CCCXCIII.—*The Reactions between Oxygen and Coal.*

By Wilfrid Francis and Richard Vernon Wheeler.

A study of the gases occluded in coal that had been exposed to the air for a long time (see Wheeler, J., 1918, **113**, 945) suggested that one reaction between oxygen and coal, or some part of the coal substance, was analogous to that between oxygen and carbon which results in the formation of a physico-chemical complex (Rhead and Wheeler, J., 1913, **193**, 461). Later work (Tideswell and Wheeler, J., 1919, **115**, 895; 1920, **117**, 794) emphasised the analogy by showing that, not only did exhaustion of coal at a slightly higher temperature than that at which "fixation" of oxygen had taken place remove part of the oxygen as oxides of carbon, but also that the coal then had a renewed capacity for attaching oxygen. To explain this "revivification," it was assumed that the molecular structure of that part of coal to which oxygen attaches itself approximated to that of carbon.

We have recently shown (J., 1925, **127**, 112, 2238; 1926, 1410) that the portion of coal most readily attacked by oxygen at low temperatures is the ulmin portion, the molecular structure of which contains a compact system of 5- and 6-membered rings, which recalls the compact 6-membered ring structure suggested for carbon by Aschan (*Chem.-Ztg.*, 1909, **33**, 561). The analogy between the oxidation of carbon and that of coal is not, however, complete. During the latter, the hydrogen-containing groupings of the ulmin molecule play an important part, whilst stable acidic (carboxylic) groupings are formed which have no counterpart in the composition of the carbon–oxygen complex formed when carbon is oxidised.

In the present research, which should be considered in conjunction with that of Tideswell and Wheeler (*loc. cit.*), whose methods of experiment we have followed, we have studied more particularly the behaviour of the hydrogen-containing groupings of the ulmin molecule during the oxidation of coal, as disclosed by the formation of water. Oxygen was circulated at a constant rate through powdered coal maintained at a constant temperature, and periodic measurements were made of the total quantity of oxygen disappearing and of the quantities of each of the products of reaction. When the reaction became slow, the oxidised coal was heated in a vacuum to a higher temperature (below the temperature of decomposition of the coal-substance), cooled to the original reaction temperature, and oxygen again admitted. This procedure was repeated several times.

The experiments can be divided into two main groups : (1) with newly-won coal, the vitrain portion of the Hamstead (Brazills) seam, Staffs.; and (2) with vitrain from the same seam after it had been transformed into soluble ulmins by prolonged atmospheric oxidation at 150° (see Francis and Wheeler, *loc. cit.*).

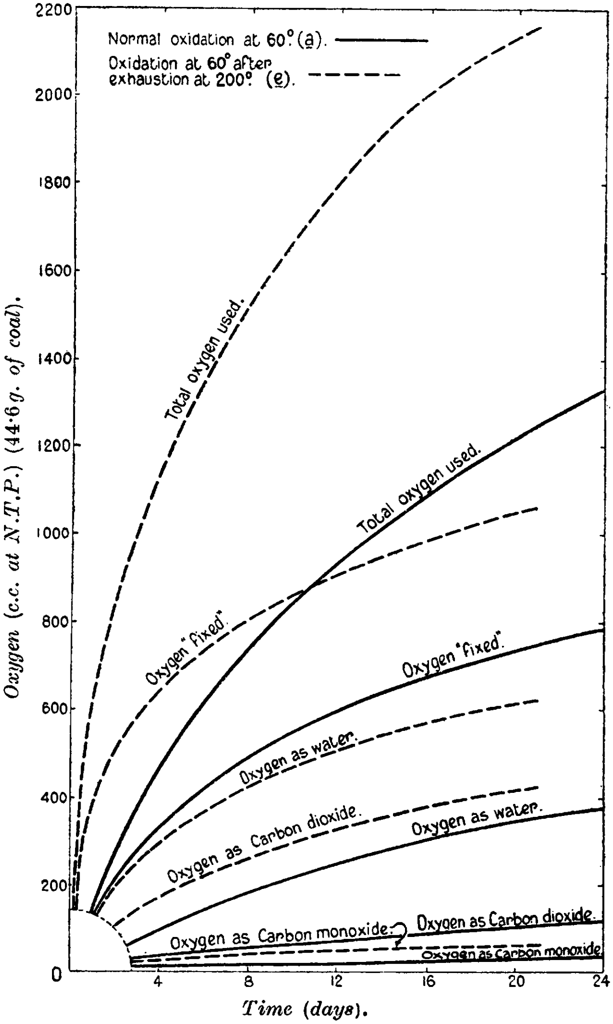
Series I. Experiments with Newly-won Coal.

The coal, ground to pass through a 40- and remain on a 60-mesh sieve (I.M.M. standard), was dried in a vacuum over sulphuric acid during 14 days and introduced into the reaction tube, where it was first heated at 60° in a vacuum and then treated with pure dry nitrogen, which was circulated through the rest of the apparatus. The weight of dry coal used was 44·6 g. The following sequence of experiments was made :

(*a*) Oxidation at 60°.
(*b*) Exhaustion at 100°, followed by oxidation at 60°.
(*c*) Exhaustion at 100°, followed by oxidation at 60°.
(*d*) Exhaustion at 185°, followed by oxidation at 60°.
(*e*) Exhaustion at 200°, followed by oxidation at 60°.
(*f*) Exhaustion at 200°, followed by oxidation at 60°.

The main results are recorded in Tables I and II and in Figs. 1 and 2, all volumes of oxygen and oxygen-equivalents being reduced to *N.T.P.* throughout. The first oxidation (*a*) at 60° can be regarded as the " normal " oxidation of the coal at that temperature. Its general course is shown in curve *a*, Fig. 1.

Fig. 1.



Carbon dioxide and monoxide were produced from the first at a rate comparable with that of the disappearance of oxygen, but

TABLE I.

Series I. The Oxidation of Newly-won Coal (44·6 *g.*) *at* 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c.			Oxygen " fixed," c.c.
			As H_2O.	As CO_2.	As CO.	
(*a*) Normal oxidation ...	35	1544	450	169	40	885
(*b*) After exhaustion at 100° (1st)	28	697	122	91	21	463
(*c*) After exhaustion at 100° (2nd)	26	564	105	72	12	375
(*d*) After exhaustion at 185°	17	781	237	127	21	396
(*e*) After exhaustion at 200° (1st)	21	2173	621	423	67	1062
(*f*) After exhaustion at 200° (2nd)	24	1914	461	403	82	968

TABLE II.

Series I. Products of Decomposition of Oxidised Coal.

Experiment.	Oxygen-equivalent of products, c.c.			
	As H_2O.	As CO_2.	As CO.	Total.
At 100° after oxidation *a*	79·8	39·7	3·5	123
At 100° after oxidation *b*	87·0	45·8	4·2	137
At 185° after oxidation *c*	352·0	269·0	39·0	660
At 200° after oxidation *d*	501·0	595·0	81·0	1177
At 200° after oxidation *e*	332·0	634·0	91·0	1057

the appearance of water in the absorption tubes was more gradual. This was no doubt because the coal, being initially dry, retained some of the water vapour first formed. There is no reason to doubt but that the production of water vapour actually corresponded with the production of oxides of carbon during the early stages as it did throughout the rest of the oxidation. As the reaction proceeded, a smaller proportion of the oxygen used became " fixed."

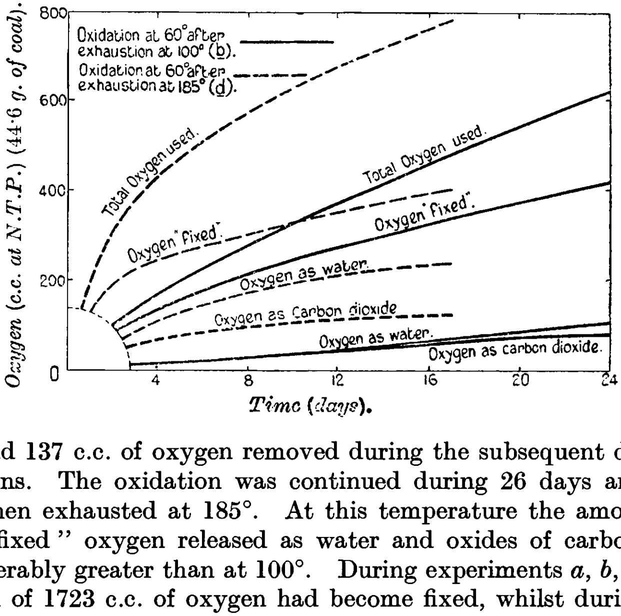
Oxidation was still continuing at a slowly decreasing rate at the end of 35 days, but the experiment was stopped and the apparatus evacuated, the temperature of the coal being raised to 100°. Considerable decomposition of the oxygenated groupings in the coal, equivalent to 123 c.c. of oxygen, occurred (see Table II), 65% of the oxygen thus removed appearing as water, 32·2% as carbon dioxide, and 2·8% as carbon monoxide.

After this exhaustion at 100°, the rate of oxidation at 60° (*b*, Fig. 2) had increased, the " normal " oxidation of the coal being continued, and the oxygen removed from the ulmins by the exhaustion, amounting to about one-seventh of the oxygen fixed during experiment *a*, being simultaneously replaced. Experiment *b* was continued during 28 days, and the coal then again exhausted at

100°. Water and the oxides of carbon were evolved in the same proportions as during the first evacuation, showing that the groupings attacked were of the same character; but rather larger quantities, equivalent to 137 c.c. of oxygen, were obtained owing to the continuance of the " normal " oxidation of the coal.

After this second exhaustion at 100°, the rate of oxidation at 60° (*c*) had again increased, in proportion with the amount of oxygen removed during exhaustion. Estimating, from the oxidation curve for experiment *a*, that during the normal oxidation of the coal the daily fixation of oxygen averaged 12 and 9 c.c. in experiments *b* and *c*, we calculate the fixations consequent on the decompositions at 100° to be 127 and 141 c.c., corresponding with 123 and 137 c.c. of oxygen removed during the subsequent decompositions. The oxidation was continued during 26 days and the coal then exhausted at 185°. At this temperature the amount of the " fixed " oxygen released as water and oxides of carbon was considerably greater than at 100°. During experiments *a*, *b*, and *c*, a total of 1723 c.c. of oxygen had become fixed, whilst during the two exhaustions at 100°, 260 c.c. had been released. Of the balance, nearly one-half (660 c.c.) was removed during exhaustion at 185° (see Table II). The proportion of oxides of carbon in the products was greater than at 100°, showing that the character of the groupings decomposed was different.

FIG. 2.



The rate of oxidation at 60° (*d*) after this treatment was initially very rapid (curve *d*, Fig. 2). This experiment was stopped after 17 days, and the coal then exhausted at 200°. The total amount of oxygen fixed as the result of all the operations up to this point was 1199 c.c. The evacuation at 200° removed as water and oxides of carbon 1177 c.c., or 98·2%. The proportion of oxides of carbon was greater than at 185°.

Oxidation at 60° (*e*, Fig. 1) was now very rapid. Considerable volumes of oxides of carbon and water were produced from the first, their quantity, in proportion to the amount of oxygen fixed, being greater than in the earlier experiments of the series. After 21 days, 1062 c.c. of oxygen had been fixed, the total amount in the coal being therefore 1084 c.c. (1199 − 1177 + 1062 c.c.). Exhaustion at 200° removed 1057 c.c., or 97·5%. The gases contained a higher proportion of oxides of carbon than those from the previous exhaustion at 200°. Oxidation at 60° (*f*), following this second exhaustion at 200°, was again very rapid. The production of oxides of carbon was greater and that of water was less than in experiment *e*, indicating the gradual elimination of groupings rich in hydrogen.

Series II. Experiments with Coal oxidised at 150°.

The material, 97% of which was soluble in aqueous potassium hydroxide, contained C, 63·8; H, 2·7%. From our previous work, we knew that extensive decomposition of the oxygenated groupings (chiefly carboxylic) of this soluble coal-ulmin would take place on heating in a vacuum. Only 9·76 g. were therefore used for the experiments. The results of a series of oxidations at 60° are recorded in Table III, and those of a series of decompositions at different temperatures in Table IV. No decomposition took place at 100°.

Although during the first oxidation at 60° (*a*), before any heat treatment, some " fixation " of oxygen occurred, there were no gaseous products, and it seems clear that the disappearance of oxygen, half of which occurred whilst it was being admitted into the apparatus, was due to adsorption and solution in the interior of the coal. Exhaustion at 220° caused a partial decomposition of the oxygenated groupings of the ulmin molecule, but the oxygen thus removed, unlike that removed during the corresponding experiments with coal, was not replaced during the subsequent oxidation at 60° (*b*). Physical adsorption of oxygen occurred, whilst there was chemical reaction resulting in the fixation of 4 c.c. of oxygen and yielding traces of oxides of carbon. Possibly water was formed also and retained by the ulmin. Heating at 320° caused considerable decomposition, and, although during the subsequent oxidation at 60° there was appreciable chemical combination with the coal-ulmin, this was by no means as great, having regard to the amount of oxygen previously removed, as might be expected from the results of the experiments with newly-won coal. The two subsequent exhaustions at 320° (after oxidations *c* and *d*) both caused some decomposition, the volumes of the products being about one-tenth of those yielded during the first exhaustion (after oxidation *b*). These results, and those of the decomposition at 420° and the subsequent oxidation at 60°, emphasise the difference in character between newly-won coal and the soluble coal-ulmin produced from it by oxidation.

TABLE III.

Series II. The Oxidation of Soluble Coal-ulmin (9·76 *g.*) *at* 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Oxygen "fixed," c.c.
(*a*) Normal oxidation ...	5	18·4	Nil	Nil	Nil	18·4
(*b*) After exhaustion at 200°	8	22·9	Nil	0·5	Trace	22·4
(*c*) After exhaustion at 320° (1st)	4	53·4	4·4	8·6	8·0	32·4
(*d*) After exhaustion at 320° (2nd)	7	45·4	1·3	4·6	6·0	33·5
(*e*) After exhaustion at 320° (3rd)	5	37·8	Nil	2·1	2·8	32·9
(*f*) After exhaustion at 420°	9	104·4	10·0	12·7	6·4	75·3

TABLE IV.

Products of Decomposition of Soluble Coal-ulmin.

Experiment.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Total.
At 220° after oxidation *a*	60·5	112·5	6·3	179·3
At 320° after oxidation *b*	71·0	381·0	31·0	483·0
At 320° after oxidation *c*	10·6	43·3	5·1	59·0
At 320° after oxidation *d*	14·9	25·0	3·7	43·6
At 420° after oxidation *e*	187·0	420·0	67·5	674·5

We explain the results of the two series of experiments as follows. The oxidation of coal takes place through the medium of an adsorbed layer (compare Tideswell and Wheeler, *loc. cit.*), which almost immediately reacts with certain external groupings of the ulmin molecule, yielding water, carbon dioxide, and carbon monoxide, and forming unstable oxygenated groupings at the points of attack. As the adsorbed layer enters into chemical combination with the coal, it is replaced by a fresh layer, the process being continuous so long as there are groupings remaining with which oxygen can combine at the temperature of experiment. The unstable oxygenated groupings formed are ultimately carboxylic in character and cause the coal-ulmin to become soluble in alkalis.

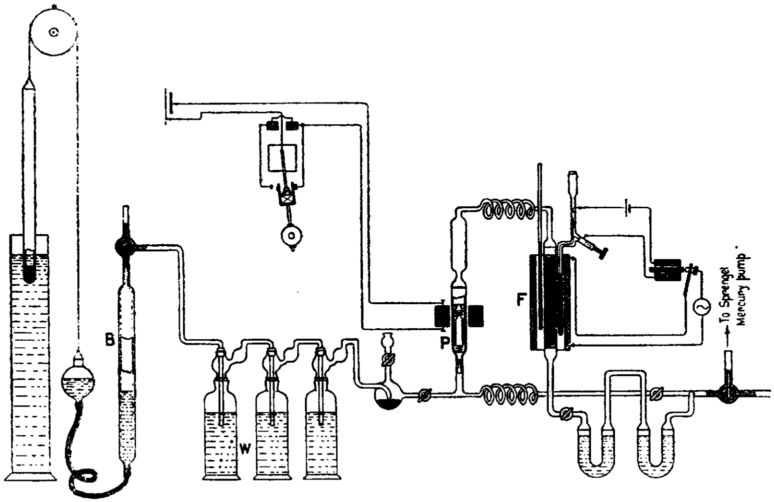
When the temperature of the coal is raised under vacuum, the oxygenated groupings that have been formed are decomposed, yielding water and the oxides of carbon, the oxygen contained in these being equal in quantity to that " fixed " during the oxidation. The coal now has an increased capacity for retaining oxygen, beyond that due to the normal oxidation, commensurate with the amount removed during exhaustion.

This process of revivification can be repeated many times, but the character of the products of decomposition at each successive exhaustion gradually changes, because groupings of slightly different character are attacked or decomposed. During exhaustion, suitable groupings near those to which oxygen has become attached furnish the hydrogen and carbon required to yield the water and oxides of carbon evolved. During the earlier exhaustions, water is the chief product of decomposition, the action being akin to dehydration. This may result in the formation of internal anhydrides from neighbouring carboxyl groupings, of lactones from suitably placed carboxyl and hydroxyl groups, or of unsaturated groupings such as are produced on the dehydration of β-hydroxy-acids. The number and type of the groupings that can be attacked depend upon the temperature at which oxidation is effected. Oxidation at 60°, as in the series of experiments with newly-won coal, is limited; but at 150°, the temperature employed to produce from that coal the soluble ulmins used for the second series of experiments, all the external groupings of the molecule are eventually attacked, leaving oxygenated (chiefly carboxylic) groupings in their place. No suitable groupings are available in such a fully-oxidised coal for the type of decomposition, permitting almost complete revivification, that obtains with a partly oxidised coal, but the decomposition (at the high temperature required) modifies the ulmin molecule profoundly, leaving a comparatively stable residue, there being but few groupings containing oxygen and hydrogen. Such revivification of this residue as can be effected is of the same character as is obtainable with carbon, and it is probable that the molecular structure of the residue approximates to that of carbon. With coals saturated with oxygen at temperatures between 60° and 150°, different degrees of revivification, by exhaustion at a higher temperature than that of oxidation, are possible.

EXPERIMENTAL.

The circulation apparatus employed for submitting the coal to the action of oxygen differed in many respects from that used by Tideswell and Wheeler (*loc. cit.*). The reaction tube in which the powdered coal was packed was supported vertically within an electrically-heated furnace (F, Fig. 3), the temperature of which could be maintained constant by means of an electric thermostat. The lower end of the reaction tube was connected by ground-glass joints to two weighed U-tubes in series. The first contained granular calcium chloride for the absorption of water, and the second, asbestos impregnated with sodium hydroxide (the top of each limb being covered by a layer of granular calcium chloride) for the absorption of carbon dioxide. These U-tubes were duplicated so that they could be periodically removed for weighing and fresh ones substituted.

FIG. 3.



Circulation of the oxygen through the coal and absorption tubes was effected by an electrically-operated glass pump, P, of special construction (see Francis, *Fuel*, 1926, **5**, 39). The oxygen entering the apparatus was first dried by bubbling through shallow layers of concentrated sulphuric acid contained in a series of large wash-bottles, W, and then passed through a mercury seal of about 1 mm. The charges of oxygen required for an experiment were contained in a graduated burette, B, over a mixture of equal parts by volume of glycerol and water. The reservoir of this burette was supported by a cord which passed over a pulley to a counterweight consisting of a tube, containing mercury, which dipped into a deep jar containing glycerol and water. The external diameter of the counterweight was equal to the internal diameter of the burette, so that as the level of the liquid in the burette rose, consequent on absorption of oxygen by the coal, the reservoir rose an equal amount and the pressure was maintained constant. The pressure was adjusted at the beginning of an experiment to be just sufficient to force the oxygen through the layers of sulphuric acid and the mercury seal.

As absorption by the coal proceeded, oxygen was drawn into the apparatus to maintain a constant pressure. The volume thus entering was measured periodically on the burette. Corrections were made for variations in atmospheric temperature and pressure and for the vapour pressure of the liquid in the burette. The oxygen, which was prepared by the action of a solution of potassium permanganate on a mixture of hydrogen peroxide and dilute sulphuric acid, was of 99·5% purity. Simultaneously with the measurements of the oxygen used, the weights of water and carbon dioxide formed were determined from the increase in weight of the **U**-tubes, and a sample of the circulating gases was analysed to determine the amount of carbon monoxide formed.

At the conclusion of an oxidation experiment, the apparatus was rapidly evacuated and the coal then raised to the required temperature during 30 hours, the gases evolved being drawn, by means of a Sprengel mercury pump, through the weighed **U**-tubes. Water and carbon dioxide were thus absorbed and estimated, and carbon monoxide was collected and measured.

The work described in this paper forms part of a research on the spontaneous combustion of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish it.

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