155. *The Solid Product of Carbonisation.*

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Properties capable of numerical evaluation of the solid product of carbonisation (coke) from a variety of materials have been studied. True specific gravity reached approximately 1·4 at 500° and 1·8 at 800°, with very slight further change to 1200°. The absence of progress to 2·25, the specific gravity of graphite, is attributed to gas (which escapes very slowly) between the layers of graphitic crystallites. The identity of substance indicated by that of specific gravity (1·85) is obscured by the varying formation of superficial graphitic films. Oxygen remaining in the substance carbonised is held responsible for the subsequent gasification from 500° upwards of nuclear carbon (see J., 1942, 252), and for the formation of an intimately pervasive micro-capillary system indicated by absorption of carbon dioxide. The terminations of these capillaries at a surface increase its rate of gasification and the reactivity of the coke. Hence, there is a causal connection between oxygen content of the material carbonised, micro-porosity or adsorption of carbon dioxide by a coke and its reactivity, and these often lie in the same order, but not necessarily so, as explained. Increasing the surface of a coke by carbonising it with admixed inert material increased reactivity but not adsorption. The micro-capillarity developed in carbonisation reached a maximum at 800—1000° and then diminished. The influence of soda and equimolecular quantities of other inorganic materials in increasing reactivity was compared and discussed.

In a typical example of that gradual progress of a carbon compound towards carbon under the influence of rising temperature known as carbonisation, there is at each temperature stage a loss of volatile matter (gaseous or liquid), and an adjustment of internal molecular structure, leaving a solid product. The liquid products are of great variety according to the material carbonised, and their expulsion is complete at about 600°. The primary gaseous products have already been examined (*loc. cit.*) and the study of the solid product is now reported.

Specific Gravity.—One change in the solid product, or coke, as the temperature rises, is in specific gravity, and Table I displays results obtained for some substances differing in constitution and behaviour on carbonisation. The method of determination was the same in each case (Greenwood and Cobb, *J. Soc. Chem. Ind.*, **1922**, **41**, 181), materials low in ash being chosen to minimise its effects on specific gravity. The description of coals is that of Seyler's classification. [In a rapid laboratory carbonisation to 800° of filter-paper and cotton-wool (both infusible) and cane-sugar (easily fusible), the specific gravities of the residues were rather lower than were obtained in the much slower carbonisations reported above, but were practically identical (*viz.*, **1·61**, **1·62**, 1·65 respectively).]

TABLE I.

Changes in specific gravity.

A. Cellulose (filter-paper), infusible (ash, $<0{\cdot}01\%$); prolonged fractional carbonisation in a vacuum: 24 hrs. at specified temperature.
B. Welsh ortho-anthracite, Stanllyd, infusible (ash, 0·92%)
C. Welsh meta-bituminous coal, Black Vein, fusible (ash, 1·84%)
D. Notts. para-bituminous coal, New Hucknall, less fusible (ash, 3·77%)
(B–D) carbonised by raising temperature at 5°/min., and 3 hrs. at specified temperature.

Specific gravity of cokes prepared at various temperatures.

	15°.	200°.	300°.	400°.	500°.	600°.	700°.	800°.	850°.	900°.	1000°.	1100°.	1200°.
A	1·60	1·61	1·41	1·38	1·42	1·59	1·70	1·82	—	1·82	1·86	1·86	1·85
B	1·44	—	—	1·45	1·45	1·49	1·63	1·76	1·80	1·83	1·71	1·70	—
C	1·29	1·29	1·30	1·34	1·40	1·50	1·64	1·77	1·80	1·85	1·86	1·87	—
D	1·27	—	—	—	1·59 *	—	—	—	1·87	—	—	—	1·88

* At 550°.

Anderson (*ibid.*, 1896, **15**, 20) found for various by-product cokes *d* 1·83, 1·85, and 1·88. Drakeley and Wilkins (*ibid.*, 1931, **50**, 333), after stamping a finely powdered typical Durham gas-coal at 10 tons/sq. in. and carbonising it at various temperatures until gas evolution had ceased, obtained cokes of *d* 1·49, 1·91, 1·94, 1·92, and 1·94 at 450°, 800°, 960°, 1000°, and 1100°, respectively, but, the ash content of the cokes being approximately 12%, the specific gravity of the ashless coke would be rather lower; *e.g.*, if a coke of *d* 1·91 contained 10% of ash of *d* 2·5 (which may well be exceeded by a ferruginous ash), the ashless coke would have the same specific gravity (1·85) as the mean of the values reported for cellulose and other cokes from 800° upwards in Table I. Smith and Howard (*Ind. Eng. Chem.*, 1942, **34**, 438) found an average value for American commercial high-temperature cokes as determined in water to be 1·9, while 525° coke gave 1·47, 700° coke 1·85, and 1000° coke 1·92. Here again necessary allowance for ash would lower the figures.

In examining the course followed by the specific gravity of the carbonised materials, as determined in our laboratory (Table I) (and consistent with results quoted from other sources), three stages are noticeable which are connected with the changes discussed by Bolton, Cullingworth, Ghosh, and Cobb (J., 1942, 252): (1) Up to 500° the alterations in specific gravity varied with the material carbonised, as did also the gaseous and liquid products, until a common *d* value of approx. 1·4 was attained at 500°. (2) From 500° up to 800°, the specific gravity rose steadily for each material to a common value near 1·8. The primary gaseous products in this stage were first methane, then hydrogen and (from oxygenated substances) carbon monoxide, and the chemical mechanism suggested was for each gas one of condensation of the type $R_1H + CH_3R_2 \longrightarrow R_1R_2 + CH_4$, where R_1 and R_2 were the newly formed, or in some cases pre-existent, benzenoid groups. (3) From 800° up to 1200°, the limit of our work (and approximately of industrial carbonisation), no further increase in specific gravity beyond 1·85 was established. Occasionally, there was a slight diminution, as found for anthracite, presumably due to the formation of closed micro-pores or fine micro-capillaries not penetrated by water in the specific-gravity determination. There was no appreciable progress towards 2·25, the density of crystalline macro-graphite. This stage of a practically constant specific gravity of 1·85 was marked by continuing emission of hydrogen and carbon monoxide.

Dr. W. T. Astbury's *X*-ray examination had shown that in the carbonised cellulose residues the two most characteristic rings as given by graphite, denoting the formation of hexagonal networks of carbon atoms in the parallel sheets of graphitic crystallites, appeared at 500°. This followed on an earlier general diffuseness which indicated a breakdown of the original structure, and some diffuseness in the rings themselves, arising from small or imperfect crystals, persisted even at 1200°.

The rapid molecular condensation in the solid, with its accompanying free escape of gas, from 500° up to 800° had been marked by pronounced increase in specific gravity. The distinguishing feature of gas emission in the stage from 800° to 1200° was its long, slow continuation over many days even under vacuum. Completion of emission at these temperatures was indeed not secured, as noted when dealing specially with the primary gaseous products. This gas, so difficult to expel, was presumably held between the sheets of the crystallites, and would prohibit that approach of the sheets to one another necessary for increase of specific gravity. The fixation of interplanar hydrogen and its effects have been investigated by H. L. Riley. It is significant that only after this 800—1200° stage does the growth of crystallites in the direction at right angles to the hexagonal-patterned planes, commence (Blayden, Riley, and Taylor, *J. Amer. Chem. Soc.*, 1940, **62**, 180). The important point for our immediate purpose is the failure of the specific gravity to exceed 1·85 even at 1200° : a much higher temperature seems to be necessary for complete graphitisation, and the corresponding specific gravity of 2·25.

Surface Film.—Account must, however, be taken of the condition of the surface film as distinct from the whole carbonised substance, and in order to do this we must consider the equilibrium $CO_2 + C \rightleftarrows 2CO$ when carbon dioxide is circulated over the surface. It has been shown (Dent and Cobb, J., 1929, 1903) that at 800° this equilibrium is conditioned by the nature and heat treatment of the " carbon " surface. The following results are relevant : (i) With coco-nut charcoal, formed without fusion, the equilibrium mixture obtained after prolonged circulation of carbon dioxide at 800° contained 9·15% of this gas when the charcoal had been previously heated for 22 hours at 900° in a vacuum, 10·7% when heated for 50 hours at 900°, and 12·10% after 48 hours' heating at 1010°. (ii) With coke from Sharlston Wallsend (Haigh Moor) coal formed with fusion (which would facilitate molecular rearrangement in a more stable form at an early stage, lending itself to graphitisation on the surface where interplanar hydrogen cannot be effective at a higher temperature), the equilibrium at 800° after 50 hours' previous heating at 900° was at 13·8% of carbon dioxide, and the same value was given by Ceylon graphite. (iii) When the graphitised surface film had been removed by slight gasification, the interior mass gave a lower equilibrium content of carbon dioxide and a higher velocity of gasification in a stream of the gas, corresponding with its structure.

The essential identity of the molecular structure formed from different substances throughout the range 800—1200° may therefore be obscured by differences in the surface films (although these are too thin appreciably to affect the specific gravity), and all the more so because the surface film usually displays its properties from the first in any reaction studied. As soon, however, as we leave the fundamental property of specific gravity, the various carbonised products display their differences in such measurable properties as porosity, powder density, surface, adsorptive power, and reactivity. These properties, *e.g.*, in the region 800—1200°, where specific gravity shows so little change, vary widely.

Percentage Porosity.—This property gives some indication of surface, although indirectly and imperfectly, since the numerical value obtained is different according to the method of determination. A porosity due to micro-capillaries can be calculated from the results of two specific-gravity determinations—one made by using water (or helium), and the other mercury, a liquid which does not penetrate micro-capillaries below some 6 μ in diameter at N.T.P. (Smith and Howard, *loc. cit.*). The results obtained by this method (Table II) show the comparative behaviour of the anthracite and meta-bituminous coals (B and C) of Table I in the same carbonisation as provided samples for the determinations there reported (Lane, Thesis, Leeds, 1934).

TABLE II.

	Micro-porosity after carbonisation at various temperatures, %.*									
Coal (see Table I).	15°.	400°.	500°.	600°.	700°.	800°.	850°.	900°.	1000°.	1100°.
B	3·03	4·8	4·7	5·1	7·4	9·8	11·9	9·9	3·1	1·0
C	1·00	5·8	14·7	17·9	18·8	20·8	20·6	18·6	17·3	14·9

* Porosity % = $100(d_{H_2O} - d_{Hg})/d_{H_2O}$.

It will be noted that the fusible coal increased greatly in micro-porosity between 400° and 500°, and that both coals reached a maximum porosity at 800—850°, and then showed a decline.

A method of dealing with a grosser pore system consists in dipping a lump of coke in molten paraffin-wax, allowing it to drain, and then weighing it in air and in water. By this method applied to three coals, each carbonised at a series of temperatures ranging from 500° to 800°, substantially the same result was obtained throughout, *viz.*, a porosity of about 55% (" The Solid Products of Carbonisation of Coal," South Met. Gas Co., 1934, p. 36).

Powder Density.—This property is useful in marking, *e.g.*, the much greater bulkiness and surface area of paper coke than of sugar coke, although these have the same specific gravity. The adsorption of a unimolecular layer of methylene-blue from solution is sometimes used as a measure of surface, it being assumed that 1 mg. of the dye corresponds to 1 sq. m. of surface (see Table III and cf. Paneth and Radu, *Ber.*, 1924, **57**, 1221).

Adsorptive Power for Carbon Dioxide.—This is one of the properties capable of numerical expression which has best repaid study : in Table IV is arranged a series of substances in order of descending oxygen content, and in other columns the adsorption values for carbon dioxide at 20° and reactivities to this gas of their cokes at 900°. A wide range of materials was examined including cokes prepared from pure substances of known constitution rich in oxygen and of very low ash content, as well as from coals of the principal types, petroleum coke, retort carbon, graphite, etc. The adsorption as estimated was a reversible secondary adsorption at 20° in c.c. of the gas (calculated to 20° and 760 mm.) per g. of powdered carbonised residue. Its magnitude will be determined by the extent of the micro-capillary system existing in the residue tested, and also by the nature of the surface. In making the estimation, not only is the total adsorption, V, determined, but also that during the first ½ hour; the latter, being expressed as a percentage, R, of the total adsorption, gives some measure of the rate of adsorption : R may diminish without appreciable alteration in V if surface graphitisation lessens ease of access of the gas to the interior of particles otherwise unchanged. This type of adsorption in micro-capillaries is confined to pores of diameter less than 12 μ (Harkins and Ewing, *J. Amer. Chem. Soc.*, 1921, **43**, 1787).

Oxygen Content and Adsorption.—Attention may be directed first to the highly contrasted adsorption (in c.c./g.) and rate of adsorption in various gases of some cokes from materials, four of very high, and two of low, oxygen content. The high values with carbon dioxide, as compared with hydrogen and oxygen, are presumably obtained because the determinations are made below the critical temperature of the dioxide (31°). This is emphasised by the still higher results with sulphur dioxide, which has an even higher critical temperature (157°). Carbon dioxide was used throughout in our survey.

TABLE III.

Oxygen content and adsorption of gases.

Material.	O_2, %, in material.	Material.	O_2, %, in material.
A. Cellulose (filter-paper)	49·4	D. Starch	—
B. Cellulose (cotton-wool)	49·4	E. Black Vein coal	3·7
C. Sugar	51·5	F. Petroleum coke	$<1·0$

	Adsorption by cokes, c.c./g.								Surface, m.^{2}/g., by M-B.	Powder density of cokes, g./c.c.	Sp. gr. of cokes.
	CO_2.		SO_2.		H_2.		O_2.				
	V.	*R.*	*V.*	*R.*	*V.*	*R.*	*V.*	*R.*			
A	45·5	100	89·0	94	1·5	75	8·3	100	6·0	0·15	1·61
B	45·0	100	85·0	98	6·9	trace	8·5	100	14·0	0·07	1·62
C	47·0	100	86·6	96	4·0	17	7·4	100	0·7	0·40	1·65
D	46·5	97	—	—	—	—	—	—	0·6	—	—
E	5·2	22	—	—	—	—	—	—	—	—	—
F	8·7	31	—	—	—	—	—	—	—	—	—

Most significant is the practical identity of adsorption given by the cokes from paper, cotton-wool, sugar, and starch, although the last two substances fused early in carbonisation, whereas the first two gave no sign of fusion at any stage and displayed the greater bulkiness and surface indicated by low powder density and high adsorption of methylene-blue. This high and identical adsorption seems to mark the formation of remarkably similar micro-capillary systems from these substances rich in oxygen. The contrasted low adsorption of Black Vein and petroleum cokes suggests that oxygen is a necessary agent in the formation of any developed micro-capillary system. The practical identity of adsorption of the cokes from paper (45·5), cotton-wool (45·0), sugar (47·0), and starch (46·5), prepared by very rapid (20 mins.) carbonisation at 800°, was confirmed by the values obtained on much slower carbonisation (3½ hours), *viz.*, 56·0, 57·0, and 58·0 for the first three respectively (see Table IV).

The formation of so similar a micro-capillary system from these fusible and infusible substances rich in oxygen would suggest that it was brought into being after a point in carbonisation had been reached at which the state of the relevant units of each substance was so far the same that subsequent treatment had the same effect. This implies that in the fusible substances the micro-capillary structure came into being after the stage of fusion had been completed with the formation of such a solid residue as was also forthcoming from the infusible substances. It is plain that, although in some other respects the solid residues from the fusible and the infusible substances might then be quite different, yet they were the same for the development of micro-capillarity. As to how this marked development was effected, a clue is provided by the fact that it occurred only in substances rich in oxygen, being present to the same extent in the cokes from paper, cotton-wool, and sugar, to nearly the same extent in cokes from oxygen-rich coals (see Table IV), but to a diminishing degree in those from materials poorer in oxygen, such as anthracite, and hardly at all in such hydrocarbon residues as petroleum coke, pitch, and retort carbon. The mode of action of the oxygen, if it is responsible for the micro-capillary structure, needs explanation. Some of the original oxygen is not effective, but is expelled in various combinations quite early. There is, however, as already indicated (J., 1942, 252), a second stage in carbonisation, from 500° upwards, marked by the evolution of oxygen in combination with carbon (mainly as the monoxide). This removal of carbon may well be responsible for the micro-porosity. The mechanism there suggested was a condensation such as $R_1{\cdot}OH + R_2H \longrightarrow R_1R_2 + H_2O$, followed by the attack of the steam so generated on carbon. It was also suggested that the carbon surviving to this stage of carbonisation was mainly nuclear aromatic carbon, so that the action of oxygen by such a mechanism would be of an intimately pervasive character affecting atomic configurations. If this view is correct, the micro-capillary structure is developed by the action of that part of the oxygen in the substance carbonised which remains in the solid carbonised residue when the first stage of carbonisation is complete, and it acts by the removal of nuclear carbon, mainly as monoxide. [Work carried out at Leeds by F. J. Dent and others for the Joint Research Committee (43rd Report, *Trans. Inst. Gas Eng.*, 1938—9) has shown that, in hydrogenation under 50 atm., nuclear carbon may be gasified readily as methane by hydrogen, in which special case a micro-capillary system could be formed without the intervention of oxygen. Under normal carbonisation conditions, however, this only occurs to a slight extent, so oxygen remains as determining in effect the gasification of nuclear carbon.]

As an illustration, attention was directed (J., 1942, 252) to a difference in behaviour between two coals, New Hucknall and Sharlston Wallsend, subjected to fractional carbonisation. They differed somewhat in oxygen content but quite disproportionately so in the emission of oxides of carbon, the latter coal giving only about a fifth as much as the former, the low-temperature emission being small from both. " A difference in

[redacted]

whereas bakelite, containing 16% of oxygen, gave 154·3 c.c. (147·2 c.c. of which were monoxide) in the same temperature range (with a negligible volume below it); consequently, the reactivity to carbon dioxide at 900° of the carbonised product was low (0·14) for petroleum coke and high (3·0) for bakelite.

Total Surface.—Although oxygen, through the capillary system it induces, becomes the basis of reactivity, it is nevertheless the whole surface over which the gas flows which is directly and immediately responsible, and whatever increases this effective surface per g. of material under test increases reactivity. For instance, paper coke and sugar coke have the same high absorption for carbon dioxide, but although the latter, fused in formation, has a high reactivity (0·6) compared with anthracite coke (0·25) formed from material of low oxygen content, yet its reactivity compared with that of paper coke (2·7), formed without fusion, is low, presumably on account of the much smaller surface bounding its micro-capillary system. If, by any means, this surface were increased, a corresponding increase in reactivity would be expected. Experiments were, therefore, made in which a series of cokes was prepared from sugar alone and from sugar mixed with purified alundum to give a gradually increasing surface of deposition for the sugar-carbon produced on carbonisation; 30 g. of each blend were used for a test of reactivity, the exact amount of the carbon present being determined by ignition. As the ratio of alundum to sugar rose from 1 : 2 to 10 : 1, the corresponding specific reactivity of the contained carbon rose steadily from 0·92 to 2·02 (that of the sugar carbon alone being 0·64) and the surface (by methylene-blue) from 3 to 20 sq. m. per g. of carbon.

Similar increases in specific reactivity were obtained when glycine coke was increased in surface by blending with alundum or kaolin before coking. The carbon dioxide adsorption of the blended cokes made from sugar and diluent alundum (or silica, kaolin, or diatomaceous earth) was also determined. Here, no increase was noted, the carbon dioxide adsorption per g. of sugar coke in the mixture being always substantially the same as that of sugar coke itself. It was plain that the carbon micro-capillary system adsorbed the gas to the same extent, whether massed in sugar coke or dispersed on extended surface in a blend, but the micro-capillaries in the blend terminated on a much wider expanse of surface, leading to increased gasification and reactivity. On this view, a surface will always have some effect, but this is greatly increased when the surface is formed by terminating capillaries. (The inorganic diluents tested separately gave no adsorption.)

Survey of Materials.—It is now possible to compare (Table IV) the results of a wider survey of cokes, prepared from typical materials placed in descending order of oxygen content, with regard to adsorption and reactivity values. A series of coals is included covering Seyler's classification, and these were treated by flotation when necessary so as to bring the ash content to about 1% and minimise its possible disturbing influence. Cokes were also tested from coals which had been allowed (see below) to take up oxygen by exposure in the air-oven at 200° for 4 weeks. Reactivity was determined in carbon dioxide at 900° on materials carbonised in 3½ hours to 800°; *V* and *R* show total adsorption and rate as on p. 580 and in Table III.

TABLE IV.

Adsorptions and reactivities of cokes from different materials.

Material and resulting coke.	O_2, %,* before carbonisation.	Adsorption of CO_2, c.c./g. by sized cokes.						Reactivity at 900°.†	Adsorption preoxidised.				Reactivity, pre-oxidised.	Ash, %, in material.
		1/5—1/12″.		1/20—1/40″.		<1/60″.			1/5—1/12″.		1/20—1/40″.			
		V.	*R.*	*V.*	*R.*	*V.*	*R.*		*V.*	*R.*	*V.*	*R.*		
Cellulose (ashless filter-paper), not fused	49·4	—	—	56	100	57	100	2·67	—	—	—	—	—	<0·01
Sugar-coke, fused	51·5	—	—	58	100	57	100	0·60	—	—	—	—	—	<0·001
Cellulose (cotton-wool), not fused	49·4	—	—	57	100	57	100	6·7 (rapid c.)	—	—	—	—	—	0·10
Coco-nut shell (carbonised at 920°)	—	70	100	71	95	—	—	8·0 (10·5)	—	—	—	—	—	0·5
Lignite (Bovy Tracy), not fused, brown	27·6	51	93	49	100	—	—	6·29	—	—	47	100	6·7	1·1
Bakelite (formaldehyde resin)	16·2	—	—	—	—	—	—	3·04	—	—	—	—	—	0·2
New Lount, meta-lignitious, not fused, black	12·1	38	54	37	84	—	—	1·28	46	98	46	100	1·7	1·25
Warrenhouse, meta-lignitious, not fused, grey	9·6	33	66	32	87	—	—	1·72	—	—	44	100	2·0	1·25
New Hucknall para-bituminous, semi-fused, dull grey	9·0	—	—	27	49	—	—	1·32	—	—	44	93	1·6	1·0
Beamshaw, para-bituminous, fused, lustrous grey	8·4	27	24	24	49	—	—	0·45	—	—	44	77	0·73	0·6
Altofts	—	4·3	15	12	15	—	—	0·39	—	—	42	93	—	—
Black Bed, ortho-bituminous, silvery	6·3	3·2	18	7·7	4·5	—	—	0·31	—	—	40	66	1·3	1·9
Haigh Moor, ortho-bituminous (Sharlston Wallsend), fused, silvery	5·9	—	—	7·0	7·5	—	—	0·20	—	—	39	89	1·1	0·6
Lupset, meta-bituminous, fused, silvery	4·4	2·6	17	5·7	9·0	—	—	0·17	37	68	38	78	0·64	1·2
Black Vein, meta-bituminous, fused, silvery	3·7	—	—	5·2	22	16	43	0·04	—	—	30	83	0·39	1·1
Two Foot Nine, semi-bituminous, dull grey	2·5	14	51	18	43	—	—	0·20	—	—	31	79	0·34	0·6
Lower New, carbonaceous, not fused, black	1·7	10	25	12	61	—	—	0·12	30	68	28	75	0·22	1·9
Stanllyd anthracite, not fused, unaltered	1·6	15	17	21	56	30	85	0·20	—	—	—	—	—	3·5
Petroleum coke	<1·0	—	—	8·7	31	—	—	0·14	—	—	—	—	—	—
Gas-retort carbon (deposited from hot gas)	<1·0	—	—	0·5	0	—	—	lowest <0·02	—	—	—	—	—	1·0
Graphite	<1·0	—	—	0·2	0	—	—	0·02	—	—	—	—	—	1·0

* The oxygen before carbonisation is calculated in the materials free from moisture, sulphur, and ash.

† Cokes of reactivity below 0·2 at 900° may with advantage be compared at a higher temperature (cf. Table VI).

Discussion of Results from Table IV.—Oxygen in the materials before carbonisation, carbon dioxide adsorption of the cokes, rates of this adsorption, and reactivities have all at various times been suggested empirically as lying in the same order. For reasons discussed above, such supposed parallelism would sometimes be quite misleading, but there is a causal connection and it is not surprising to find these properties with such a series of coals as that in Table IV (carbonised and tested under the conditions described) lying in nearly the same order. As judged by the values for V and R, it would appear that, with all the substances of high oxygen content, a micro-capillary system has been established by carbonisation which gives a rapid access and high adsorption of carbon dioxide; this effect is very much lessened in the fusible coals of low oxygen content from Black Bed (6·3%) downwards, increased again somewhat in the infusible carbonaceous coals, and finally almost obliterated in the substances with less than 1% of oxygen and very low reactivity. The lowest reactivity (with very low adsorption) was shown by gas-retort carbon. This is presumably due, not only to the negligible oxygen content of the gas from which it is formed, but also to its mode of formation—slow deposition by the decomposition of hot gas—which would facilitate the building up of a closely-knit, impervious carbon structure.

The comparative freedom of access of carbon dioxide was also brought out in the adsorption shown by materials of different sizing. It made no difference until the lower adsorptions (again from Black Bed downwards) were reached, but from that point onwards was noticeable. (It was suggested above that the cause of the fall in the true specific gravity of anthracite from 900° upwards, as determined in water, was the minute capillaries not penetrated by the water.)

Addition of Oxygen.—The foregoing study of the influence of oxygen contained in materials undergoing carbonisation was supplemented by experiments in which oxygen was added to coals directly, and the influence on the reactivity and adsorption of the cokes determined. For all the coals in Table IV, the results are given of passing air slowly over them for 4 weeks while they were heated in an air-oven at 200°, before carbonisation. In nearly every case marked increase in adsorption and reactivity of the coke resulted; the proportional increase was most pronounced with the coals of lowest oxygen content, but one striking result was the high and similar adsorption of carbon dioxide (40—47 c.c./g.) given by most of the cokes from the oxidised coals. The only exceptions showing little or no increase were lignite and anthracite, at the two ends of the series. Lignite may be presumed to be already so far provided with oxygen that the very little it fixed had no further effect. With anthracite, preliminary experiments showed that at 200° its oxygen fixation was practically nil, and this inertia may be explained by the extensive aromatic condensation which it had already undergone during formation, with development of graphitic crystallite structure (Blayden, Riley, and Taylor, *loc. cit.*). When heated at 325°, however, anthracite fixed 7·9% of oxygen in 27 hours and the cokes showed an increase in reactivity from 0·35 to 0·93 (at 950°). Heating in nitrogen caused no such increase. In another series of tube experiments, Haigh Moor bituminous coal was heated at 150° in air, with collection of the gases evolved, during periods increasing up to 12 hours, and the reactivities of the corresponding solid products after carbonisation determined. Parallel blank experiments were made using nitrogen instead of air, and the determinations corrected accordingly. The corrected results from oxidation of 100 g. of coal in these experiments after 12 hours were : total oxygen consumed, 4·07 g.; oxygen in water, 1·48 g.; in carbon dioxide, 0·39 g.; in carbon monoxide, 0·23 g.; fixed (by diff.), 1·97 g. The reactivities of the coked residues rose steadily from 0·5 to 0·9, but all those from the nitrogen " blanks " had the same reactivity as that from the untreated coal, *viz.*, 0·5, a result uniformly forthcoming in other similar tests.

It was noticeable that the loss of oxygen as carbon dioxide and water (3·3 g. in 12 hours) in treatment of the coal in nitrogen at this low temperature had no effect on the reactivity of the coke, but that oxygen taken up during the heating in air was more firmly fixed and had a marked effect in raising the reactivity of the coke, presumably by its expulsion of carbon as monoxide at a higher temperature, where it would influence the structure as suggested above. The maximum oxygen fixed (in 28 hours at 150°) was 3·89%, and the corresponding increase in reactivity of the coke was to 1·87. The coking property was practically destroyed at an early stage in the oxidation with only a slight increase (0·1) in reactivity, but both oxidation and reactivity continued to increase steadily. The same was noted with the other fusible coal (New Hucknall) similarly tested. [In view of the marked increase in reactivity brought about by oxygen, it was not surprising that 7 and 24 months' storage of a newly mined and powdered coal ($\frac{1}{6}$—$\frac{1}{10}$″) raised the reactivity of the coke from 0·2 to 0·4 and 0·5 respectively.]

These results, obtained by the direct action of oxygen on bituminous coals, lignite, and anthracite (for further details, see G. Milner, Ph.D. Thesis, Leeds, 1933), are in full accord with the view expressed above from quite other considerations. The causal connections between oxygen content, adsorption, and reactivity so far indicated may be expressed as follows : oxygen remaining in the solid product after the first stage of carbonisation (sometimes including fusion) becomes responsible from 500° upward for the subsequent gasification of carbon, mainly as monoxide, and the consequent formation of an intimate micro-capillary system, which in such a process as gasification of the solid product of carbonisation in carbon dioxide increases the effect of the surface it underlies and so becomes the basic, though not the sole, determinant of reactivity. The extent of this micro-capillary system is indicated by the adsorptive power for carbon dioxide.

Influence of Carbonisation Temperature.—So far, our discussion of adsorption and reactivity has been for clarity based upon comparative results obtained from solid products carbonised at one temperature, 800°, reactivities being all determined at 900°. The influence of carbonisation temperature will now be considered.

Adsorption of carbon dioxide was measured on the solid products obtained by the prolonged vacuum carbonisation of cellulose (filter-paper) at successive temperatures up to 1200° as described in J., 1942, 252. The volumes of carbon dioxide (c.c. at 20° and 760 mm.) adsorbed per g. of solid at 20° were :

Temp.	200°	300°	400°	500°	600°	700°	800°	900°	1000°	1100°	1200°
Vol.	2·5	20·1	27·1	43·9	50·6	57·6	65·3	72·0	74·3	73·4	59·4

Such results are, however, somewhat affected by the time of heating; *e.g.*, the paper coke adsorbed 65·3 c.c. per g. after the prolonged vacuum carbonisation at 800°, 57 c.c. after the 3½ hours' slow carbonisation to 800° (as usually employed in our tests; see Table IV), and 45·5 c.c. after the rapid 20-minutes' carbonisation used in our first preparation of cokes from paper, cotton-wool, sugar, and starch (Table III), suggesting some increase here in the micro-capillary system with time, although, as noted earlier, the filter-paper gave a coke of practically the same adsorption as did the cotton-wool, sugar, or starch, whether the carbonisation had been slow or rapid. The prominent features in the values for adsorption of the paper coke prepared in a vacuum at different temperatures were the sudden rise at 500°, marking the formation of the micro-capillary system as established, the steady and rapid rise between 500° and 900° as the system developed, and the fall from a maximum at 1000°, becoming rapid between 1100° and 1200°, the highest temperature of the carbonisation.

The same rise and fall of carbon dioxide adsorption are reported (" The Solid Products of the Carbonisation of Coal," South Metropolitan Gas Co., 1934, p. 34) as occurring with cokes prepared from a Durham gas-coal, but the maximum was for a coke prepared at 700°, above which temperature adsorption was less and slower. In a few experiments with wood charcoal a higher maximum (about 800°) was obtained. When the coal was carbonised in a tube under vacuum, with a periodical introduction of hydrogen intended to minimise any graphitic formation which would tend to lower adsorption, the attainment of a maximum with subsequent falling away was still just as pronounced.

In the determination of micro-porosity (Table II) made on the solid products throughout the carbonisation range (15—1100°) of anthracite and a meta-bituminous coal, and based on the difference of penetration of water and of mercury, the micro-capillary system which mercury would not penetrate, and that which would be effective in carbon dioxide adsorption, are little different, the limiting diameters being estimated at 6 μ and 12 μ respectively, but the volume of the micro-capillary system is more directly measured by that of the penetrating water. It is seen there that with both anthracite and meta-bituminous cokes this volume reached a maximum at 850° and then shrank.

All these facts point to a rapid growth in the micro-capillary system from 500° upwards during carbonisation and the attainment of a maximum at a temperature which varied somewhat with the material tested. The lowest value for the maximum was 700° for a gas-coal (see South Metropolitan Gas Co., *loc. cit.*), 850° for anthracite and a meta-bituminous coal, and 1000° for cellulose (filter-paper), the last having been subjected to prolonged fractional carbonisation under vacuum. Beyond the maximum, there was a marked shrinkage in volume of the micro-capillary system, which seems, therefore, to be of general occurrence somewhere in the temperature range 800—1200°, although, as noted above, there is no increase in specific gravity.

What may be taken as interesting visual evidence of the shrinkage and a consequent increasing coherence appears in " Photomicrographs of Sulphuric Acid Dispersion of Cokes, carbonised to Various Temperatures " obtained in the South Metropolitan work (Fig. 14 therein). The coke produced at 1030° differed widely from those of lower temperature in giving " a colourless solution containing suspended in it black particles of substantially the same size as the original particles of coke taken for test." This may be taken as due to a consolidation with rising temperature of the carbon structure, opposite in effect to that of the carbon monoxide and finally overcoming it, with consequent diminution in micro-capillarity and reactivity. In approximately the same temperature range the progress of the superficial carbon towards graphite, as demonstrated by equilibrium measurements, will also tend to diminish reactivity during gasification in carbon dioxide, more particularly during its early stages. These two causes of diminishing reactivity, *viz.*, shrinkage of the capillary system and superficial graphitisation, are usually but not necessarily coincident in operation. The results of experiments recorded in Table V illustrate both effects as arising from increasing temperature (and time) of carbonisation.

TABLE V.

Reactivity at 900°, and adsorption by solid products from different temperatures of carbonisation.

A. Filter-paper, $(C_6H_{10}O_5)_n$, infusible. B. Cane-sugar, $C_{12}H_{22}O_{11}$, fusible. C. New Hucknall coal, para-bituminous, semi-fusible.

	Temp.	Gasification (mins.) in CO_2, and corresponding reactivity. 5.	20.	40.	60.	90.	120.	150.	180.	Mean re-activity.	CO_2 adsorption, c.c./g. *V.*	*R.*
A	800°	(4·63)	3·77	2·82	2·37	2·23	2·17	—	—	2·67	56·0	100
	1000 (40 mins.)	2·00	2·00	2·23	2·17	2·00	1·84	—	—	2·04	—	—
	1000 (240 mins.)	(1·18)	1·50	1·55	1·68	1·72	1·53	—	—	1·60	51	85
B	800	0·60	0·60	0·58	0·59	0·59	0·59	0·60	0·60	0·60	58·0	100
	1000 (40 mins.)	(0·38)	0·43	0·48	0·53	0·54	0·56	0·56	0·57	0·52	47	76
	1000 (240 mins.)	(0·30)	0·36	0·41	0·45	0·48	0·50	0·52	0·54	0·47	41	45
C	800	—	—	—	—	—	—	—	—	1·32	27	49
	1400 (25 hrs.)	—	—	—	—	—	—	—	—	0·27	0·7	0

The results for cane-sugar show the fall in reactivity from 0·60 to 0·52 brought about by raising the temperature of carbonisation from 800° to 1000°, and the further fall to 0·47 with a more prolonged time of heating at 1000° The value after 5 mins.' gasification (0·38; shown in parentheses and not used in calculating the mean reactivity) shows the lowered reactivity of the surface preheated to 1000° owing to its graphitisation, and this again was more pronounced with the longer exposure at 1000°. Since, however, the gasification of carbon in the whole 120 minutes of the test was only about 8%, the extent of graphitisation was very small, confirming the indications of specific-gravity measurements, although its existence was in full accord with results as obtained in a study of the equilibrium in the reaction $C + CO_2 \longrightarrow 2CO$ and reported above. The adsorption of carbon dioxide, V, was lessened from 58 to 41 c.c./g., and there was a reduced rate of adsorption, R falling from 100 to 45, mainly, it may be assumed, because of a diminished freedom of access through the graphitising surface layer.

The reactivity of the paper coke was much greater (2·67) than that of the sugar coke (0·6). The paper and the sugar contained substantially the same high percentage of oxygen and developed equally the micro-capillary system as indicated by adsorption of carbon dioxide, but the paper did not fuse on carbonisation, and gave a bulkier coke with lower powder-density (0·15 as against 0·4), which presumably meant a greater extent of surface per g. bounding the micro-pores and increasing reactivity. As with the sugar coke, the reactivity of the paper coke and the adsorption both diminished after preheating to 1000°. The reactivity of the paper coked at 800° after 5 mins.' gasification was higher (4·63) than that found subsequently (2·67). This is probably due to the more reactive surface atoms with greater free energy or unsaturated bonds, and is commonly found with unfused material, particularly at lower temperatures. The atoms would form graphitic crystallites on further heating, and the paper coke displayed the lowering reactivity of a graphitising surface (1·18) in the 5-min. sample after 240 mins.' heating at 1000°, although not so markedly as the fused sugar coke. The rate of adsorption was also lowered after this prolonged heating, but again less than with sugar coke. A single example is provided in Table V of the influence of long exposure (25 hours) at a much higher temperature (1400°), above the normal range of our experiments, on New Hucknall (para-bituminous) coal. The reactivity was greatly lowered, from 1·32 to 0·27, and the adsorption almost obliterated, by the combined effects of shrinkage and graphitisation.

Reactivities at High Temperatures.—The comparison of reactivities of the solid products of carbonisation towards carbon dioxide is conveniently made at 900°, but the reactivity has also been determined up to 1500° (Blakeley and Cobb, Gas Research Fellowship, *Trans. Inst. Gas Eng.*, 1934). Roughly, the reactivities were multiplied 100-fold when the temperature was raised from 900° to 1400°. The temperature coefficient of reactivity R_{t+10}/R_t decreased with increasing temperature, but the numerical difference between the reactivities of two solid products increased greatly. A complication in these determinations arises from an alteration in the material itself under the severe heat treatment as gasification proceeds; this was shown to have an appreciable effect but not to invalidate the general relation of results obtained. (The original paper should be consulted for details.) Some typical results are given in Table VI, including tests of materials which at 900° are only slightly reactive.

TABLE VI.

Specific reactivities at different temperatures.

	900°.	1000°.	1100°.	1200°.	1300°.	1400°.	1500°.
Holmside (Durham) coke, carbonised at 920° ...	0·50	2·47	9·2	19·5	52·0	100	—
Same, after 15 mins. at 1400°	0·15	1·10	—	—	—	—	—
Coconut shell, carbonised at 920°	10·5	40·6	137	196	—	—	—
Ceylon graphite	0·04	0·59	3·96	14·0	—	81·2	—
Petroleum coke	—	1·2	—	10·7	—	18·6	29·7
Retort carbon	—	—	2·8	4·2	8·8	—	15·2

Reactivity at Low Temperatures.—From 600° downwards, the reactivity of the solid product of carbonisation towards carbon dioxide has usually fallen to a point at which the method described above for its determination in inapplicable. It becomes more practicable to substitute oxygen (as air) for carbon dioxide and to measure the percentage of the oxygen consumed by the carbonised product as indicated by the expression $100(CO_2 + \frac{1}{2}CO)/(CO_2 + \frac{1}{2}CO + O_2)$, where CO_2, CO, and O_2 represent percentages in the effluent gas (Bolland and Cobb, *J. Soc. Chem. Ind.*, 1933, **58**, 153—159T).

Influence of Inorganic Additions on Reactivity.—It was reported by Lessing and Banks (J , 1924, **125**, 2344) that the course of carbonisation was affected by the presence of certain inorganic salts. This was confirmed in our laboratory by experiments on coal, undertaken primarily to determine the effect as regards sulphur and nitrogen compounds (Marson and Cobb, Gas Research Fellowship, *Trans. Inst. Gas Eng.*, 1925), but amplified by tests on reactivity (*ibid.*, 1926). These were all made on cokes prepared from coal of low ash content (to minimise its possible interference) to which inorganic compounds had been added before carbonisation, and a remarkable heightening of the decomposition of both steam and carbon dioxide was found to result from the addition of soda, lime, or ferric oxide. Moreover, it was demonstrated that almost the same result could be obtained from cokes to which the addition had been made by impregnation with inorganic salts after carbonisation. A method of determining the reactivity towards carbon dioxide of these special and ordinary cokes, which has been used ever since with slight modifications, was reported by Branson and Cobb (*ibid.*, 1927, p. 357) and a necessary working scale connecting a defined reactivity with decomposition of carbon dioxide or steam was published (Key and Cobb, *J. Soc. Chem. Ind.*, 1930, **49**, 439T).

Other work on the various factors influencing the reactivity in gasification of cokes has been carried out in our own and other laboratories and also on a larger scale, but we now deal with experiments on the reactivity of the solid products of carbonisation from an organic substance with and without inorganic additions. Cane-sugar was chosen as being of known constitution, of negligible original ash content ($<0{\cdot}001\%$), and as yielding, after fusion and further heating, a coke of rather low reactivity, 0·6. The properties of this coke have already been given in detail. Impregnation of the coke with inorganic additions was carried out at room temperature, soluble salts being used, and penetration of the solution sometimes being aided by evacuation.

In Table VII is shown the influence of adding soda (as sodium carbonate) in gradually increasing quantity, the complete figures being given in this case for the percentage of carbon dioxide decomposed by **5 g.** at 900° at periods up to 120 mins. There was a continuous and large rise of carbon dioxide decomposition with the increase of carbonate added. Moreover, if a corresponding table is calculated, each figure being corrected for the carbon gasified during the progress of a test, it is shown that there was a gradual rise in the % of carbon dioxide decomposed as gasification proceeded. This would be expected because of the growing concentration of alkali, particularly with the more rapid rates of gasification.

TABLE VII.

Influence of added Na_2O *on* CO_2 *decomposition,* %.

Additions, %, of Na_2O as Na_2CO_3.	5 mins.	20 mins.	40 mins.	60 mins.	80 mins.	120 mins.	Mean.
Sugar coke (alone)	8·2	7·5	7·2	7·6	7·6	7·8	7·6
+ 0·09 Na_2O	12·3	13·7	14·8	15·8	16·8	16·8	15·0
+ 0·21 Na_2O	20·2	22·3	24·2	24·8	24·9	24·9	23·5
+ 0·35 Na_2O	26·8	28·5	30·3	32·1	32·9	33·7	30·7
+ 0·6 Na_2O	45·2	49·1	49·3	50·9	52·6	49·3	49·4
+ 0·8 Na_2O	62·6	72·0	76·0	65·8	56·2	52·1	64·1
+ 1·0 Na_2O	68·2	69·7	74·8	73·2	67·6	58·9	68·7
+ 1·3 Na_2O	82·0	81·0	74·7	74·6	66·4	56·2	72·5
+ 1·4 Na_2O	86·1	87·2	79·4	73·2	68·1	48·9	73·8

A comparative survey made with equivalent additions of different inorganic substances, 0·01 g.-mol. of oxide per 100 g. of sugar coke, gave the following descending order of mean reactivity at 900° (Key–Cobb scale) : BaO, 13·0; Fe_2O_3, 10·0; Na_2O, 8·8; Li_2O, 7·7; SrO, 6·4; CaO, 3·8; K_2O, 3·4; NiO_3, 3·3; PtO_2, 2·7; Ce_2O_3, 1·7; CuO, 1·5; ThO_2, 1·4; Al_2O_3, MnO_2, MgO, ZnO, and Ag_2O 0·8—0·6; sugar coke 0·6. These results embody the correction for carbon gasified, but the order is not altered thereby.

The most pronounced effects were shown by the strongly electro-positive elements, lithium being the most effective weight for weight. The additions were made by impregnation with dissolved salts, usually carbonate or nitrate, and differences in fusibility, volatility, ease of decomposition and reducibility (as, *e.g.*, with ferric oxide) would tend to invalidate the comparison as one dependent solely on an inherent property of the inorganic element added; for instance, although lithium, sodium, and potassium cokes showed reactivities increasing during gasification, those with calcium, strontium, and barium showed decreasing reactivities, explained by the fact that, whereas the alkaline-earth oxides or carbonates are not fused at 900°, the alkaline carbonates are fused, and on that account would be more closely retained on the changing surface of the carbon during its gasification.

Various explanations of the marked increase in reactivity brought about by some of these inorganic additions were considered. It seemed possible that it might be due to some change in the carbons, brought about in the preliminary heating to 900° with the inorganic additions, before being gasified in the reactivity test; but when sugar coke impregnated with soda (1·4%) was given this pre-heating, it was found that, although only 10% of the soda was removed by extraction with water for 12 hours (Soxhlet) and some remained even after boiling in concentrated hydrochloric acid for a further 24 hours (suggesting some degree of fixation of the soda by the coke), yet the coke residue had a very much lower reactivity than that of a normal 1·4% soda-coke and even lower than that of one made up with the much smaller soda content of the residue after extraction. The enhanced reactivity of the soda-coke cannot then be attributed to change in the carbon during pre-heating. Further evidence was forthcoming from determinations of the repeated adsorption of carbon dioxide by cokes pre-heated as before containing soda and baryta. The following results were obtained :

	V, c.c./g.	*R*.	Reactivity.		*V*, c.c./g.	*R*.	Reactivity.
Sugar coke	47	100	0·6	Sugar coke + BaO	49	95	32
Sugar coke + Na_2O	49	77	5·4				

Thus the change in total adsorption was insignificant, and that in rate of adsorption was slight, and as there was no appreciable change in micro-structure, the reason for the greatly enhanced reactivity must be sought elsewhere.

Now, Dent and Cobb's experiments with graphite (*loc. cit.*) showed that, although the approach to equilibrium on passing carbon dioxide over graphite at 800° was greatly accelerated by sodium carbonate, yet the equilibrium figure (13·8% of dioxide) was unaltered, so catalysis is indicated. Its mechanism will be treated summarily, since it is still under investigation. A mechanism for carbon dioxide and an inorganic oxide RO may be represented thus :

$$A\left\{\begin{array}{ll}\text{(i)} & RO + CO_2 \longrightarrow RO{\cdot}CO_2 \\ \text{(ii)} & RO{\cdot}CO_2 + C \longrightarrow RO + 2CO\end{array}\right\}\text{The result is } CO_2 + C \longrightarrow 2CO_2\text{, which reaction also occurs directly and independently of catalysis.}$$

The analogous mechanism for steam in its simplest form is :

$$B\left\{\begin{array}{ll}\text{(i)} & RO + H_2O \longrightarrow R(OH)_2 \\ \text{(ii)} & R(OH)_2 + C \longrightarrow RO + CO + H_2\end{array}\right\}\text{Here, too, the ultimate result } H_2O + C \longrightarrow CO + H_2\text{, also occurs directly.}$$

Although the decomposition of the carbonate by carbon as in A (ii) occurs readily below 900° (the temperature of reactivity determination in carbon dioxide) with sodium carbonate (F. J. Dent), and the formation of sodium hydroxide as in B (i) was indicated by an initial fixation of steam at 1000° (the usual temperature of reactivity determination in steam) (A. J. Wilson), yet the application of this explanation to lime and other activating substances offers obvious difficulties, particularly when still higher temperatures are considered at which their carbonates and hydrates cannot exist, but enhancement of reactivity continues.

A possible explanation of the enhanced reactivities may be based on the energy of free electrons, as involved in the catalytic action at the surface of metals, carbon being itself a conductor. The following sequence of elements is in the ascending order of the maximum kinetic energy of their free electrons (Nyrop, *J. Soc. Chem. Ind.*, 1931, **50**, 752) : K, Na, Li, Ca, Mg, Ag, Al, C, Cu, Zn, Pt, Cr, Fe, Ni, Mn. On comparing that order with the one given above (p. 587) for reactivities induced by the impregnation of salts of the elements, it would appear that, in general, the oxides and salts of those elements possessing electronic energies greatly different from that of carbon were actually more efficient catalysts but, as there explained, disturbing factors enter which cannot be evaluated.

Summary and Conclusions.—This work, following upon the study of the primary gaseous products of carbonisation (J., 1942, 253), is applied to cellulose (filter-paper and cotton-wool), sugar, coals of different types, anthracite, petroleum coke, retort carbon, graphite, etc., and is mainly directed to tracing some properties capable of numerical expression.

(i) The specific gravity, whatever it may be initially and in the first stage of carbonisation, reaches a common value of *ca.* 1·4 at 500° and rises with temperature to 1·8 at 800°, then remains nearly constant at about 1·85 up to 1200°, the highest temperature of our experiments. The steady period, 800—1200°, is marked by the long-continuing emission of hydrogen and carbon monoxide, and this gas, by lying between parallel sheets of graphite crystallites, probably prevents their coalescence and consequent increase of specific gravity. Although all the materials tested have this bulk density from 800° to 1200°, yet a superficial graphitic film is also formed, but is not thick enough to exercise any appreciable influence on the specific gravity. Fundamentally, therefore, the solid product was always the same carbon, over a wide range of temperature for all the materials tested, but differences in physical structure emerged which determine differences in behaviour and appearance.

(ii) The micro-capillarity of the solid product, as indicated by reversible carbon dioxide adsorption at room temperature, or by the difference in specific gravity as determined in mercury and water, increased from a carbonising temperature of *ca.* 500° to a maximum at 800—1000° (according to substance and method of carbonisation) and then diminished. The micro-capillary system so formed was most fully developed in the solid product from a material rich in oxygen, such as cellulose, and became negligible when the material contained little or no oxygen. The following explanation seems applicable. Oxygen left in the solid residue at 400—500°, at which temperature the formation of graphitic crystallites was first prominent, is the agent by which carbon is gasified as oxides, mainly from nuclear carbon in the hexagonal network, by the reaction $R_1OH + R_2H \longrightarrow R_1R_2 + H_2O$, followed by the attack of steam on carbon (see J., 1942, 252), thereby giving rise to a very intimate micro-capillary system.

(iii) The reactivity of the solid product towards carbon dioxide at any particular temperature depends on the nature of the carbon, and the extent of surface over which the gas flows, but a primary determinant of the surface effective in gasification is the extent of the underlying micro-capillary system, not because of gas flow through these capillaries (which is very small), but because their terminations at any surface render it so discontinuous and open to attack. In the absence of such a system the surface is comparatively inert. Reactivity therefore depends largely on the oxygen which remains in the solid product at 400—500° and generates the capillary system as the temperature rises further. There is, however, another important factor. When sugar coke was mixed with inert alundum, the extent of the micro-capillary system and the adsorption on coking were unaffected, but the increase of surface bounding the micro-capillaries brought the reactivity up from 0·6 to 2·02, comparable with that of paper coke.

It was found that if a coal was allowed to take up oxygen by prolonged heating in air at 150°, the quantity of oxygen fixed by the coal and the reactivity of the coke rose gradually together. Heating in nitrogen had no such effect although carbon dioxide and water were expelled. Values of oxygen in the original material, and of adsorption, rate of adsorption, and reactivity of the solid products of carbonisation, were obtained for a wide range of substances (Table IV).

It was deduced that, although there was no scientific basis for placing the reactivities of the solid products of carbonisation in the same order as the oxygen contents of the original materials, or as the adsorption or rate of adsorption by the carbonised product, yet there was a causal connection between the oxygen expelled from combination with carbon from 500° upwards, the micro-capillary system (indicated by adsorption) which it generated in the solid product of carbonisation, the surface effective in gasification, and the reactivity.

In the results for the wide range of coals in Table IV, the order of oxygen content, adsorption, and reactivity was nearly the same. This is comprehensible. The greater the previous molecular condensation with loss of easily expelled oxygen (irrelevant to these phenomena), the closer would be the correspondence expected between the oxygen content of materials and the adsorptions (or reactivities) of their cokes. All coals have already undergone such condensation in their formation from vegetation. A comparison after heating to (say) 400° would presumably heighten the degree of correspondence.

(iv) When the temperature of carbonisation was increased, the consequent shrinkage of the micro-capillary system, which began at 800—1000° with different materials, lowered both adsorption and reactivity (they nearly disappeared in a coke heated at 1400° for 25 hours). Superficial graphitisation increased these effects. The reactivity increased rapidly with rise of the temperature of gasification in carbon dioxide, but the temperature coefficient of reactivity diminished.

(v) The influence of inorganic constituents on sugar coke, chosen as being of known constitution, rather low reactivity (0·6), and negligible ash content, was studied by impregnation with soluble salts. Reactivity was continuously and greatly raised as the proportion of added soda was increased in stages to 1·4%. Equivalent additions (0·01 g.-mol. of oxide per 100 g. of the coke) of different inorganic substances showed that alkalis and alkaline earths were the most effective in raising this reactivity (*e.g.*, BaO, 13·0; K_2O, 3·4). In spite of this increase, the adsorption after the preheating as applied in a carbon dioxide reactivity test was the same for soda coke and baryta coke as for the coke alone. Also, Dent and Cobb had shown that, although sodium carbonate accelerated the approach to equilibrium on passing carbon dioxide over graphite at 800°, yet the equilibrium figure obtained (13·8% of dioxide) was the same. Catalysis was therefore indicated as the cause of the enhanced reactivity.

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