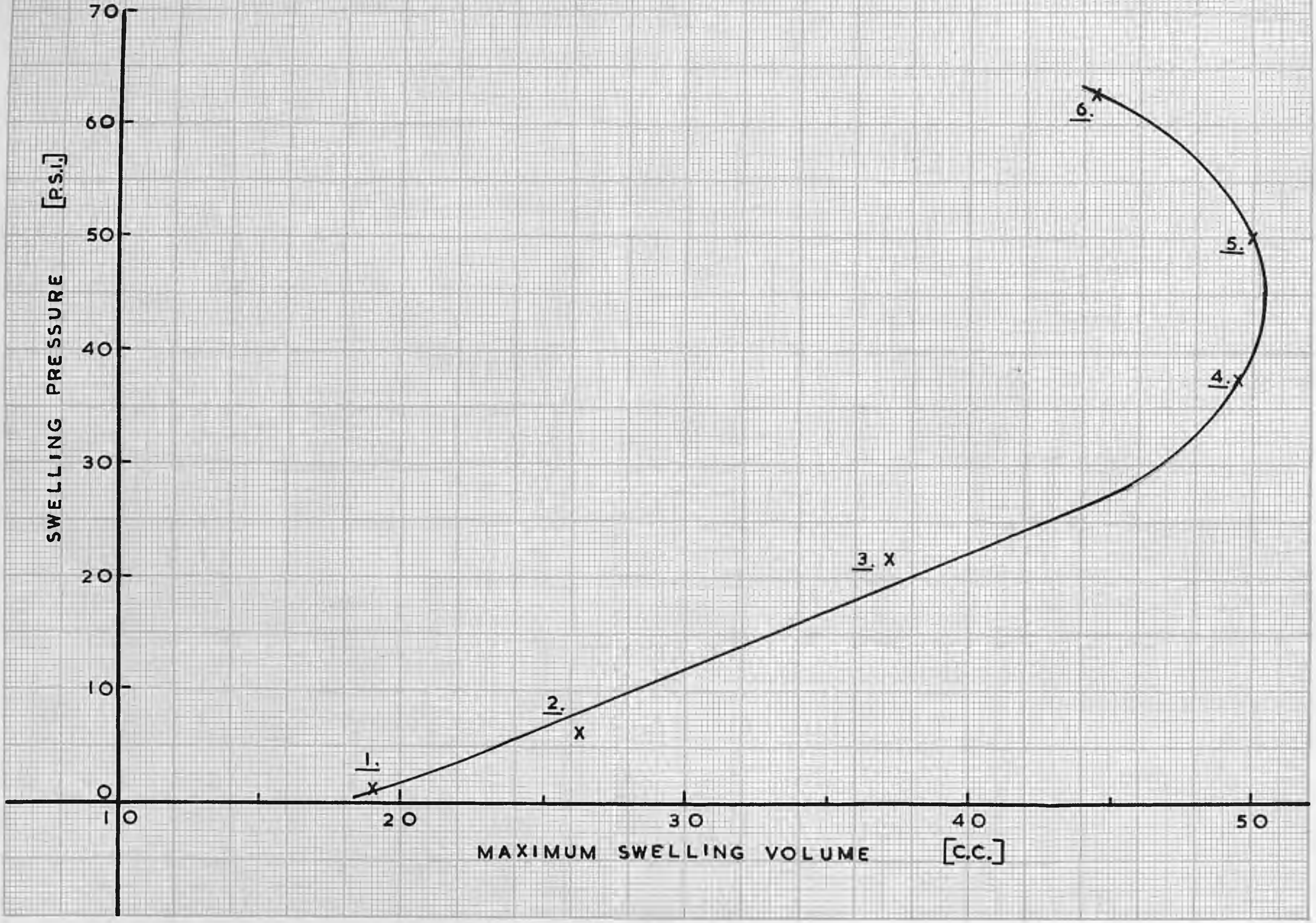

70
60
50
40
30
20
10
0
SWELLING PRESSURE [P.S.I.]
10
20
30
40
50
MAXIMUM SWELLING VOLUME [C.C.]
1.
2.
3.
4.
5.
6.

FIG. XIV

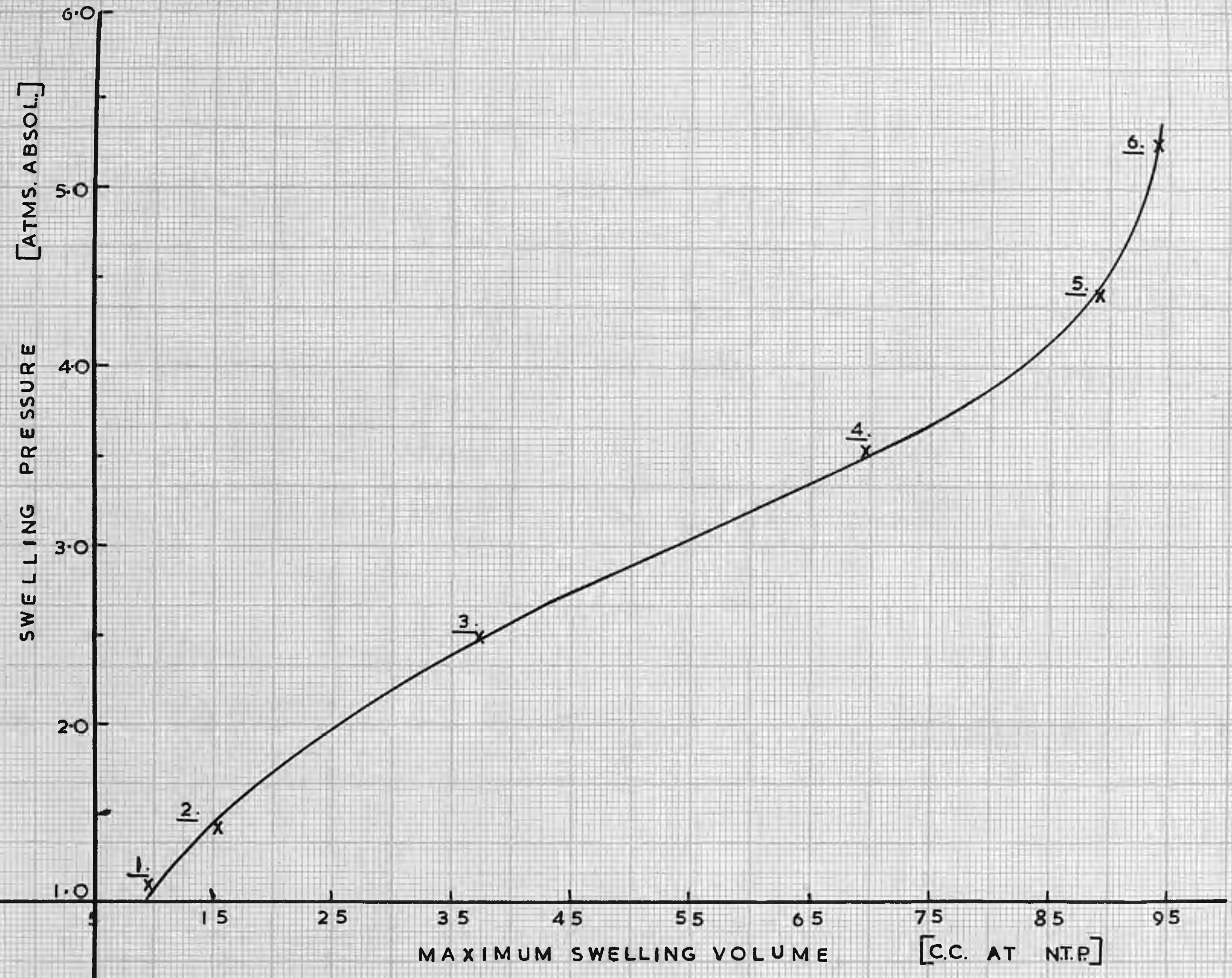

6·0
5·0
4·0
3·0
2·0
1·0
SWELLING PRESSURE [ATMS. ABSOL.]
5
15
25
35
45
55
65
75
85
95
MAXIMUM SWELLING VOLUME [C.C. AT N.T.P.]
1.
2.
3.
4.
5.
6.

FIG. XV

Table XX.

Test No.	Maximum Swelling Volume c.c.s.	% of actual Coal Vol.	Swelling Pressure Lbs/sq.in.	I.S.T. (°C).	T.M.S. (°C.)
K.5	19.03	159	1.25	375	398
K.6	26.25	219	6.25	380	405
K.7	37.3	310	21.9	375	400
K.8	49.5	412	37.5	375	405
K.9	50.2	419	50.0	378	410
K.10	44.4	369	62.5	383	411

Table XXI.

Test No.	Maximum Swelling Volume c.c.s.	% of actual Coal Vol.	Swelling Pressure Lbs/sq.in.	I.S.T. (°C.)	T.M.S. (°C.)
K.11	23.1	193	1.25	380	393
K.12	24.5	204	3.1	378	400
K.13	24.9	207	6.25	380	400
K.14	31.4	261	25.0	378	397
K.15	33.1	268	37.5	378	397
K.16	35.6	297	46.9	378	400
K.17	35.0	292	62.5	378	397

did not collapse suddenly and frequently the maximum pressure was maintained with only slight subsidence. Thus it appeared that this coal "set" quite quickly, that the change from the "plastic" to the "non-plastic" state was quite sudden and that any intermediate stage of "residual" plasticity was short indeed.

The effect of progressively increased pressure on the pore structure of the residue can be clearly seen in Fig. XVI; the applied pressures from left to right were 1.25, 6.25, 21.8, 50.0 lbs/sq.in.

FIG. XVI

A second series of tests was carried out in which the average heating rate was 2.0°C/min. instead of the standard value of 2.5°C/min; these results are shown in Table XXI. (P.61) The general trend for the swelling volume to increase with applied pressure, noted in the previous series, is again obvious up to a swelling pressure of some 50lbs/sq.in. when there is a slight drop with higher applied pressure. These results will be referred to in the subsequent discussion (Part VIII).

Section (iii) - Pressure-Volume Relationship for Sacriston Coal by Constant Pressure Method.

The effects described in the previous section made it highly desirable that a similar series of constant pressure results be obtained for the Sacriston coal, to demonstrate if any such effects had been overlooked by the previous study under constant volume conditions. The completion of a full series of results under these conditions was unfortunately curtailed by the development, in the electrical generator, of a rather disturbing defect. Repeated attempts to eradicate the defect by minor experimental adjustments were fruitless and the time available did not allow the final elimination of this fault. Nevertheless the few results obtained, considered in conjunction with those of the previous section, bring to light a number of very interesting points as to the behaviour of the two coals when "plastic."

These tests were carried out on a 7.5 gm. sample of undiluted coal of fixed size grading, as this appeared to offer a better basis of comparison with the previous section. To accommodate this reduced sample volume, the central silica sheath of the morganite crucible, normally 0.7cm. O.D., was reduced to 0.45cm. O.D.; in all other respects the procedure was identical to Section (ii), a heating rate of 2.5°C/min. being used. The swelling-volume-temperature curves for four tests at swelling pressures of 1.25, 4.69, 9.38, and 18.76 lbs/sq.in. are shown in Fig.XVII and the following two points are worthy of note at this stage, viz:-

(i) The swelling volume-temperature relationship is not so strictly linear as in the case of the Kingshill coal, the curves being distinctly "S" shaped.

(ii) The range of "plasticity" does not tend to increase as the applied pressure rises and in fact the opposite effect is noticeable to a slight extent. If the series had been completed in full, the results would have thrown some light on the effect of the addition of inert sand and also the difference in pressure-volume relationships determined at constant pressure and constant volume. As it is, the conclusions as to these effects remain somewhat speculative and a discussion of these factors will be delayed till later; a comparison of the swelling volumes at similar swelling pressures is given in Table XXII column two being for tests at constant pressure on the undiluted coal, while column three is for the diluted coal tested at constant pressure.

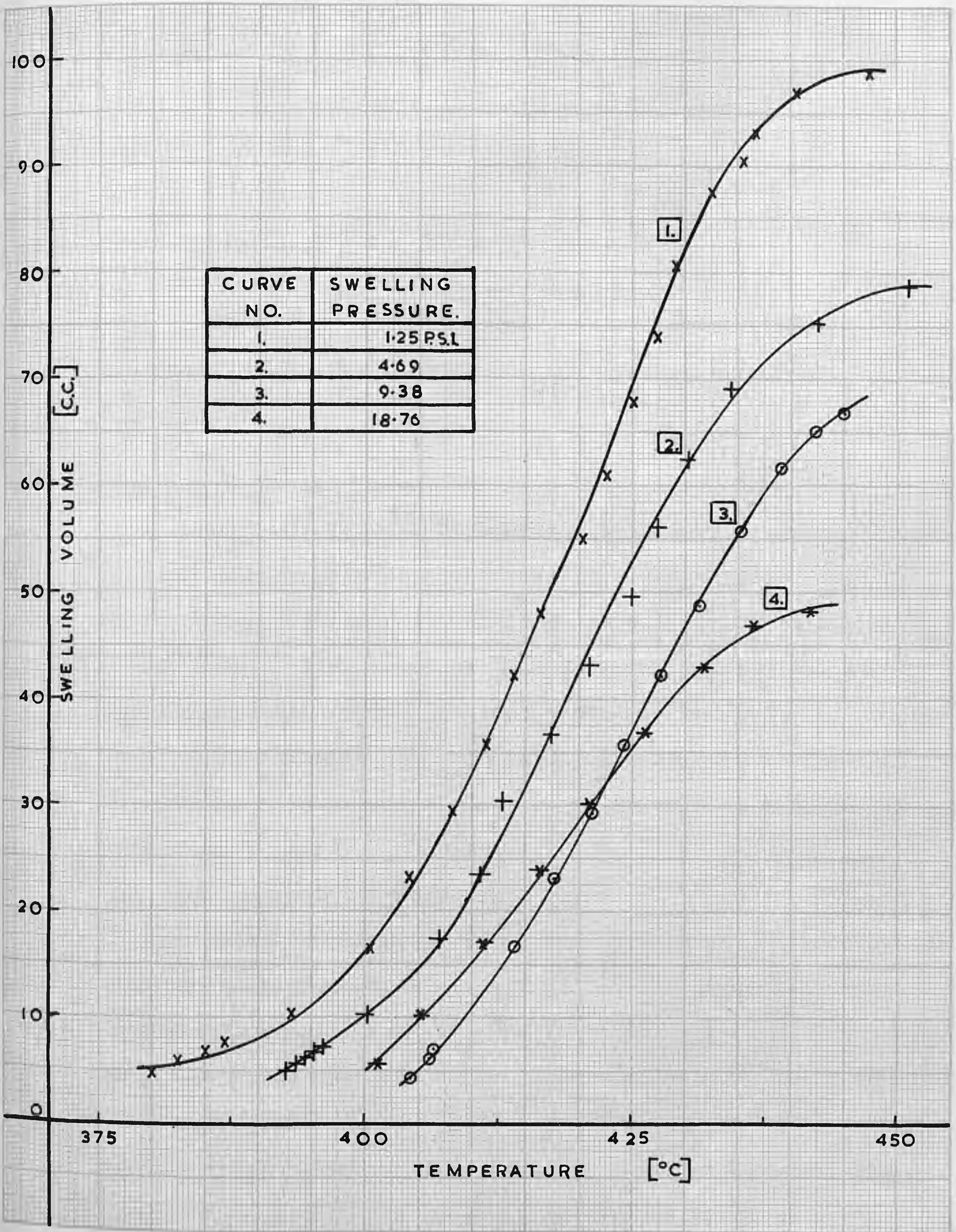

CURVE NO.
SWELLING PRESSURE.
1. 1·25 P.S.I.
2. 4·69
3. 9·38
4. 18·76
1.
2.
3.
4.
SWELLING VOLUME [C.C.]
TEMPERATURE [°C]
0
10
20
30
40
50
60
70
80
90
100
375
400
425
450

FIG. XVII

Table XXII.

Swelling Pressure (Lbs/sq.in.)	(1) Pure Coal Const. Pr.	(2) Diluted Coal Const. Vol.
1.25	97.4c.c.s.	59.0 c.c.s.
4.69	78.9	50.0
9.38	67.0	43.5
18.76	48.5	36.0

It will be seen that the diluted coal tested at constant volume was always less strongly swelling than in the other case.

Section (iv): Investigation of Swelling Mechanism.

This final section records several observations made of the swelling mechanism; the majority of these are concerned with the early stages of swelling and only a few with the later ones. Almost all of this work was carried out on the Sacriston coal and the aim was to observe the swelling process and to obtain information which might assist in a satisfactory explanation of the above results. The work is divided into two stages, viz:-

(i) Initial Swelling Stage.

Actual swelling of individual particles was preceded by pronounced fissuring on the surface of the particles, and started in certain petrographic bands which developed a highly cellular structure while the adjoining ones were still intact; the surface of such bands had a pronounced nodular character with not infrequent exudations of black pitch-like material, itself highly cellular internally. Fig.XVIII shows a ½"

FIG. XVIII

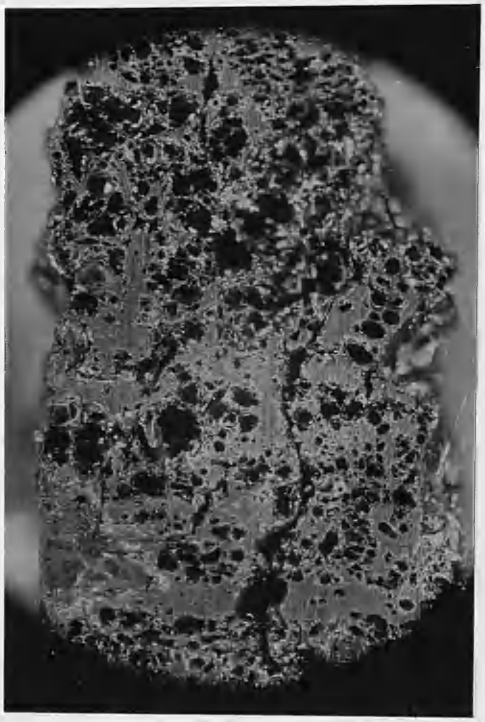


FIG. XIX

particle of coal heated to 338°C at 2.5°C/minute and illustrates surface fissuring and the inception of swelling at the top and bottom regions; the internal cellular structure of the same particle is shown in Fig.XIX with a central unswollen region. When heated to a slightly higher temperature the internal cell structure became very highly developed as can be seen from Figs. XX and XXI which is of a $\frac{1}{4}$" particle heated to 348°C and viewed at magnifications of (x8) and (x15) respectively. The initial swelling mechanism was apparently similar in much smaller particles as seen in Figs. XXII, XXIII, which are of +36 B.S.S. (+0.017) particles heated to 344°C.

A closer study of this initial swelling indicated that it started quite suddenly at a fixed temperature. This is clearly indicated by the change in apparent density of a number of +$\frac{1}{4}$" particles heated to three progressively higher temperatures; the apparent density was measured by displacement in benzene.

Table XXIII.

Final Temperature (°C).	Initial Apparent Density (gms/ccs.)	Final Apparent Density (gms/ccs.)	% Change in Apparent Density.
325	1.28	1.27	0.8
338	1.28	1.08	15.6
345	1.28	0.98	23.5

Further tests indicated that at a temperature just above this "primary" swelling temperature, i.e., about 338°C, the degree of swelling or synonomously the decrease in apparent density, was controlled largely by the particle size of coal

FIG. XX

FIG. XXI

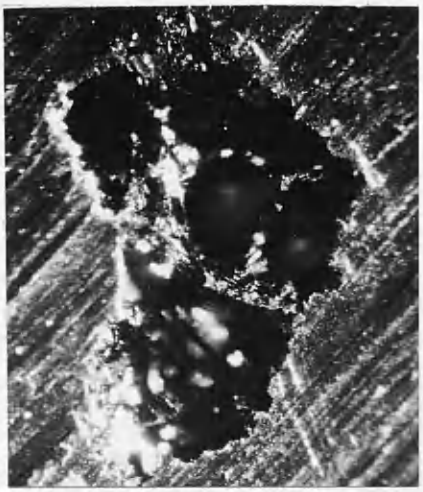


FIG. XXII

FIG. XXIII

FIG. XXIV

FIG. XXV

used. Thus the results of a series of tests in which different size fractions were heated to 338°C are contained in Table XXIV.

Table XXIV.

Particle Size.	Apparent Density Before Test gms/ccs.	Apparent Density After Test gms/ccs.	% Change in Apparent Density.
-1/16" + 16B.S.S.	1.32	1.06	19.7
-16 + 22	1.28	1.08	15.6
-22 + 36	1.28	1.14	11.0
-36 + 52	1.28	1.22	4.7
-52 + 72	1.30	1.25	3.8
-72 + 100	1.30	1.28	1.5

The progressive decrease in the % change in apparent density with decreased size will be noticed, and it was observed that the results conformed approximately to the expression -

$$\%\ \text{Change in Apparent Density} \propto L^3 \propto V$$

L = Particle Dimension
V = Particle Volume.

This relationship suggested that the early change in apparent density was controlled largely by internal gas pressure within the particles. It was considered that such a difference in "primary" swelling should be reflected in a difference in the Initial Swelling Temperature (I.S.T.) of bulk samples of differently sized particles. 10 gms. samples of three size fractions were heated at 2.5°C/minute and the I.S.T. determined were as follows:-

Size Fraction.	I.S.T.
-1/16" + 16 B.S.S.	375°C
-52 + 72 B.S.S.	385°C
-100 +200 B.S.S.	392°C

The following points were noted:-

(i) I.S.T. of the bulk sample sizes fall with a progressive increase in particle size.

(ii) If the -1/16" + 16 B.S.S. size is considered the difference between the "primary" swelling temperature of the particles and the I.S.T. of the bulk sample was over 30°C which is quite considerable.

(iii) It was observed that once swelling started in the finer particle bulk sample, its rate rapidly increased and the rate subsequently appeared to be controlled solely by temperature and to be independent of initial particle size. Further reference will be made to these observations in Part VII.

(ii) Observations of Semi-Coke Structure near End of Swelling.

In spite of the excessive degree of swelling of Sacriston coal, the structure of the semi-coke throughout the major portion of the swelling stage was very regular and comprised a sponge-like mass at all stages, the cell wall thickness becoming progressively decreased as new pores developed; only towards the end of the range did the foam structure collapse and the material coalesce into a non-swollen residue. During the foam stage the coke was a lustrous tarry black which turned to a duller grey-black after the swelling had passed its maximum. It was observed that in the foam state the cell walls very frequently contained small transparent "windows" covered by a brown film of what appeared to have been a liquid or highly fluid material; the transparency of these windows depended largely on the extent of swelling, being relatively opaque when swelling was small and quite transparent later. The friable nature of these films made their reproduction difficult but two such "windows" are shown in Figs. XXIV and XXV. The relatively sharp boundary between coke material and the "window" will be apparent as if the former had been ruptured and that rupture covered over with a thin brown film. Fig. XXV shows that the film material has an internal structure and it would appear that small particles, possibly of the coke substance proper, are dispersed in the film. It was a notable feature that at temperatures near and above the temperature of maximum swelling, 445°C, this film was frequently found wanting and open "windows" were now apparent, indicating a disappearance of the film-forming constituent. This disappearance was accompanied by an alteration in the colour of the semi-coke from tarry black to the grey black of the final residue. It would be suggested that this film material plays an essential role in the coking process and its possible mode of action will be discussed subsequently.

PART VI.

PHYSICO-CHEMICAL CONSIDERATIONS OF THE PLASTIC STATE.

Solvent analysis was one of the earliest methods used in the elucidation of the causes inducing "plasticity" in coking coals. The initial results suggested that the so-called bitumens, i.e., the (β) and (γ) fractions of Wheeler's scheme, (44), or the solid and oily bitumen of Fischer's scheme (45), controlled the agglutination and swelling of coking coals. However, the work of such workers as Fischer, (45), Brocke & Schmitz (46), etc., proved conclusively that the presence of bitumens was by no means specific with regard to coking properties. A final stumbling block to the older hypothesis, that swelling was controlled entirely by the amount of bitumen present, came with the results of Kester and Junge (47), who found no correlation of coke making properties with the amount of extract obtainable from a representative number of coking coals. Recently Kiebler, (48), and Kreulen, (49, 50), have considered solvent extraction to be a process involving the dispersion of a colloidal system in liquids of progressively lower surface tension, and this approach has thrown considerable fresh light on the nature and relationship of the several fractions so obtained. Nevertheless a comprehensive explanation of the different coking properties shown by coals of varying rank, on the basis of information obtainable by this method, has proved impossible. The more promising results of alternative methods of approach will now be considered.

The methods of the physical chemist, applied to the study of the colloidal nature of coal, have thrown considerable fresh light on coal structure in relation to the coking process. Perhaps the most significant of several such fresh investigations was that measuring the internal surface area of coals by heat of wetting in methanol, and the variation of that factor with coal rank, (51,52). Griffith and Hirst (51) showed that there was a marked minimum in the internal surface-rank curve in the region of coking coals, and it was shown in addition, that the internal surface-carbonisation temperature curve was characteristic in the case of these coals. Thus the internal surface area rose with carbonisation temperature to a maximum at 350-375°C and then dropped progressively to a flat minimum in the range 450-475°C; a further rise was obtained at higher temperatures. Furthermore, it was shown on comparison of this curve with the expansion-temperature curve for the behaviour of the coal in the Sheffield Laboratory Coking Test, that the initial maximum in the former curve was co-incident with the initial contraction temperature of the latter and that swelling of the coal took place during the time that the internal surface was dropping to the minimum; swelling ceased at the turning point in the internal surface-temperature curve. A notable feature of such curves was the fact that at no stage in the carbonisation process did the internal surface fall to zero thus precluding any interpretation of the results on the basis of a "melting" phenomenon which would have resulted in a product of very low internal surface; the minimum value attained indicated that the internal surface at this stage was equivalent to about half the initial value. Any theoretical interpretation must take these fresh experimental observations into account.

In formulating such an account Hirst (53) postulates a micelle structure for coal of the "globular" type with aggregates of differing degree of polymerisation making up the micelle; the central region is made up of the heaviest cross-linked aggregates surrounded by those of progressively less complex nature, the latter apparently being relatively loosely bound to the former. This latter assumption, suggested by the "plastic" nature of the coal at low temperatures, (54) is confirmed by the findings of Bangham and Franklin (55), who concluded from a study of the co-efficient of thermal expansion that the intra-micellar structure contained units bound by both van der Waal and covalent bonds. Heat will cause these loosely bound, less complex, surface aggregates to attain a considerable mobility to the extent that they will act as boundary lubricants for the movement of the individual micelles, and once fully developed they will confer on the mass the ability to form "films" under suitable conditions. The thermal oscillations of the micelle nuclei will result in their frequent collision, and cohesion of these take place probably on account of the polar nature of the central nucleus. Thus the nuclei tend to conglomerate and this process will result in a decrease in internal surface area; this latter decrease will take place at a progressively decreasing rate at higher temperatures due to the larger nature of conglomerates involved and also to the disrupting effect of the evaporation of progressively more complex molecules as the temperature is raised. Consequently at some higher temperature mobility will cease due to these two factors, swelling of the mass will cease and a rise in the internal surface can be expected due to the disappearance of the boundary lubricants. The effective range of "plasticity" of the mass will be controlled by the ease with which the lubricants and other products of pyrolysis can escape, i.e., by the permeability of the material and by the total amount of lubricating agent present or available. In coking coals, as has been mentioned, the permeability is undoubtedly low and it may well be that the supply of potential lubricating agents from the break down of the more highly polymerised molecules will be greater in these coals due to their lower initial oxygen content; both factors tend to give pronounced "plastic" properties to this range of coals. Hirst likewise stresses the micellar shape as a factor controlling the extent of mobility attained and it is suggested that coking coals are favoured in this respect by a regular micellar shape, while lower rank coals may be more irregular in this respect and, due to their higher oxygen content, may even have a number of micelles cross-linked to one another. This latter view is consistent with the fact that reduction of these coals causes greater "plasticity" and it would be interesting to determine whether such reduction is accompanied by aby decrease in internal surface area. Coals of rank higher than those in the coking range lose the ability to become "plastic", not only on account of their slightly greater internal surface, but also due to the further loss of oxygen and hydrogen which allows a more rigid and highly covalent structure to be attained, precluding any marked intermicellar movement. Oxidation, known to seriously impair "plastic" properties, is effective, on this basis, by restricting intermicellar movement possibly by cross linking these through the readily oxidisable (β) compounds. Such a view of the effect of hydrogen and oxygen seems preferable to that proposed by Berkowitz (56), who, in discussing "plasticity" and swelling from a similar standpoint, regards the effect of the former to be due to increased volatile matter content and of the latter to be caused by an enlargement of the pores, i.e., by increased permeability.

It may be summarised that "plasticity" in coking coals has its origin in a unique combination of essentially physical factors in the structure of bright coals. The main criteria appear to be a low permeability, synonymous with low internal surface, combined with a suitable micellar structure which, in the case of coking coals, is intermediate between the more highly covalent structure of the higher rank coals and the more irregular and possibly cross linked one of coals in the lower rank range. "Plasticity" on this basis is not controlled, essentially, by the presence or absence of coal "bitumens" but by the inter-relationship of these and the above physical structure; the chemical effects of oxidation and reduction are important in so far as they affect this inter-relationship. Although much information is still required as to the structure of the coal micelle and the intermicellar arrangement, such a theory of coking coals is markedly superior to the older one based on the results of "solvent" analysis.

Finally, it is proposed to discuss the work of Riley and his co-workers, (57,58,59,60) on the X-ray diffraction studies of carbonaceous materials in so far as they are relevant. It must be emphasised that the interpretation of the observed line broadening effects, on the basis of alteration of crystallite size, has been criticised from a crystallographic point of view (61) and from the point of view of the coal technologist the significance of the hypothetical crystallites is not at once apparent. On the basis of average crystallite dimensions for a Durham coal, and assuming a micellar size determined by Bangham (62) it can be deduced that a single micelle will contain somewhere in the region of 700-800 crystallites. Whether such crystallites are in any way related to the molecular units present in the micelle remains to be seen. Cricumstantial evidence in support of the interpretation of the observed effects from a molecular basis is to be found, perhaps, in the fact that a closely similar series of effects was observed (60), for coal tar pitch. It seems unlikely that a cause, other than molecular similarity in the two cases, could be reproduced so exactly, especially when the respective origins of coal and pitch are considered.

From the standpoint of "plasticity" in coking coals the important deductions from the above interpretation are:-

(i) A Coking coal is characterised by a progressive increase in the "C" dimension, of the cylindrical crystallite as the carbonisation temperatures is raised to 550°C,

(ii) Crystallographically the (α), (β) & (γ) fractions of "solvent" analysis are similar, apparently consisting of a layer-plane or turbostratic system, on the basis of the similarity of the patterns of these materials with those shown by Biscoe and Warren, (63) for amorphous carbons.

Solvent extraction indicated that the former effect was connected directly with the presence of the bitumens, the removal of these leaving a residue which did not show this effect and which was non-swelling. It was thus considered that the bitumens formed a "mobile" turbostratic system as opposed to the "rigid" one of the (α) fraction; on heating the mobility of the former allowed them to move and it was considered that they then layered themselves on existing crystallites, giving the observed increase in "C" dimension. No speculation as to what motivated such a layering was made, e.g., whether it was due solely to energy considerations of a disorder-order change or whether chemical considerations were involved. The authors indicated (59) that oxidation of a strongly swelling coal, to the point where this property was completely destroyed, was accompanied by the elimination of the characteristic maximum in the "C" dimension-temperature curve. It was demonstrated further that the amount of extractable material had not altered appreciably as a result of oxidation and it was also shown that the (γ) fraction which resembled the whole coal in giving a maximum in its "C" dimension-carbonisation temperature curve, continued to do so after oxidation. Oxidation had thus not destroyed completely the "mobile" nature of the (γ) phase but had suppressed the layering of these molecules on the existing crystallites; these facts stress the close inter-relationship of all phases during the "plastic" state and suggest that the state of the (α) phase as regards extent of oxidation may be a very important point in regard to the growth of these crystallites. It is thus apparent that some degree of inter-action of the several phasespresent is essential for the development of coking properties, and the lack of this inter-action, either by oxidation or by change of coal rank, leads to a material with non-swelling properties. The fundamental concepts of this approach are by no means contradictary to those of the micellar one but the obscure significance of the crystallites involved in the former and the difference in size of the units involved in the two cases, make a detailed comparison highly speculative; the desirability of carrying out such a comparison of these two interesting approaches is obvious.

PART VII.

DISCUSSION OF RESULTS : SECTION 1.

The results contained in (Section IV) Part V, are conveniently discussed first in a separate section as they are concerned with the primary stages of swelling where the factors of importance are slightly different from those in the subsequent stages; the significance of the latter are discussed subsequently (Part VIII).

The observations made on the occurrence of fissuring prior to swelling, and of the inception of that swelling in certain petrographic bands are in keeping with those of Thiessen and Sprunk (64) who found no change in internal structure in a coking coal, below 330-335°C; the surface became progressively fissured and cracked above 130°C. Above 335°C vacuoles formed internally, in the translucent attritus, and these developed progressively with rise in temperature, similarly, no doubt, to the structure developed on heating particles of "bright" Sacriston coal to 10°C above the "primary" swelling temperature, i.e., to 348°C (Fig.XX). The exact cause of this fissuring is not obvious since very little change in the coal can have been effected at temperatures as low as 130°C; it would appear that it is possibly related to the desorption process which is consider:ed, e.g., by Hirst (52) to take place in the pre-swelling range; this desorption will also include removal of colloidally held moisture. Thus even minute volumes of gas entrapped within the coal particles could build up sufficient pressure to cause fissuring in the essentially brittle coal.

With reference to the "primary" swelling temperature i.e., that at which the swelling of the individual particles starts, two observations suggest that this temperature is controlled by more than one factor; these observations are:-

(i) the relatively rapid increase in the degree of swelling, for a given particle size, as the temperature is raised (Table XXIII), and

(ii) the close dependence of the degree of swelling at one temperature, on the particle size Table XXIV.

In this respect Mott (15), showed that this "primary" swelling temperature was co-incident with the initial contraction temperature of an aggregate sample under load while Hirst (52) demonstrated that the latter temperature corresponded to the first maximum in the heat of wetting-temperature curve, at which inter micellar movement becomes possible for the first time. It is now suggested that the two factors controlling the "primary" swelling temperature are:-

(i) The temperature at which inter-micellar movement becomes possible, i.e., at which the coal "softens" and its yield point drops.

(ii) Progressive build up of internal pressure by volatile matter entrapped within the inter-micellar pores; the magnitude of this pressurefor a given coal, will be controlled largely by particle size. With reference to (ii) it should be noted that the total amount of volatile matter required to build up the necessary pressure, will be small indeed and it is probable that the bulk of this originates from gas adsorbed on the coal surface. When the pressure from (ii) exceeds the yield point the particle will distend rapidly; as the yield point will be independent of particle size, the factor controlling the "primary" swelling temperature viz., the internal pressure, will be particle size dependent.

When the swelling of aggregates of single size fractions is considered, notable features are the discrepancy between the "primary" swelling temperature of the particles and the initial swelling temperature of the aggregate (340°C and 380°C respectively) and the fact that the latter is also particle size dependent. Such a difference, between the two swelling temperatures, is readily appreciated when the swelling mechanism is considered. Swelling of individual particles starts at "primary" swelling temperature, but due to the inhomogeneous distribution of swelling constituents the mass at this stage can hardly be regarded as "plastic." This primary swelling is "free" in that the particles can expand, under virtually no load, into the voids of the original aggregate; once all such voidage is filled further swelling is resisted by frictional effects in the crucible and also by the small applied pressure, i.e., 1·3 lb/sq.in. Due to the inhomogeneous nature of the mass its permeability will be high and this in conjunction with a low rate of generation of volatile matter at these temperatures (Fig.XXVl)

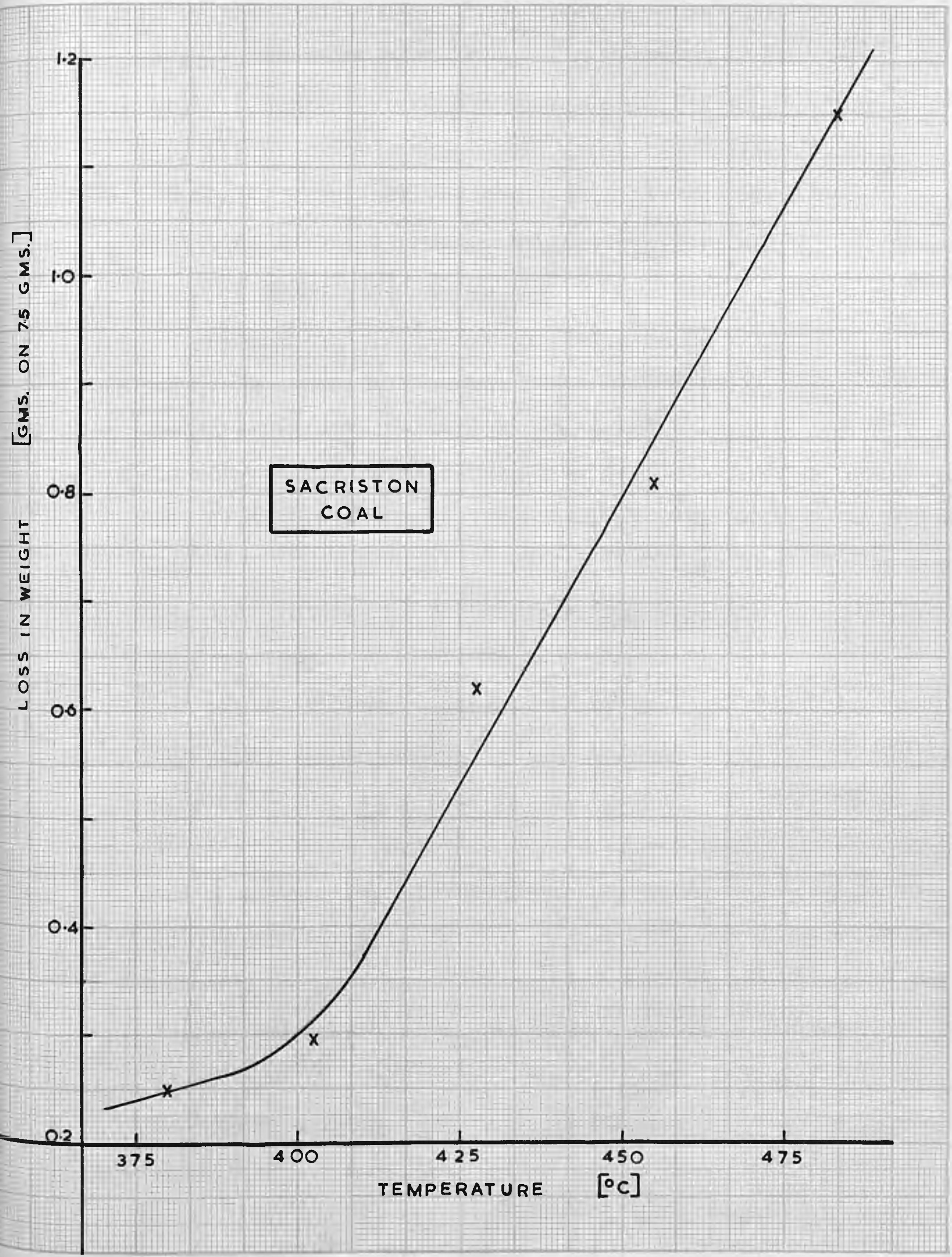
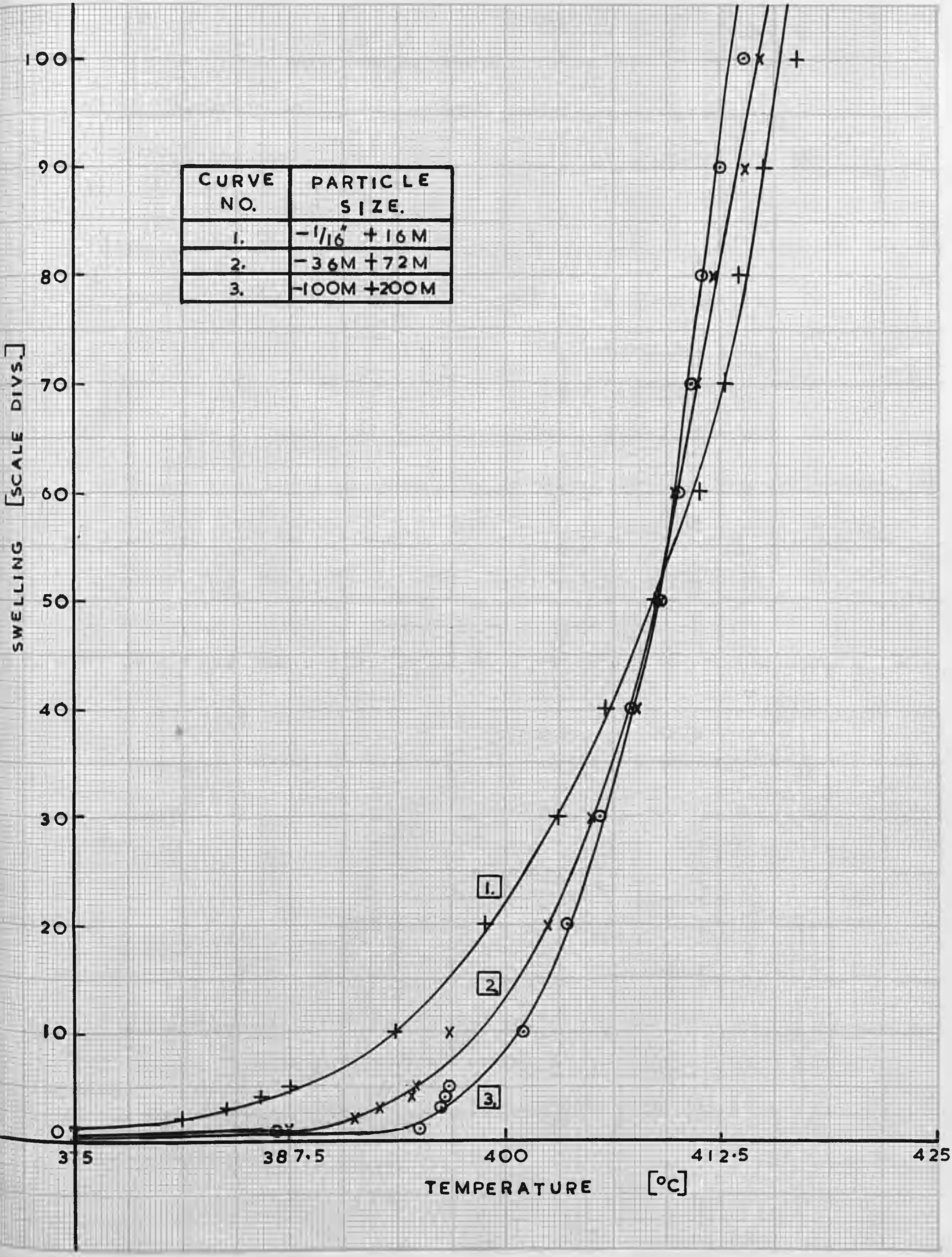

1·2
1·0
0·8
0·6
0·4
0·2
LOSS IN WEIGHT [GMS. ON 7·5 GMS.]
SACRISTON COAL
375
400
425
450
475
TEMPERATURE [°C]

FIG. XXVI

implies that further swelling is delayed. Only when the rate of generation of volatile matter begins to increase appreciably, i.e., above 380°C (See Fig.XXVI) will swelling of the aggregate take place; this stage is no doubt, preceded by one in which the inhomogeneous nature of the mass is lost and in which the permeability is dropping due to progressive elimination of any remaining voids. The fact that the initial swelling temperature of aggregates made up of finer particles, is higher than for ones of coarser particles is a result of (i) the higher value for the "primary" swelling temperature of the smaller particles, and (ii) the fact that it will take longer for all the inter-particle voidage to be eliminared with a consequent fall in permeability.

It is interesting to observe, Fig.XXVII, that once swelling starts the rate of swelling is largely independent of initial particle size and apparently depends largely on the temperature for a given rate of heating; in fact the rates of swelling of the finer coal samples appear to be a little greater than for the coarser one, at higher temperatures, and this may reflect the lower permeability of the former due to better dispersion of non-fusible constituents. A significant observation regarding the initial swelling temperature is that it is not accompanied by any radical alteration in the form of the heat of wetting-temperature curve, (52), and that consequently no pronounced alteration in internal surface or in inter-micellar arrangement


CURVE NO.
PARTICLE SIZE.
1. −1/16" +16M
2. −36M +72M
3. −100M +200M
1.
2.
3.
SWELLING [SCALE DIVS.]
100
90
80
70
60
50
40
30
20
10
0
375
387·5
400
412·5
425
TEMPERATURE [°C]

F I G. XXVII

accompanies this temperature; this is considered evidence in support of the view that the initial swelling temperature is controlled largely by the rate of thermal decomposition.

Evidence in support of the above interpretation is to be had from the corresponding values of the "primary" swelling temperature and the initial swelling temperature for the lower rank Kingshill coal. The former was found to be in the region of 360°C, i.e., some 20°C higher than for the Sacriston coal, while the latter temperature was 378°C. Thus the first observation is explained by the fact that the lower rank of this coal will give a higher permeability; this fact is deduced from the work of Hirst (51) who showed that the internal surface area rose with decrease in rank. Thus the pressure necessary to cause swelling of the individual particles will not be built up till a higher temperature is reached. The fact that the initial swelling temperatures of the two coals are nearly the same, in spite of the higher permeability of the Kingshill coal, is readily explained by the higher rate of gas generation of this coal, in the temperature range 350-375°C (Fig.XXVIII).

Cell Wall "Window" Structure.

This structure (Figs.XXIV and XXV) is undoubtedly related to the cenosphere structure described by Carlile (65) and reflects the superlative film forming ability of the Sacriston coal. The relatively sharp boundary of such "windows" suggests that they are not merely excessively thin

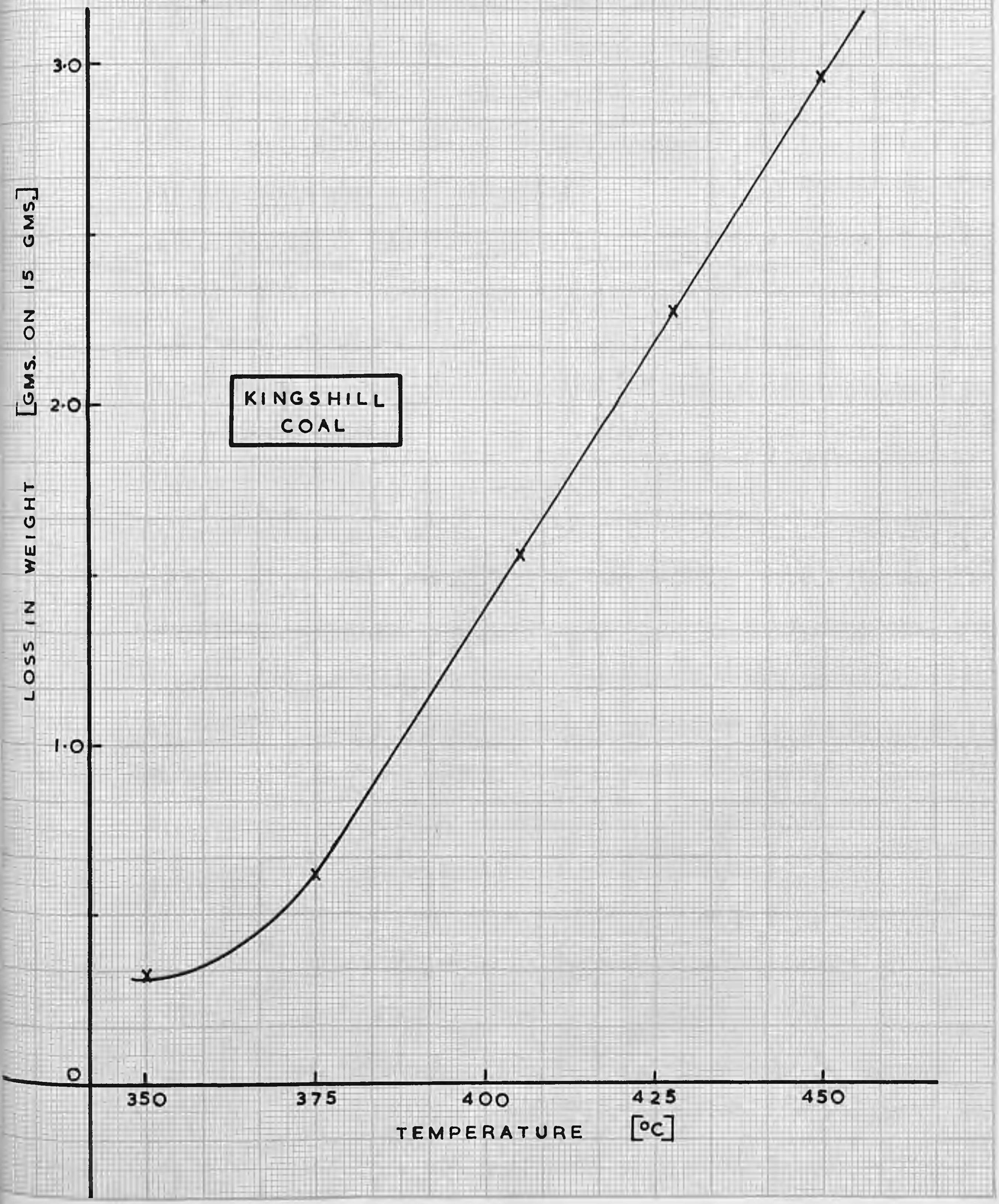

KINGSHILL COAL
LOSS IN WEIGHT [GMS. ON 15 GMS.]
3·0
2·0
1·0
0
350
375
400
425
450
TEMPERATURE [°C]

FIG. XXVIII

portions of the cell wall, but it seems possible that they comprise local regions in which there is present an excess of "lubricating" agents which confer "plasticity" on the coal material; the structure of Fig.XXV suggests that the films can disperse the cell wall material and the opacity of the "window" may well depend on the degree to which the latter material has drained off, as described by Carlile for cenospheres. It will be appreciated that as long as these films form swelling will probably continue since the rupture which might have appeared in the cell wall at that point is effectively sealed. A visual inspection of the semi-coke from the Kingshill coal (Fig.XVI) suggests that in this coal no such phenomen occurs, at least to this extent and that rupturing of the cell walls is quite frequent. Although little quantitative significance can be attached to this observation it will be useful when discussing the different behaviours of the two coals near the end of the "plastic" range.

PART VIII.

DISCUSSION OF RESULTS : SECTION II.

A cursory survey of the swelling behaviour of the Sacriston and Kingshill coals might suggest that little similarity of basic principles could be expected as the former coal swells less under higher pressures in contradiction to the latter. These discrepancies merely stress, however, the significance of permeability as a factor in the swelling mechanism.

The importance of this physical factor has been stressed directly by Mott and Hirst (27 & 53) and the results of workers such as Bangham, McKee and Pirani (66), Kramers, Pirani and Smith (67), Blayden, Gibson and Riley (11), on the behaviour of poorly swelling materials have stressed the effect of fast heating rates as a means of offsetting inherently high permeabilities, and thereby setting up the internal pressure so essential for swelling and coking. Consequently it would appear that the two main factors controlling the swelling of a "plastic" coal are:-

(i) The permeability of the material. Low permeability is the sine qua non of swelling, its magnitude in relation to (ii) below controlling the rate of swelling and the range over which it is effective controlling the degree of swelling.

(ii) The rate of generation of thermal decomposition products.

A simple interpretation of the swelling mechanism appeared possible on the basis of these two quantities and such an interpretation is formulated and tested in the subsequent paragraphs.

Theoretical Approach to Swelling Mechanism.

Once swelling of the "plastic" mass has started, under constant pressure conditions, the instantaneous rate of swelling may be expressed thus:-

$$dV/dt = R - Pd.S. \qquad (3)$$

where

(dV/dt) = Time rate of volume swelling (c.c. at N.T.P./min.)

(R) = Time rate of generation of volatile matter (c.c. at N.T.P./min.).

(Pd) = Pressure difference between the inside and the outside of the "plastic" mass (ATMS.); this is equivalent to (P_A-1) where (P_A) is the absolute pressure (ATMS.).

(S) = Specific Permeability of the mass (c.c. at N.T.P./ATMS./Min.).

Of these four factors (d^V/dt) and (Pd) can be measured experimentally, while (R) and (S) are unknown factors.

It is doubtful whether a reliable value of R could be determined directly because the tar vapours are not stable at the temperatures at which they are evolved. Alternatively (R) could be calculated from the rate of evolution of volatile matter on the weight basis if a value for the average molecular weight of the volatile matter were known. An estimate could be made from the molecular weight of some portions of high temperature coal tar, but any such value could be regarded only as a rough approximation.

However, values of (R) may be estimated indirectly from experimental measurements of (d^V/dt) and (Pd) as follows. The curves (Figs.XXVI & XXVIII) relating loss in weight of the coal to temperature are characterised by a relatively constant gradient over the temperature ranges when the coals are "plastic" suggesting that the rate of generation of volatile matter in grams per degree is constant over a fairly wide temperature range. If the assumption is made, that the molecular weight of the volatile matter does not alter appreciably over the swelling range, then it can be deduced that (R), in cubic centimetres per minute, is constant over the swelling range. This assumption is reasonable when the short temperature range over which swelling takes place is considered. Furthermore it can be expected that the permeability S will approach a constant value at higher pressures. This follows from the nature of the plastic coal. It is almost certain that permeability to gas is due to tiny holes or pores, probably located at "non-fusible" durain or fusain particles. As the pressure increases, these holes will be closed by the flow of plastic material from the surrounding vitrain particles. In this case the curve of $Pd/^{dV}/dt$ should become linear and have a negative slope and, of course, the value of R can be obtained by extrapolating back to $Pd = 0$.

Experimental Verification of the Determination of (R).

(i) Kingshill Coal: The curves from which the experimental values of $(^{dV}/dt)$ and (Pd) are taken are those of Fig.XIII; the gradients of these curves in cubic centimetres per degree, taken at a temperature of 390°C must be multiplied by 2.5 to convert them to centimetres per minute. These latter values are shown in column $(d^{v''}/dt)$ of Table XXVI and are corrected to N.T.P. in column (d^{v}/dt).

Table XXVI.

P_A (ATMS.)	Pd (P_A-1) (ATMS.)	Temp. (°C.)	$d^{v''}/dt$ (c.c./Min.)	d^{v}/dt (ccs. at N.T.P. /min.)
1.08	0.08	390	1.40	0.63
1.42	0.42	"	2.47	1.42
2.50	1.50	"	4.72	4.85
3.57	2.57	"	6.24	7.88
4.40	3.40	"	5.68	10.20
5.25	4.25	"	4.65	10.00

A plot of (d^{v}/dt) / (Pd) is shown in Fig.XXIX. The sharp rise in (d^{v}/dt) with rising (Pd) is at once apparent and the decided break in the curve at a value of (Pd) = 3.5 ATMS. likewise is notable. Thereafter it appears that the relationship between the two parameters assumes the conditions stipulated by equation (3) if (S) becomes constant, i.e., a linear relationship of negative gradient. The fact that this condition is reached at values of (Pd) near the limit of the apparatus prevented the extension of the relationship to higher values of (Pd), which might have established the relationship more exactly and would have made the subsequent extrapolation to (Pd) = 0 more justified and exact. Nevertheless the trend of results is in keeping with a constant value of (S) being attained at higher pressures and consequently it was deemed permissible to extrapolate the short

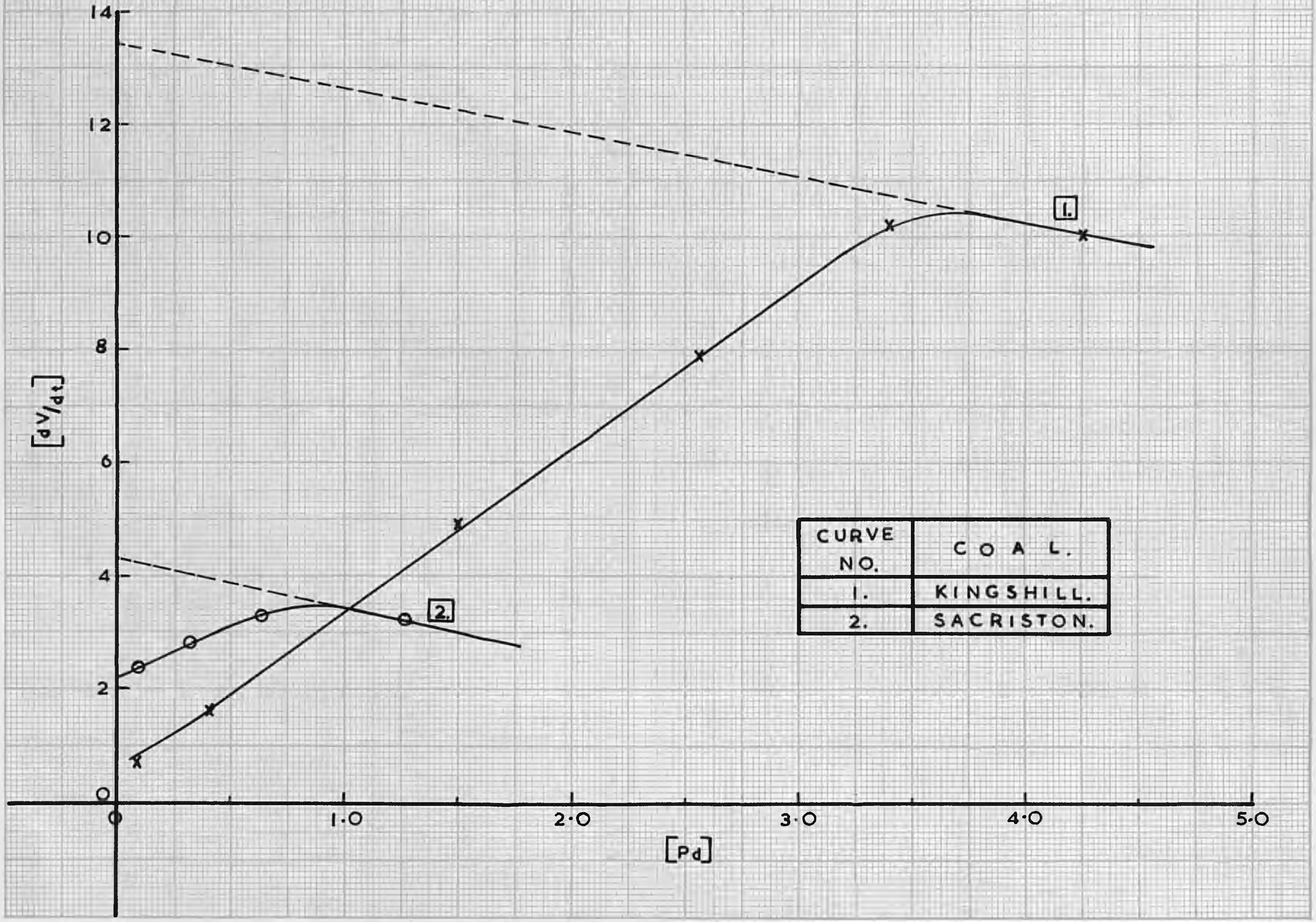

14
12
10
8
6
4
2
0
[dV/dt]
1·0
2·0
3·0
4·0
5·0
[Pd]
1.
2.
CURVE NO.
COAL.
1.
KINGSHILL.
2.
SACRISTON.

FIG. XXIX

linear portion to obtain a value for (R) at (Pd) = 0. The value for the rate of generation of volatile matter thus obtained is 13.4 c.c./minute; this value is for a 15 gms. sample.

It was considered that a check as to the validity of this figure could be obtained by correlating this value of (R) with the slope of the volatile matter - temperature curve (Fig.XXVIII), thereby determining a figure for the average molecular weight of the volatile matter evolved. If this value were of the correct order of magnitude this could be regarded as circumstantial evidence in support of the determined value of (R), and thus on the subsequent interpretation.

Thus (R) = 13.4 ccs. at N.T.P./min.; $d^{V.M.}/dt$ = 0.08 grams/min.

$\therefore$ Molecular Wt. = 133.

This value while possibly a little high is considered reasonable, taking into account the method of determination. Weiss and Downs (68) give a value of 116 as the average molecular weight of 43% of the contents of a coke oven tar; the remaining 57% comprising pitch, resins, etc., would undoubtedly be of higher molecular weight than 116. Furthermore, it is to be expected that the cracking undergone by the primary tar will yield a product with a relatively lower molecular weight so that primary tar may well have a value above 150 and if this is considered in conjunction with a molecular weight, for the gas phase, of 20, (69), the average molecular weight for the primary volatile material can not be much below 100, and may well be greater. Thus the value of (R) obtained by this indirect method appears to be reasonably accurate at least to a degree comparable to that obtainable by any alternative method; the method is now applied to the determination of (R) for the second coal.

(ii) Sacriston Coal.

The experimental results utilised are those contained in Fig.XVII. The decided "S" shaped nature of these curves has been referred to previously and this will be discussed more fully later; it was deemed advisable to take the gradients of these curves for use in the determination of (R) near the centre of each where conditions approximate to the linear nature of those corresponding curves of the Kingshill coal. These values, suitably corrected to a time basis and subsequently to N.T.P. are drawn up in Table XXVII.

Table XXVII.

P_A (ATMS.)	Pd (PA-1) (ATMS.)	Temp. (°C.)	$d^{V''}/dt$. (ccs./min.)	d^{V}/dt (ccs.as N.T.P./min)
1.08	0.08	418	5.61	2.35
1.32	0.32	419	5.39	2.80
1.64	0.64	423	5.11	3.28
2.27	1.27	419	3.51	3.15

The plot of (d^{V}/dt) / (Pd) is shown in Fig.XXIX. The trend of results is identical with that of the previous coal, the turning point being at a value of (Pd) = 0.8 Atms. The same downward trend of values of (dv/dt) at higher values of

(Pd) is to be observed and it is unfortunate that the entire pressure range could not be covered, for reasons referred to earlier, as some doubt still exists as to the exact form of this latter portion of the relationship where (S) apparently tends to reach a constant value. The enforced curtailment of this series of tests, by an electrical defect similar in nature to others which had hampered the progress of this research necessitates that the method for the determination of (R) by this indirect method, be regarded only as tentative; it follows naturally that any quantities deduced from values of (R) so determined, e.g., specific permeability, (S) can only be considered on a similar basis. Nevertheless the close similarity in trend of the (d^v/dt) / (Pd) relationships and the negative inclination of these at higher values of (Pd) is regarded as evidence in support of the general accuracy of the method for the determination of (R). The value of (R) obtained by extrapolation for the Sacriston coal is 4.3 c.c./minute, for a 7.5 grs. sample. When this value is correlated with the slope of the volatile-temperature curve (Fig.XXVI) a value for the average molecular weight of the volatile matter of 122 is obtained, in fair agreement with the value of 133 given by the Kingshill coal.

It may be finally concluded that the proposed method for the determination of (R) has been proved tentatively correct; final confirmation will be obtained when the relationship between (dv/dt) and (Pd) is shown to be accurately linear beyond the turning point in the relationship shown in Fig.XXIX.

Specific Permeability Values.

It is now proposed to apply the above determined values of (R) to calculate the specific permeabilities of the two coals, in order to study the effect of pressure, temperature, volume and coal rank on (S).

Table XXIX.

Pd (ATMS.)	d^{v}/dt (ccs. at N.T.P./Min.)	S (ccs. N.T.P./ Min/ATMS.)	"Corrected" S (Sc).
0.25	1.04	49.4	98.8
0.50	1.70	23.4	46.8
1.0	3.28	9.1	18.2
1.5	4.68	5.8	11.6
2.0	6.10	3.7	7.4
2.5	7.72	2.3	4.6
3.0	9.20	1.4	2.8
3.5	10.38	0.86	1.72
4.0	10.20	0.80	1.60
4.25	10.00	0.80	1.60

Table XXIX.

Pd (ATMS.)	d^{v}/dt (ccs. at NTP/Min.)	S (ccs.at NTP/Min./Atms.)
0.2	2.52	8.9
0.4	2.86	3.6
0.6	3.2	1.8
0.8	3.4	1.1
1.0	3.4	0.9
1.2	3.2	0.9
1.4	3.0	0.9
1.6	2.8	0.9

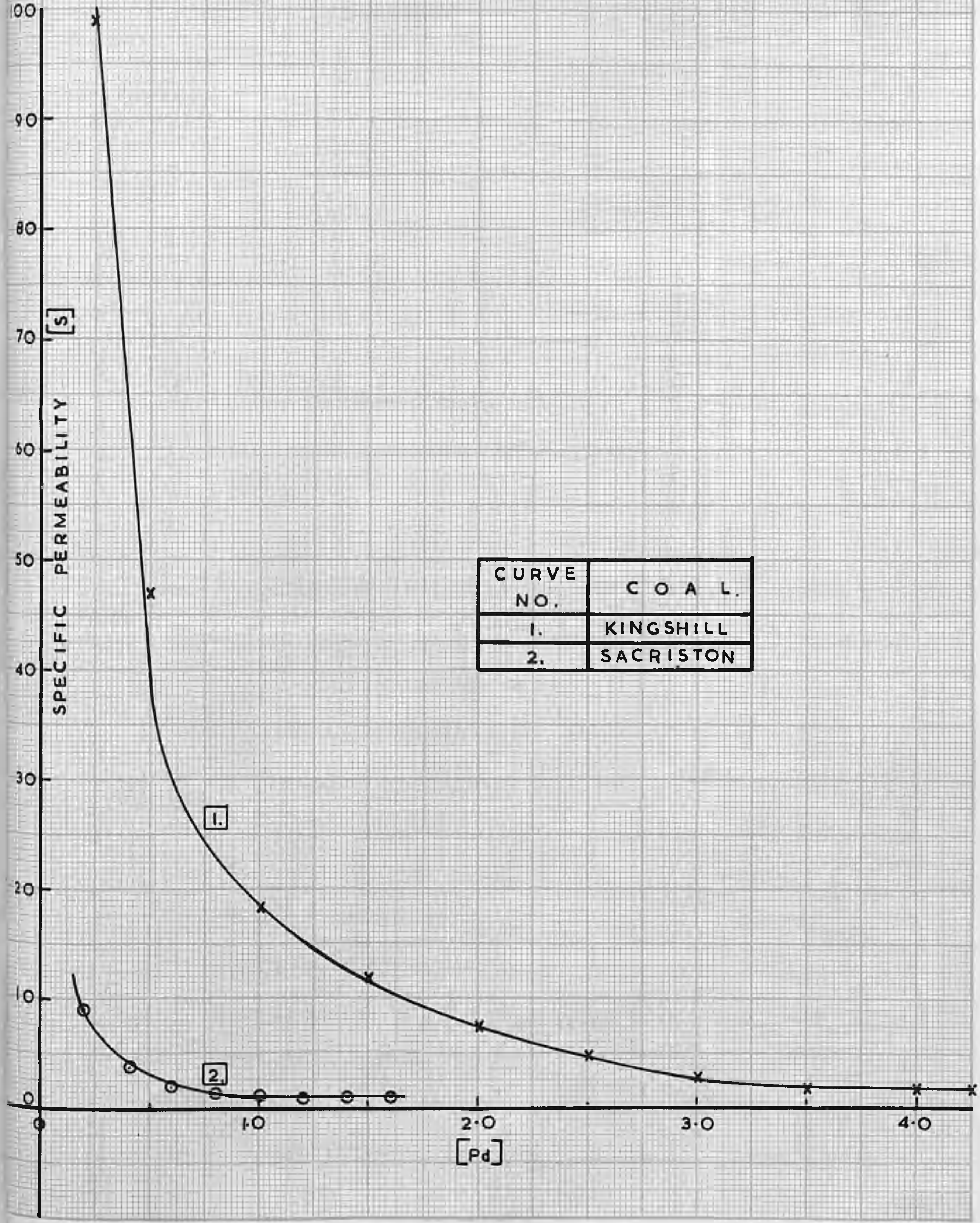
Thus

$$S = (R - d^{v}/dt) / Pd. \qquad (4)$$

Values of (S) calculated from equation (4) are shown in Tables XVIII & XXIX for the Kingshill and Sacriston coals, respectively. In order to make the values of (S) in the two coals strictly comparable it is necessary to correct the Kingshill values for the fact that the sample weight in this case was twice that of the Sacriston, so that the distance through which gas had to diffuse was twice in this case what it was with a sample half that size. This corrected value is listed in Table XXIX under the column (Sc). It should likewise be noted that (R) must be halved for the Kingshill coal, to make it strictly comparable to the value for the Sacriston coal.

Variation of Specific Permeability with Pressure.

A plot of specific permeability against (Pd) for the two coals is shown in Fig.XXX whence it can be seen that (S) for the Kingshill coal decreases continuously as the applied pressure is raised to 59 lb/sq.in. and that this drop occurs most rapidly in the range 1-11 lb/sq.in; the Sacriston coal has its (S) value initially much lower, less critically affected by pressure and attains a steady value when 11-12 lb/sq.in. pressure has been applied. Any discussion of such a variation of (S) with (Pd) must suggest why it should occur in the first place. Hirst (58) found that a pressure of three tons per square inch had very little effect on the internal surface of the "plastic" coal; it would appear that an explanation of the effect of such low pressure as 60 lb/sq.in., on the basis of reduced permeability



100
90
80
70
60
50
40
30
20
10
0
SPECIFIC PERMEABILITY [S]
0
1·0
2·0
3·0
4·0
[Pd]
1.
2.
CURVE NO.
COAL.
1. KINGSHILL
2. SACRISTON

FIG. XXX

of the actual "plastic" coal, due to compression, is quite out of the question. The most likely explanation is one which considers the petrographic inhomogeneity of the coal sample; this is supported by the fact, recorded previously that the anomalous effect of pressure in increasing swelling could be obtained using a synthetic mixture of durain and vitrain. It is relevant here to note that in the synthetic mixture (Test B.2) heated under pressure, some of the larger particles of durain were observed to have undergone "swelling" in that elongated pores were present as if the particle had been distended by high internal gas pressures. These latter pressures could easily be built up if the particles of durain are visualised surrounded by a highly impermeable "plastic" mass under considerable pressure. The final constant (S) value may only be attained once the durain particles have been effectively "dispersed" in the "plastic" coal, possibly by the former first distending and thereby permitting of a more thorough dispersion by the latter. The observed difference as to the magnitude of the effect of (Pd) on (S), in the case of the two coals, could be explained by the following two points:

(i) The mobility of the "plastic" Sacriston coal will, for reasons suggested by Hirst (59) and others, probably be higher than in the lower rank Kingshill coal, so that a given pressure would be more effective in dispersing a given amount of infusible material.

(ii) Differences in the amount and characteristics of the non-fusible materials. These factors are probably of equal importance; the size and distribution of the non-fusible materials will undoubtedly affect the pressure required to attain a final steady (S) value in conjunction with the ratio of fusible : non-fusible material. The nature of the non-fusible material may well be a further factor of importance since it is known that certain durains have limited swelling ability.

It is difficult to assess the relative significance of these several factors. It is considered that in the Sacriston coal mobility of the "plastic" mass is high, the amount of non-fusible material small and possibly finely distributed in contradistinction to the Kingshill coal where the amount and distribution of the non-fusible material are less favourable to swelling; the long steady drop of (S) with increase in (Pd) is consistent with the progressive dispersion of non-fusible material in the Kingshill coal.

The higher final value of (S) attained by the Kingshill coal, i.e., 1·6 as compared to 0·9 is regarded as significant. The steady value attained will be controlled presumably by the permeability of the coal actually "plastic", and, as indicated from the heat of wetting investigations (57) this is higher the lower the coal rank. The higher steady (S) value given by the Kingshill coal may also be a reflection of its initial higher content of non-fusible material.

Variation of Specific Permeability with Volume and Temperature.

(i) Kingshill Coal: Linear nature of the volume-temperature curves, (Fig.XIII) indicates that over the major portion of the swelling range (d^v/dt), and therefore (S), is constant; the variation of (d^v/dt) due to increased temperature from the lower to the upper end of the curves, is not significant. Only towards the end of the "plastic" range does the gradient decrease, indicating a rapid increase in (S). The independence of (S) with volume implies that the specific permeability of the whole sample is independent of the average cell wall thickness and is controlled simply by the total thickness of material to be traversed. It is perhaps not a little surprising to find (S) so relatively independent of temperature but the observed effect may only be the result of two opposing influences. Thus the decrease in viscosity with temperature of the "plastic" material may well be offset by an increase due to progressive pyrolysis and polymerisation, so that the net effect over the relatively short "plastic" range, i.e., 25-30°C is the one observed. At higher temperatures the latter tendencies predominate when boundary "lubricants" decompose faster and result in the observed increase in permeability. On the basis of the hypothesis as to the effect of pressure in reducing (S), it might be expected that a progressive decrease in (S) would take place under one pressure on continued application, i.e., a lower pressure applied for a longer time being as effective as a higher one for a shorter time in reducing the permeability; the limited time available under any one pressure would prevent such an effect being observed.

(ii) Sacriston Coal The curves of Fig.XVII are different from those of the Kingshill coal in being decidedly "S" shaped and the extent of this effect is seen on comparing the values of (S) at two different temperatures on any single curve, e.g.

Table XXX.

Curve No.	Temperature (°C).	(S)
2	400 419	9.9 5.0
3	410 418	3.6 1.8

In each case there is a pronounced decrease in (S) with increasing volume of swelling and temperature. If it is assumed that the effect of volume of swelling is similar, in this coal, to the Kingshill coal, i.e., that (S) is independent thereof, the entire effect is attributable to temperature. This temperature effect may arise from the two following sources, viz:-

(i) Reduction of (S) by a progressive dispersion of non-fusible material, facilitated by the low viscosity of the

"plastic" material and a relatively longer "plastic" stage.
(ii) The nature of the "plastic" coal may be such that in the early stages the viscosity of the mass is reduced by temperature rise, in a similar manner to that observed for coal tar and hydrocarbons (70), leading to a decrease in (S). It is also possible that effect (ii) may be complimentary to effect (i).

It is considered appropriate at this stage to discuss the possible influence of the crucible design on the shape of the volume-temperature curves and thus on the values of (S). Any effect arising from this source must be from a variation in the effective permeability of the asbestos discs throughout the test. It might be argued that the observed variations of permeability with temperature and pressure were due to, or largely masked by variations in the permeability of the asbestos paper which became progressively chocked with "plastic" coal. If this were indeed the case it is surely to be expected:-

(i) that the anomalous expansion of the Kingshill coal under higher pressure would in fact, have been obtained with the more highly fluid Sacriston coal.

(ii) that the "S" shaped nature of the swelling volume temperature curve, would have been found with the Kingshill coal, if it had been the result of progressive "chocking" of the asbestos paper.

Finally the fact that the "window" structure, referred to previously (Part VII) disappeared at approximately the temperature at which swelling of the Sacriston coal ceased, is taken as evidence in support of the observed variations in permeability being considered as true variations in the coal mass.

Further Observations on the Specific Permeability.

(i) It will be recalled that in Table XXI, Part V, the results of tests carried out on the Kingshill coal, under constant pressure conditions, and at heating rates which varied from 1·75°C/min. to 2·25°C/min. (average for a number of tests was 2·0°C/min. as quoted) were recorded. These results were analysed in a manner similar to that described above, and values of (S) were calculated. While little emphasis can be placed on these results due to the variation of heating rate in different tests, the trend of results suggested that (S) at any single value of applied pressure, was approximately independent of heating rate. This does not imply that the degree of swelling at lower heating rates, for a given applied pressure will be the same as that at higher values, for reasons given in the following paragraphs; the results of Table XXI indicate in fact that the degree of swelling is actually lower at lower heating rates, as is to be expected. It will be interesting if the above trend of results, i.e., that (S) is independent of heating rate is finally confirmed as it is in keeping with the hypothesis as to the cause of the constancy of (S) at higher applied pressures.

(ii) The fact has been mentioned previously that (S) for the Kingshill coal only attains its final steady minimum value when the applied pressures are of the same order of magnitude as the upper limit of applicable pressures, i.e., 62·5lb/sq.in. The difficulty of maintaining such pressures over the entire "plastic" range with the chance of leakage of "plastic" coal round the top alundum disc or of ruptures of the entire crucible, may be overcome as follows. A pressure of 62.5 lb/sq.in. may be applied at the start of the "plasticity" and maintained for a short time; this will have the effect of causing (S) to attain its minimum value. Thereafter the pressure may be reduced to a more convenient value and the minimum (S) may then be calculated in the usual manner from the function (d^V/dt) at this lower pressure; there is no reason to expect that (S), once it has attained its minimum value, will again increase when the applied pressure is reduced. Such a procedure would only be applicable to coals where (S) does actually drop to its minimum value under an applied pressure not greater than 62.5 lb/sq.in.

Pressure-Volume Curves of Sacriston & Kingshill Coals.

(i) Curves at Constant Pressure.

The relationship between the final swelling volume, in cubic centimetres at N.T.P. and the swelling pressure for the Kingshill Coal is shown in Fig. XV. The final swelling volume, under a given pressure, may be regarded as the time integral of equation (3) over the "plastic" range, provided certain modifications are applied. Thus

$$V_F = \int_{t_1}^{t_2} dV/dt = \Big[(R - Pd.S'')\,t\Big]_{t_1}^{t_2} \qquad (5)$$

In equation (5) (S'') is the average permeability over the entire swelling range, taking into account the "tail" at the end of the curves in Fig.XIII; the value of (S'') will vary, in approximately the same manner as (S) with increase in (Pd). Thus a slight rise in (Pd) will reduce (S'') considerably and (V_F) can be expected to rise sharply as shown in Fig.XV. At higher values of (Pd) the effect of the latter in decreasing (S'') becomes smaller and eventually ($Pd.S''$) formerly decreasing, now starts to increase and this is reflected in the flattening off of the curve at higher values of (Pd).

In the case of the Sacriston coal, the complete expansion pressure-swelling volume curve could not be completed, but the total expansion, in cubic centimetres at N.T.P. at the four steady pressures used, were as follows:-

Table XXXI.

Swelling Pressure (ATMS.)	Maxm.Swelling Volume. (c.c.at N.T.P.)	Swelling Pressure (ATMS.)	Maxm.Swelling Volume. (c.c.at N.T.P.).
1.08	40.5	1.64	41.7
1.32	39.0	2.27	42.0

Thus there is a very slight increase in the swelling volume as (Pd) is raised but the effect is not so marked as for the Kingshill coal. It is worthy of comment that the distinct

"S" shaped nature of the four curves in Fig.XVII means that the average permeability (S'') for use in equation (5), is considerably higher than the minimum value for any given value of (Pd). Furthermore the fact that the "S" shaped nature is more pronounced at lower values of (Pd) means that the average permeabilities for the four curves are very nearly the same; hence the values of (V_F) obtained in the four cases above are not widely different.

(ii) Pressure-Volume Relationship at Constant Volume.

This relationship, determined for the Sacriston coal only, is shown in Fig.XII. The swelling volumes plotted in this latter graph can, for the purpose of analysis, be separated into two fractions, i.e.,

$$V_F = Vo + V_1 \qquad (6)$$

where V_F = Total swelling volume (c.c. at N.T.P.)

Vo = Swelling volume prior to the application of pressure (c.c. at N.T.P.). This quantity is synonymous with the volume of volatile matter entrapped in the "plastic" coal prior to the application of pressure.

V_1 = Volume of volatile matter entrapped between the time of application of pressure and the end of swelling, i.e., till the maximum in the swelling pressure-temperature curve (c.c. at N.T.P.).

(Vo) and (V_1) may be expressed on a basis similar to (V_F) of equation (5), viz:-

$$Vo = (R - Pd_o.S_o)\ t_o \quad (7) \qquad V_1 = (R - Pd_1S_1)\ t_1 \quad (8)$$

where

R = Time rate of generation of volatile matter (c.c. at N.T.P./Min.)

Pd_0 = Pressure difference applied to the sample during the early swelling stage (ATMS.). This is constant at 0.09 Atms.

Pd_1 = The average pressure difference applied during the time of application of pressure. (Atms).

S_0 = Specific Permeability during the early swelling stage (c.c. at N.T.P./Min/ATMS.)

S_1 = The average Specific Permeability during the time of application of pressure (c.c. at N.T.P./Min./Atms.).

t_0 = The time range of early swelling (Min.).

t_1 = The time range during which pressure is increasing to its maximum value (Min.).

The factor (Vo) is related directly to (t_0) increasing as the latter increases, i.e., as the "constant volume" at which the application of pressure is started increases; it must be recalled, however, that any value of (S_0) calculated therefrom is an average value only due to the effect of temperature on the specific permeability of this coal. The main difficulty either in predicting the variation of (V_F) with maximum swelling pressure or in deducing any value of (R) or (S) therefrom, is encountered when the quantity (V_1) is considered. Thus for any single test carried out at constant volume, (R) and (t_1) will be constant. Difficulty will be encountered in obtaining an accurate value for (Pd_1) since this is the average pressure difference applied; the variation of pressure with time has been shown previously (Fig.X) from which it can be seen that taking (Pd_1) as half the maximum swelling pressure is only approximately correct. The main difficulty is encountered, however, when (S_1) is considered. Thus, as the tests at constant pressure indicated, (S) varies not only with pressure but also with temperature for this coal, so that any value of (S_1) deduced from (V_1) could only be regarded as an average of all these several effects and consequently of little value. The trend of (V_F), increasing with increase in the maximum swelling pressure undoubtedly reflects (i) the decrease in the quantity $(Pd_o.S_o.t_o.)$ as (t_o) decreases, i.e., as the constant swelling "volume" decreases, and (ii) the tendency for $(Pd_1.S_1.t_1)$ to decrease in the earlier stages due to the effect of pressure reducing the specific permeability (S_1). Investigation indicated that in the later stages of Fig. XII, the effect of (i) masked the tendency for $(Pd_1.S_1.t_1.)$ to increase once (S_1) had attained a more stable value while (Pd_1) and (t_1) were increasing continuously.

It is possible to calculate instantaneous values of specific permeability, (S), from the pressure-temperature curves of Fig.X, replacing the quantity (v) of equation (3) by a factor $(^k/P)$ where (P) is the applied pressure in atmospheres. The values of (S) were actually calculated in this manner and were found to be slightly higher than the values listed in Table XXIX ; this no doubt reflects the presence of the inert silica sand in these earlier tests. The values of (S) so deduced were considered to be liable to error due to the difficulty of obtaining accurate values of (dP/dt) from the curves of Fig.X, which are measured over a relatively short temperature range. The values of (S) deduced from tests at constant pressure are considered more accurate.

In conclusion it may be stated that little useful quantitative information can be obtained from the tests run at "constant volume" conditions, due to the approximations which have to be made and to the average values of any quantities deduced therefrom. The final relationship between the swelling volume and the maximum swelling pressure appears to be of an unduly complex nature and precludes the further application of this type of test.

Length of the "plastic" Zone : "Residual" Plasticity.

Attention has been focussed mainly on the specific permeability of the "plastic" material, and on the variation of that quantity with temperature and pressure. Another point worthy of note is the range of temperature over which this factor is operative, i.e., the length of the "plastic" zone. This is decidedly different in the case of the two coals tested, i.e., 60°C for the Sacriston and 30°C for the Kingshill coal. Such a difference implies either that the former coal has an excess of "lubricating" material or alternatively that what it has is stable as such to higher temperatures, than is the case with the Kingshill coal. The latter view is considered the more probable and is confirmed, to some extent, by the observations made regarding the persistence of the "window" structure (Part VII) to high temperatures. Other factors may well be of indirect importance in affecting the length of the "plastic" range. The inherently lower permeability of the Sacriston coal ensures that loss of these "lubricating" agents is restricted and the effect of reduced permeability in lengthening the "plastic" range is to be seen in the results of the Kingshill coal which had a longer "plastic" range at higher pressures. The oxygen content is a further factor affecting the stability and effectiveness of these lubricating agents; higher oxygen low rank coals may suffer from these agents becoming chemically bound, by oxygen to the stable cross-linked non "plastic" micelle phase, at temperatures below that at which they would normally decompose, thereby reducing the effective "plastic" range.

The difference in the behaviour of the two coals at the end of the "plastic" range has been referred to and this difference is considered significant; the fact that high rank coals retain a certain "residual" "plasticity" has previously been demonstrated by Mott (27). It would appear that an essentially rigid and possibly cross-linked structure , is formed near the end of the "plastic" stage in lower rank coals possibly as a result of the incorporation of the "lubricating" agents into the non "plastic" material in a manner described above. Higher rank coals would appear to pass through a transition stage in which a certain amount of "lubricant" still remains but not in sufficient quantity to prevent the ready egress of volatile matter; such a behaviour is consistent with the view that in these higher rank coals the end of "plasticity" is caused by the gradual decomposition or volatilisation of certain molecular constituents over an appreciable temperature range. This difference in the behaviour may be of importance when considering the fissuring behaviour of cokes. If in fact, as suggested by Davis and McCartney (33), the after contraction of all semi-cokes are approximately constant, the observed differences in fissuring behaviour must be due to some such effect. If the semi-coke has a small "residual" "plasticity" at higher temperatures it may be capable of resisting the initial forces causing fissuring to a better degree; this may be especially the case in the layer adjacent to the oven wall which layer is being heated rapidly and in which the main longitudinal fissures appear to have their origin.

"Absolute" Swelling Pressures.

By "absolute" swelling pressure is meant the pressure required to confine the initial bulk sample to its original volume; the only swelling occurring is to the extent of the voidage of the aggregate. The order of magnitude of this pressure can be obtained from equation (5), viz.,

$$V_F = \int_{t_1}^{t_2} \mathrm{d}V/\mathrm{d}t = \Big[(R - Pd\, S'')\, t \Big]_{t_1}^{t_2} \qquad (5)$$

by suitable substitution. The "absolute" swelling pressures calculated in this way were as follows:-

Table XXXII.

Coal	Sample Weight (Grs.)	"Absolute" Swelling Pressure. (Lb./sq.in. Absol.)
Kingshill	7.5	231
Kingshill	15.0	74
Sacriston	7.5	83

These values are undoubtedly high as the value of (S) taken was the minimum value attained and not an average value over the entire range. The pronounced variation of this pressure with sample size is notable and this point tends to emphasise the fact that the "absolute" swelling pressure is dependent largely on such experimental factors as sample size, crucible design, etc.; any figures quoted can be discussed only in relation to the particular experimental set up in which they were determined. Thus the higher values quoted by Mott, (27), are due to the nature of the particular crucible which he used; "absolute" swelling pressures, of the same order of magnitude as those measured by him were calculated by appropriate correction of specific permeability figures (determined in this research) for the crucible dimensions which he utilised. Thus the advantage of such measurements of specific permeability over ones of "absolute" swelling pressure is obvious.

CONCLUSION.

The significant features of the foregoing research are:-

(i) The representation of the swelling process in terms of two fundamental properties of the "plastic" state, namely the specific permeability (S) and the time rate of generation of volatile matter (R).

(ii) The ability of the experimental technique to estimate the latter two properties with reasonable accuracy.

Such a simple and fundamental analysis of the swelling process is desirable and it will undoubtedly facilitate the explanation of the coking behaviour of different coals when applied to a representative range of coals. Thus the more complex quantities of swelling pressure at constant volume, or swelling volume at constant pressure, suffer from the defect that they are functions of the experimental conditions. In this respect it has been indicated that the properties of specific permeability and time rate of volatile matter generation may be applied to a given set of conditions for the determination of any required swelling pressure-swelling volume relationship.

It is fully appreciated that the analysis, as it stands at present, can be considered as only tentative, regarding the method of derivation of (R), the time rate of generation of volatile matter. The linear relationship of

(Pd) to (d^v/dt), required for complete justification of the method, was not conclusively obtained for either of the coals tested. In the case of the Kingshill coal, where the (Pd) - (d^v/dt) relation only attained the requisite linear form at values of (Pd) near the limit of the apparatus, time did not permit of the modification of the latter to accommodate higher values of (Pd), and there was no indication, at the start of the investigation, that pressures greater than 62.5 lb./sq.in. would be required. The analysis will be finally confirmed when the (Pd) - (d^v/dt) relationship is proved to be linear and of negative gradient, over a representative range of (Pd) values.

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SUMMARY.

(i) The significance of the "plastic" state, in relation to the properties of blast furnace coke, is discussed and the importance of swelling pressure is emphasised.

(ii) The aims of the investigation are drawn up. They include the development of a method, using di-electric heating, for the measurement of the swelling pressure of "plastic" coals and the study of the variation of this property with coal rank, etc.

(iii) Previous methods of measuring swelling pressure are reviewed and their sources of error indicated.

(iv) The theory of di-electric heating is described and the possibility of this technique giving uniform volume heating, in a coal sample is put forward.

(v) The experimental apparatus is described.

(vi) A detailed account of the development work entailed in the application of this novel technique is given. The most striking point arising from the development work is the critical effect of small amounts of oxygen in reducing the swelling properties of a coal.

(vii) The finally adopted experimental method is described. The results are presented in the following four sections, viz:-

- (a) Swelling Pressure - Swelling Volume relationship for a Durham (Sacriston) coal by a "constant volume" method.
- (b) Swelling Pressure - Swelling Volume relationship for a Scottish (Kingshill) coal by a "constant pressure" method.
- (c) Swelling Pressure - Swelling Volume relationship for the Durham coal by a "constant pressure" method.
- (d) An investigation of swelling mechanism.

(viii) Recent work on the physico-chemical nature of coal and carbonised coal is reviewed in so far as it is relevant to the investigation.

(ix) The results of (d) paragraph (vii), are discussed and compared with previous similar investigations.

(x) The swelling pressure-swelling volume relationships obtained by the "constant pressure" method, are analysed. Specific permeability figures are deduced therefrom and the variation of these with pressure, temperature and volume, for the two coals tested, is discussed. An analysis of the swelling pressure-swelling volume relationship, obtained by the "constant volume" method, indicated that little useful information could be deduced from this complex relationship.

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