CCCLVI.—*The Combustion of Charcoal in Oxygen, Nitric Oxide, and Nitrous Oxide. Part I. The Adsorption of Oxygen.*

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THE combustion of charcoal in oxygen has frequently been studied, and three explanations of the mechanism have been advanced. Lang (*Z. physikal. Chem.*, 1888, **2**, 168) observed that the products of combustion varied with the velocity of the stream of oxygen, the yield of carbon monoxide decreasing with increasing velocity and ultimately becoming zero; he concluded that the primary product is the dioxide which, in contact with an excess of incandescent carbon, is reduced to monoxide.

The second explanation, that carbon burns in the first instance to monoxide which is subsequently oxidised to dioxide by excess of oxygen in the presence of water vapour, was advanced by C. J. Baker (J., 1887, **51**, 249) and by H. B. Baker (*Phil. Trans.*, 1888, **179**, *A*, 571); the former showed that when dried charcoal is allowed to absorb dry oxygen and then heated to 450°, the gas evolved consists mainly of carbon monoxide, and the latter reached the same conclusion from his experiments on the combustion of charcoal in dry oxygen. Dixon (J., 1899, **75**, 630) supported this explanation and disputed Lang's results.

The third explanation, based on previous suggestions of Brodie (*Annalen*, 1873, **169**, 270), Berthelot (*Bull. Soc. chim.*, 1876, **26**, 102), and Armstrong (*J. Soc. Chem. Ind.*, 1905, **24**, 473), was adopted by Rhead and Wheeler (J., 1912, **101**, 846; 1913, **103**, 461, 1210), who found that charcoal, which had been previously exhausted at 950°, readily absorbed or occluded oxygen at low temperatures, and the gas could not be completely removed, even by the most efficient pumping, provided the temperature was kept low and constant. If the temperature was raised, however, oxygen was liberated in the form of carbon monoxide and dioxide until the saturation capacity of charcoal for oxygen was reached. Rhead and Wheeler therefore concluded that "the first product of combustion of carbon is a loosely formed physico-chemical complex which can be regarded as an unstable compound of carbon and oxygen of an at present unknown formula, C_xO_y," which decomposed with rise of temperature, giving monoxide and dioxide. The formula C_xO_y implied that one oxygen molecule became attached to several carbon molecules; the evolution of heat resulting from this adsorption caused some oxygen molecules to acquire one carbon atom each, giving the dioxide, and others to be torn apart in the process, leaving the carbon molecule as monoxide. This process continued until the carbon became "saturated," after which there was alternate formation and decomposition of the complex. A similar view is held by Wartenberg and Sieg (*Ber.*, 1920, **53**, 2192), Lowry and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1413), Taylor and Neville (*ibid.*, 1921, **43**, 2055), and Blench and Garner (J., 1924, **125**, 1288). Richardson (*J. Amer. Chem. Soc.*, 1917, **39**, 1845), however, did not find any evidence of the formation of such a compound from his studies on the reverse action of carbon dioxide on charcoal at relatively high pressures.

Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361) considers in his theory of adsorption that the adsorbed molecule is held by either the primary or the residual valency forces of the atoms composing the adsorbing surface. At the surface of charcoal, for example, one of the primary bonds of each carbon atom might be unsaturated, or at least partly free to exert an influence, and one adsorbable atom or molecule of the gas would be bound for each carbon atom. Thus "with oxygen the adsorbed layer consists of oxygen atoms chemically combined with the carbon atoms which form the surface" (*ibid.*, 1915, **37**, 1154). These atoms or molecules constitute a layer and are said to be chemically or quasi-chemically united to the surface atoms of charcoal. Keyes and Marshall (*ibid.*, 1927, **49**, 156), however, suggest that the oxygen molecules or atoms attached to the surface can be regarded as being in a special state of valency strain such as to enable this first layer to adsorb a second layer of molecules of the same or of a different species. Further layers could be held by continually decreasing forces until the final layer differed but little from the free gas.

The present investigations deal with the systematic study of the behaviour of certain gases towards charcoal at various temperatures, and it seems highly probable that such layers of adsorbed oxygen and nitric oxide partaking of the "special state" exist on the surface of charcoal; this special state of oxygen (on the surface of charcoal) is, therefore, treated as the basis for an explanation of combustion of charcoal in oxygen, *i.e.*, as an alternative to that of Rhead and Wheeler (*loc. cit.*). Attempts, using both dynamic and static methods, are now described to elucidate the mechanism of combustion of charcoal by a comparative study of its combustion in oxygen, in nitric oxide, and in nitrous oxide, and the work of previous investigators is correlated.

Little work of a systematic nature has been done on the combustion of charcoal in nitric or nitrous oxide. It has long been known that a glowing piece of charcoal burns more vividly in nitrous oxide than in air and is extinguished when immersed in nitric oxide. This behaviour has been explained on the assumption that nitrous oxide is more easily decomposed than nitric oxide, the former being unstable above 520° and the latter above 1000°. On the other hand, one might expect nitric oxide to be a better supporter of combustion than nitrous oxide because their heats of formation are — 21,575 and — 17,470 cals. respectively. There is an anomaly here which demands explanation.

EXPERIMENTAL.

Preparation of Materials.—The charcoal employed in most of the previous work was obtained from wood, although such charcoal is known to be variable in properties, but in this investigation sugar charcoal was used. The gases were carefully purified and all volumes are reduced to 0° and atmospheric pressure.

Sugar charcoal. Recrystallised cane sugar was heated in a loosely covered porcelain dish first gently and then strongly. The charcoal thus obtained was submitted to the action of chlorine in a Jena-glass tube maintained at a dull red heat for 8 hours; after being cooled, it was digested repeatedly with boiling distilled water, collected, washed until free from hydrogen chloride, dried in an air-oven at 200°, and finally heated strongly in a vacuum for 2 hours (yield, 25%).

The product still contained chlorine (see experiments with nitric oxide, Section A), and was therefore heated to 1050° in a silica tube in a vacuum and treated with a current of nitric oxide, which displaced a considerable amount of chlorine. The charcoal was then coarsely powdered and sifted, 30—60-mesh particles being used in the quantitative experiments; on incineration it gave 0·12% of ash.

Before each experiment, either qualitative or quantitative, the purified charcoal was heated to 1100° and exhausted for 5 hours under the successive action of " Hyvac " and Sprengel pumps.

Oxygen. The oxygen used for the experiments in Section A was prepared by heating recrystallised potassium permanganate and collected over air-free water; it contained 0·2% of impurity unabsorbed by alkaline pyrogallol. For all the other experiments, the gas was obtained by electrolysing a solution of recrystallised barium hydroxide in pure conductivity water, and was passed through heated tubes containing copper oxide and phosphoric oxide before being collected over mercury.

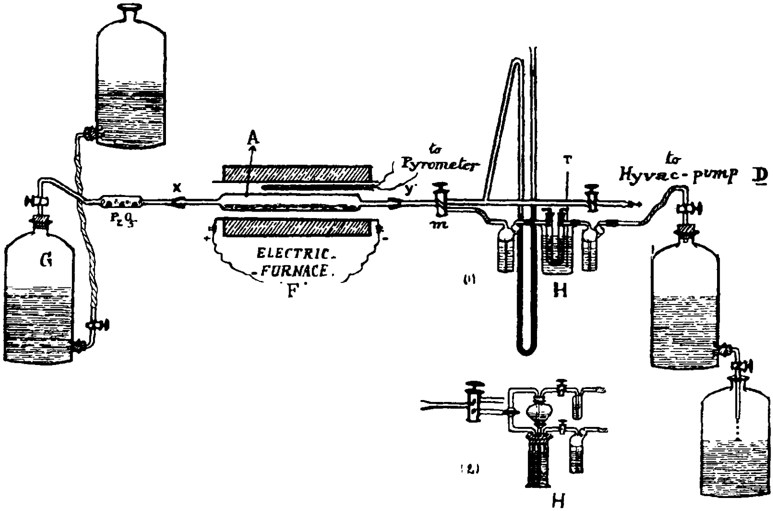
Nitrous oxide. For qualitative experiments nitrous oxide was prepared from hydroxylamine hydrochloride and sodium nitrite or was taken from a cylinder; it was stored over distilled water, traces of oxygen being removed by shaking with alkaline pyrogallol. For the quantitative work, it was solidified by means of liquid air, fractionated, and collected over mercury or in an evacuated two-litre bulb.

Nitric oxide. Nitric oxide was prepared by the potassium nitrate and ferrous sulphate method and collected over air-free distilled water. For the absorption experiments described in Section B, it was dissolved in ferrous sulphate solution and expelled by heating. Absorption with alkaline sodium sulphite showed the presence of 0·1% of residual gas. For other experiments it was liquefied, fractionated, and passed successively through tubes of sodium hydroxide and phosphoric oxide.

Carbon monoxide and dioxide. The monoxide was prepared from formic acid by the action of sulphuric acid, and the dioxide from calc-spar by the action of dilute hydrochloric acid. For quantitative work these gases were collected over mercury, and for the streaming method experiments they were collected over air-free distilled water and saturated sodium bicarbonate solution, respectively.

Nitrogen. Nitrogen, prepared from urea by the action of sodium hypobromite solution, was washed with caustic potash solution and collected over mercury.

FIG. 1.



Section A. Ignition Temperatures of Sugar Charcoal in Oxygen and Nitrous and Nitric Oxides: The Reaction Products below the Ignition Points.

Moissan (*Compt. rend.*, 1902, **135**, 921) studied the inflammation of diamond, graphite, and amorphous wood charcoal in a stream of oxygen; his results may be summarised thus:

	Diamond.	Graphite.	Wood charcoal.
Evolution of gas begins at	720°	510°	200°
,, ,, is abundant at ...	790	600	—
Ignition begins at	800—850	690	345

Manville (*ibid.*, 1906, **142**, 1190, 1523) found that the temperatures of formation of carbon monoxide and dioxide during the oxidation of wood charcoal varied with its previous heat treatment. No similar work is recorded on the combustion of charcoal in nitric and nitrous oxides.

Procedure.—The silica tube *A* (Fig. 1) containing 4—5 g. of sugar charcoal was connected with ground joints *x* and *y* to a gas reservoir

G and a three-way tap *m* respectively. The latter was connected with the pump *D* and with reagents for detecting carbon dioxide and monoxide as shown in *H*. The tube *A* was heated electrically by the furnace *F* to 1150° in a vacuum and cooled. A regular stream of the required gas, dried by a 6″ column of phosphoric oxide, was then passed from the gas holder *G*, and the temperature of the furnace was raised gradually until a flame was observed. At intervals of 10°, the temperature was maintained constant for 3 minutes, and the effect of increasing the rate of the gas stream was observed while the issuing gas was tested for cyanogen or oxides of carbon. The results are shown in Table I. Separate experiments were carried out for the detection of free oxygen produced in the interaction of nitric oxide and nitrous oxide with charcoal. Experiments were also conducted to detect the possible conversion of the dioxide into monoxide and *vice versa* in presence of charcoal. The reagents used for detecting the gases were: For carbon dioxide, baryta solution; for carbon monoxide, (1) in experiments with nitric oxide, dilute palladous chloride solution, (2) in other experiments, iodine pentoxide; for oxygen, (1) alkaline pyrogallol solution, (2) the red colour developed by catechol in the presence of ferrous sulphate and caustic potash (Binder and Weinland, *Ber.*, 1913, **46**, 255)—in using this reagent air was completely displaced by hydrogen; for cyanogen, absorption with caustic potash solution, followed by the Prussian-blue test.

Section B. Absorption of Gases by Charcoal at 0°*: The Gases evolved in a Vacuum at* 0° *and subsequently at Higher Temperatures.*

With a view to elucidate the mechanism of combustion, it is necessary to study the absorption by charcoal (*a*) of oxygen, nitric oxide, and nitrous oxide, and (*b*) of the reaction products. The power of charcoal to retain oxygen has been studied by previous investigators. Angus Smith (*Proc. Roy. Soc.*, 1863, **12**, 424) attempted to recover oxygen, absorbed by charcoal, by the agency of heat, and found that carbon dioxide was produced. C. J. Baker (*loc. cit.*) observed that charcoal which had adsorbed moist oxygen at room temperature yielded carbon dioxide when it was heated to 100°, whereas dried charcoal which had absorbed dried oxygen yielded only traces of gas (mainly monoxide) when heated to 450°. McLean (*Trans. Roy. Soc. Canada*, 1921, **15**, 73) and other workers showed that no oxygen as such could be pumped off above 200°, the gases evolved consisting of the oxides of carbon. On the other hand, Dewar (*Proc. Roy. Soc.*, 1904, *A*, **74**, 122) observed that oxygen absorbed by charcoal at the temperature of liquid air could be recovered without change on raising the temperature. Lowry and

TABLE I.

	Detection of			Flame observed	
Gas.	CO_2 at	CO at	O_2 at	at	Observations.
O_2	280—290°	280—290°	—	510°	A surface glow was observed at 470°, and scintillations at 510°.
N_2O	460—470	460—470	Nil	710	(1) A faint blue phosphorescence (visible only in the dark) was seen at 540°; its intensity increased with rise in temperature in a slow stream but disappeared in a rapid stream of N_2O.* (2) Yellowish-green flashes were observed at 710°.* (3) No cyanogen was detected.
NO	70	>450	Nil	Not obs. up to 1150°.	(1) The NO was completely decomposed: the issuing gas from the reaction tube did not give brown fumes on exposure to air. (2) No cyanogen found, but a considerable amount of chlorine was detected in preliminary experiments.†
CO_2	—	>200° (traces)	—	—	Reduction of CO_2 is very slow.
CO	>290° (traces)	—	—	—	It seems that the auto-oxidation of CO begins at 290°. Engler and Grimm (*Ber.*, 1897, **30**, 2921) showed that a mixture of CO + H_2O reacts with the evolution of CO_2 at 300°. Cleminson and Briscoe (J., 1926, 2148) found that in the auto-oxidation of CO in presence of carbon CO_2 is not produced up to 300°.

* A similar blue phosphorescence and yellowish-green flashes were observed when a mixture of CO and N_2O was passed under reduced pressure through a similar tube at 710°.

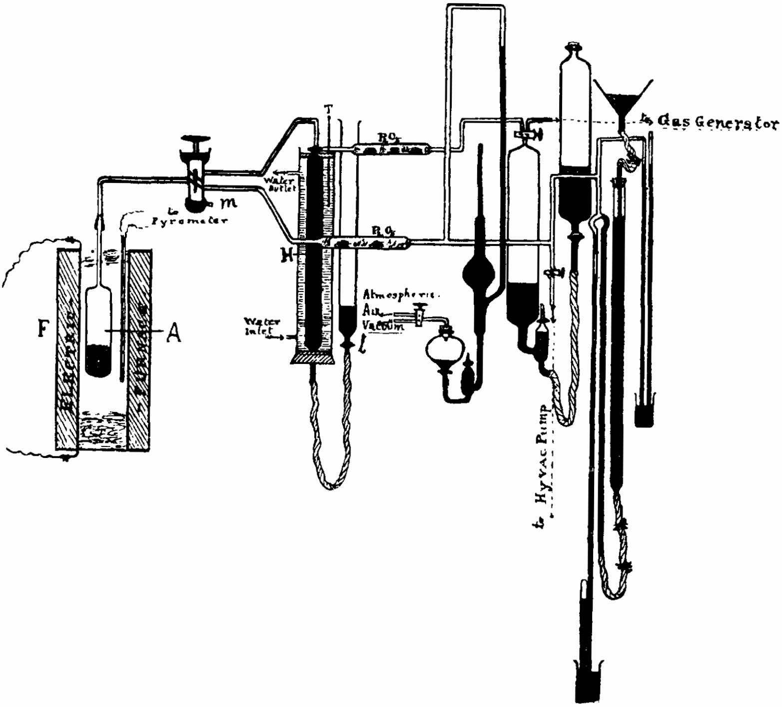
† This chlorine had been retained by charcoal: nitric oxide treatment (see p. 2664) was therefore subsequently included in the process of purification, and all observations in Table I were repeated and confirmed with the purer charcoal.

Hulett (*loc. cit.*) studied the absorption of oxygen over long periods of time, and concluded that "adsorption and surface condensation proceed simultaneously, the fixed oxygen being held by charcoal as a surface compound or compounds." Similar work with oxides of nitrogen has not been carried out before.

A determination has been made (*a*) of the volumes of oxygen, nitrous and nitric oxides, carbon monoxide and dioxide, and nitrogen absorbed and retained by charcoal at 0°, and (*b*) of the quantity and composition of the gas evolved when the charcoal was subsequently heated in a vacuum.

Procedure.—The apparatus used is shown in Fig. 2. It was tested for leaks by being kept under high vacuum over-night. Purified sugar charcoal (5 g.) in the silica tube *A* was heated to 1150° in the furnace *F* and exhausted for 4—5 hours by means of the Hyvac pump followed by the Sprengel pump. At 1100—1150° a slow but continuous evolution of gas was observed and the pressure recorded on a McLeod gauge could not be reduced below $1{\cdot}32 \times 10^{-2}$ cm. Hg (possibly owing to the softening of the silica vessel or to the reaction between carbon and silica); on lowering the temperature to 950° the pressure fell to $1{\cdot}1 \times 10^{-3}$ cm. Hg.

FIG. 2.

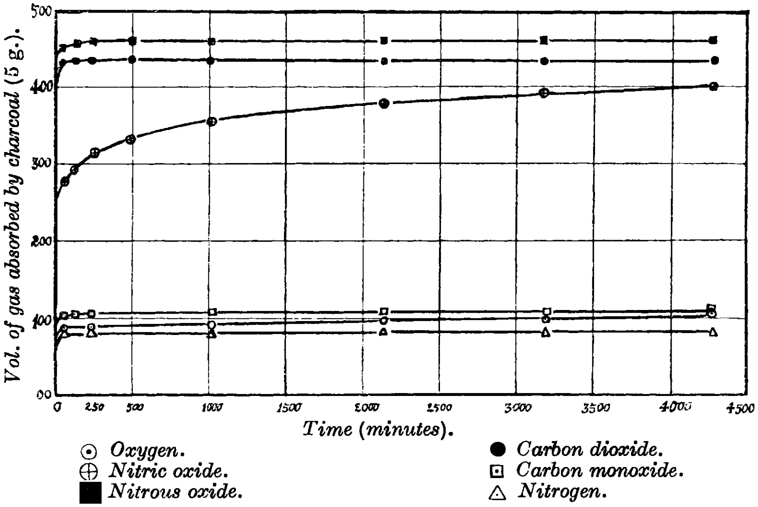


After the above heat treatment, the furnace was removed and the bulb allowed to cool. It was then surrounded by finely powdered ice and kept at 0° for ½ hour: the absorption was then allowed to proceed by connecting the silica tube *A* with the gas burette, *H*, by means of the tap, *m*. The volume of the gas absorbed at the barometric pressure was recorded at regular intervals by means of the

TABLE II.

Time (mins.).	Gas (c.c.) absorbed by 5 g. of charcoal.					
	O_2.	NO.	N_2O.	CO_2.	CO.	N_2.
5	74·0	199·4	429·4	407·4	94·4	75·6
10	81·0	—	437·4	421·4	100·4	77·6
20	84·6	242·4	442·4	426·2	103·4	79·1
30	86·0	259·6	446·4	429·2	—	80·8
45	—	—	449·4	431·8	—	80·8
60	86·4	277·4	452·4	—	104·0	81·0
120	87·6	294·6	455·4	432·4	104·8	81·8
240	88·8	310·4	459·4	432·4	105·3	82·2
480	—	329·3	460·4	432·4	105·3	82·2
1080	91·0	345·4	460·4	432·4	105·3	82·2
2160	93·8	376·4	460·4	432·4	105·3	82·2
3240	99·0	389·4	460·4	432·4	105·3	82·2
4320	102·0	403·6	460·4	432·4	105·3	82·2

FIG. 3.



levelling tube, *l*. The results are shown in Table II and plotted in Fig. 3. The absorption of nitrogen, nitrous oxide, and the oxides of carbon was complete after 4 hours, but that of oxygen and nitric oxide was incomplete even after 72 hours. After the absorption had proceeded for 72 hours, the charcoal in silica tube *A* was exhausted at 0° by means of the Sprengel pump and the evolved gas was analysed. In the preliminary experiments with 1 g. of charcoal, it was found that most of the first four gases was evolved in the first hour, but that oxygen and nitric oxide required 4—5 hours' continuous pumping. In the series with 5 g. of charcoal, the evacuation was extended to 5 days for the complete removal of the last two gases, whereas one day's pumping was sufficient in the experiments with the other gases. The Sprengel pump was worked for 10 hours a day, and the pressure recorded at intervals of 2—3 hours. In the nitric oxide experiments, this reduced the pressure to $1{\cdot}1 \times 10^{-3}$ cm. each day, but more gas was evolved over-night; this evolution of gas diminished gradually and the same pressure remained constant after the fifth day.

The charcoal was next heated to various temperatures, at each of which the gas was allowed to accumulate for 2 hours, and was then pumped off and analysed. At each temperature the Sprengel pump was allowed to work for 2 hours after the " click " of mercury was heard, and the pressure of $1{\cdot}1 \times 10^{-3}$ cm. was registered before the temperature was again raised.

In the nitric oxide experiments, the fluctuation in pressure noted at 0° was also found at temperatures up to 125°, but above this temperature the gas was readily removed. In order to compare the gas adsorbed by charcoal with that evolved on heating, separate experiments were carried out in which charcoal, exhausted at 150°, was suddenly heated to 450°, 600°, or 750°, and the gas allowed to accumulate. The temperature was then allowed to fall to 150°. In none of these experiments was the gas evolved ever reabsorbed or fixed by charcoal, thus indicating that the gas held in charcoal was different from the gas evolved.

In the analysis of the gas, oxygen and oxides of carbon were estimated by absorption with standard reagents, nitrous oxide by explosion with carbon monoxide, and nitric oxide by absorption in a saturated solution of alkaline sodium sulphite, followed by ferrous sulphate treatment in order to ascertain if absorption was complete.

The analytical results of a set of experiments with each gas are given in Tables III—VI, the weight of charcoal being 5 g. and the volume of the silica bulb 50·4 c.c. in each case.

TABLE III.

Experiments with oxygen.

O_2 absorbed = 152·4 c.c.

Temp. of evacuation.	Gas evolved, c.c.	Composition,			
		CO_2.	CO.	O_2.	Residue.
0°	133·5		—	133·5	—
25	0·2				
50	0·1	—			
75	1·1	0·8	0·0	—	0·3
100	0·3				
150	0·4				} *
300	7·4	5·2	2·2	—	0·2
450	10·4	4·6	5·7	—	0·1
600	10·6	2·8	7·7	—	0·1
750	10·3	0·5	9·7	—	0·1
900—950	5·4	0·0	5·1	—	0·3

* A sudden increase of pressure occurred at 280°.

The results in Table III show that (1) no oxygen escapes above 0°; (2) a small quantity of gas is evolved between 0° and 280°; (3) at and above 280° a sudden increase in pressure is observed, the gas consisting of a mixture of oxides of carbon.

TABLE IV.

Experiments with nitric oxide.

NO absorbed = 454 c.c.

Temp. of evacuation.	Gas evolved, c.c.	Composition,				
		CO_2.	CO.	NO.	N_2.	
0°	231·5	4·3	—	130·8	96·4	*
25	15·0	2·2	—	10·9	1·9	
50	41·8	9·8	—	27·0	5·0	
75	19·5	5·8	—	12·4	1·4	
100	31·3	12·1	—	16·4	2·8	
125	4·5	2·3	—	1·8	0·6	
150	1·3	1·1	—	0·1	0·1	†
300	21·6	15·6	5·0	—	1·0	
450	28·4	12·4	15·3	—	0·7	
600	28·0	7·0	20·6	—	0·4	
750	28·8	0·9	27·5	—	0·4	
900—950	11·8	0·0	6·0	—	5·8	

* A trace of nitrogen peroxide is suspected in the gas evolved below 125°, for the mercury of the pump was slightly affected.

† No gas was evolved between 150° and 280°.

The results with nitric oxide show that (1) a large amount of nitrogen is present in the gas pumped off at 0°, *i.e.*, charcoal interacts with nitric oxide and fixes the oxygen; (2) on raising the temperature, nitric oxide is pumped off, along with carbon dioxide and nitrogen, up to 125°, beyond which no nitric oxide escapes from the charcoal; (3) no appreciable amount of gas is evolved between 150° and 280°, but here a sudden increase in pressure occurs such as is observed in the experiments with oxygen, and the gas evolved above 280° consists of a mixture of the oxides of carbon.

TABLE V.

Experiments with nitrous oxide.

N_2O absorbed = 510·8 c.c.

Temp. of evacuation.	Gas evolved, c.c.	Composition,*		Temp. of evacuation.	Gas evolved, c.c.	Composition,*	
		N_2O.	N_2.			N_2O.	N_2.
0°	509·0	509·0	—	300°	0·1	—	0·1
25	1·5	1·5	—	450	0·1	—	0·1
50, 75, 100	0·4	—	0·4	600	0·1	—	0·1
125, 150	0·2	—	0·2	750—950	0·2	—	0·2

* Oxides of carbon were absent.

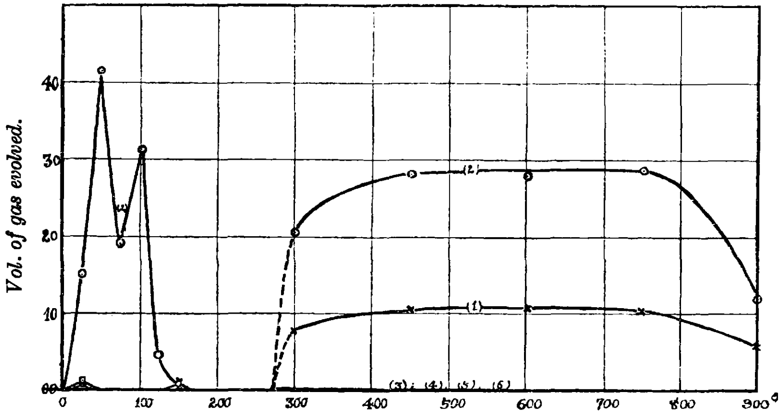
Table V shows that nitrous oxide is completely pumped off at 0°, *i.e.*, it neither reacts with nor is retained by the charcoal; the gases detailed in Table VI behave similarly, and hence if they are produced in the reaction between charcoal and nitric oxide, they will not be reabsorbed or fixed by charcoal when the temperature is lowered.

TABLE VI.

Experiments with carbon monoxide, carbon dioxide, and nitrogen.

Gas absorbed.....	CO = 155·8 c.c.				CO_2 = 482·8 c.c.				N_2 = 132·7 c.c.			
		Composition,				Composition,				Composition,		
Temp. of evacuation.	Gas evolved, c.c.	CO_2.	CO.	Res.	Gas evolved, c.c.	CO_2.	CO.	Res.	Gas evolved, c.c.	CO_2.	CO.	N_2.
0°	155·0	—	155·0	—	482·0	482·0	—	—	132·5	—	—	132·5
25	1·0	—	1·0	—	0·8	0·8	—	—	0·5	—	—	0·5
50, 75, 100	0·2	—	—	0·2	0·6	0·4	—	0·2	0·2	—	—	0·2
150, 300 .. 950	0·7	—	—	0·7	0·7	—	—	0·7	0·3	—	—	0·3

FIG. 4.

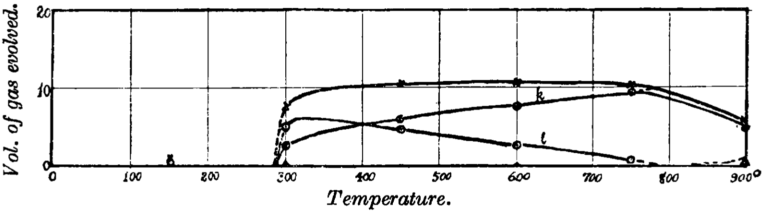


The volume of the gas evolved during the heat-treatment of charcoal in a vacuum, in the experiments with (1) *oxygen;* (2) *nitric oxide;* (3) *nitrous oxide;* (4) *carbon dioxide;* (5) *carbon monoxide;* (6) *nitrogen.*

The foregoing results, at temperatures higher than 0°, are represented graphically in Figs. 4, 5, and 6.

The outstanding results of these experiments are: (1) The absorption by charcoal of oxygen and nitric oxide increases with time and so differs from that of carbon monoxide and dioxide, nitrous oxide, and nitrogen. (2) Charcoal retains oxygen on absorption at 0° in some form of complex which breaks down at and above 280° with formation of monoxide and dioxide. (3) Nitric oxide partly decomposes into nitrogen and oxygen when absorbed by charcoal at 0°, the oxygen being retained as in (2); further, a considerable amount is held by charcoal and interacts with the above complex, giving carbon dioxide and nitrogen up to 150°; at and above 280°, the carbon–oxygen complex decomposes as in (2). (4) Nitrous oxide, nitrogen, and carbon monoxide and dioxide do not react with charcoal at 0°.

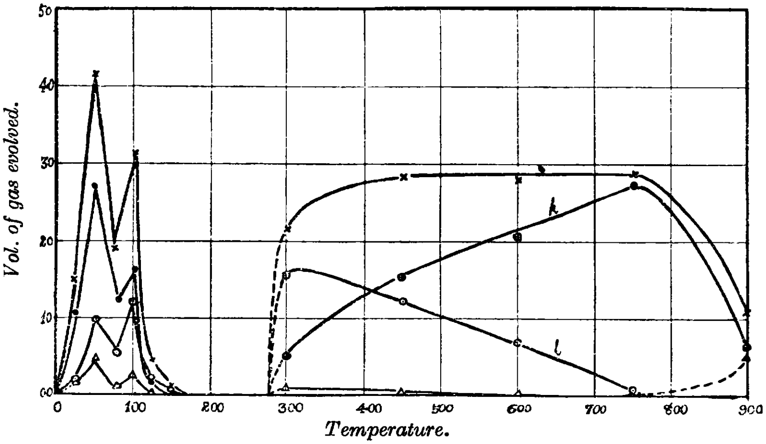
FIG. 5.



Composition of the gas evolved during the heat-treatment of charcoal in experiments with oxygen.

× *Volume of gas.* ○ *Carbon dioxide.*
⊗ *Carbon monoxide.* △ *Residual gas or nitrogen.*

FIG. 6.



Composition of the gas evolved during the heat-treatment of charcoal in experiments with nitric oxide.

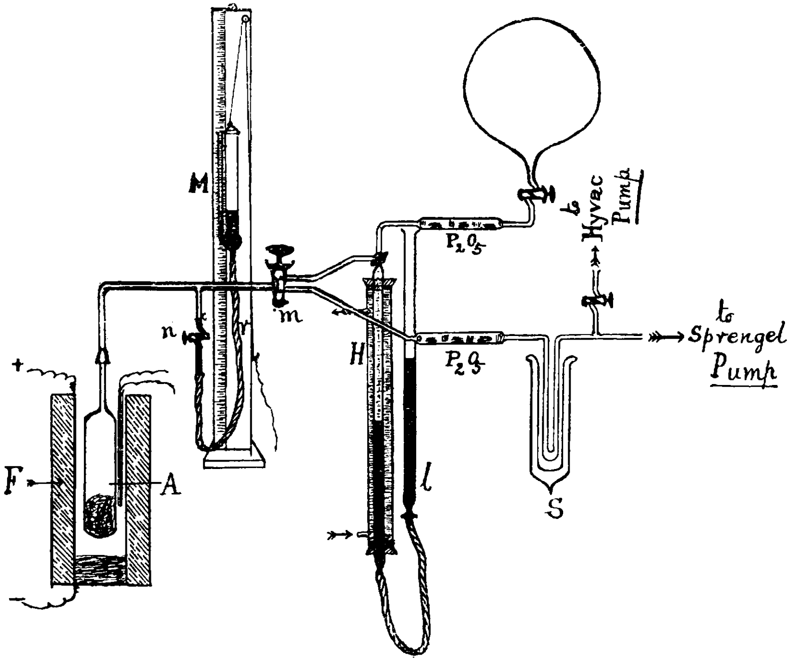
× *Volume of gas.* ⊕ *Carbon monoxide.* ● *Nitric oxide.*
⊙ *Carbon dioxide.* △ *Nitrogen.*

Section C. The Interaction of Charcoal at 470° *with Nitrous Oxide, Carbon Dioxide and Monoxide.*

Since these three gases do not react with charcoal at 0°, it is important to examine the products at temperatures sufficiently high to cause reaction. All the reactions have therefore been carried out at 470°, this being the lowest temperature at which nitrous oxide reacts (see Table I).

Procedure.—The apparatus used is shown in Fig. 7. Purified sugar charcoal (5 g.) contained in the silica tube, *A*, was previously heated and exhausted at 1100° for 4 hours. The temperature was then kept constant at 470°. A measured volume of the gas was next admitted from the burette, *H*, and the pressure adjusted as rapidly as possible (1—2 mins.) to 1 atm. by means of the levelling tubes, *l* and *r*. The taps, *m* and *n*, were now closed, the reaction allowed to proceed for one hour, and the tap *m* opened so as to connect with the trap, *S*, immersed in liquid air; the reaction was thereby arrested, nitrous oxide and carbon dioxide being removed from the reaction chamber and condensed in the trap. The remaining nitrogen and carbon monoxide were then pumped off, and the reaction chamber was completely evacuated at 470°, the tap *m* closed, the liquid air removed, and carbon dioxide and nitrous oxide were collected.

FIG. 7.



The subsequent heat treatment of charcoal in a vacuum was then carried out by raising the temperature of the furnace to 600°, 750°, and 900° and collecting the gases evolved at each temperature as described in Section B. Three experiments were performed with each gas and similar results were obtained. The analyses of the gases evolved in a set of experiments, given in Table VII, show that

TABLE VII.

Experiments with nitrous oxide, carbon dioxide, and carbon monoxide at 470°.

Gas admitted..............	N_2O = 30·3 c.c.					CO_2 = 13·0 c.c.			CO = 10·8 c.c.		
Temp. of evacuation.	Comp. of gas evolved,* c.c.					Comp. of gas evolved,* c.c.			Comp. of gas evolved,* c.c.		
	CO_2.	CO.	N_2O.	N_2.	Total.	CO_2.	CO.	Total.	CO_2.	CO.	Total.
470°	6·4	1·2	2·6	27·8	38·0	12·4	0·3	12·9	0·1	10·6	10·7
600	1·2	3·1	—	0·2	4·5	—	—	—	—	—	—
750	0·2	5·5	—	0·1	5·8	—	—	—	—	—	—
900—950	—	1·1	—	0·1	1·2	—	—	0·2	—	—	0·2

* In each of the three cases under these headings there was a residue of 0·2 c.c.

(1) the nitrogen of all the nitrous oxide that has decomposed is evolved along with unchanged nitrous oxide at 470°; (2) a part of the oxygen of the decomposed nitrous oxide appears at 470° and the remainder is evolved between 470° and 900°, always in the form of oxides of carbon; (3) at 470° charcoal neither retains carbon monoxide or dioxide nor removes oxygen from these gases.

From these observations it may be concluded that the reaction between charcoal and nitrous oxide proceeds with the evolution of nitrogen and the fixation of oxygen in the same manner as is observed in the experiments with oxygen and nitric oxide (p. 2671); this fixation of oxygen is not observed in the reaction of charcoal with carbon monoxide or dioxide.

Discussion.

The above results show that the combustion of charcoal depends upon adsorption. Nitrous oxide, carbon dioxide and monoxide, and nitrogen are adsorbed by charcoal and can be removed by lowering the pressure, but oxygen and nitric oxide are adsorbed and cannot be so removed. McBain (*Phil. Mag.*, 1909, **18**, 916) has defined the processes as (*a*) *adsorption* when there is a condensation of the gas on the surface of a solid; (*b*) *absorption* when there is a solution of the gas in the interior of the solid; (*c*) *sorption* when there is a chemical reaction between the gas and the adsorbent in addition to adsorption or absorption. It is apparent that in case (*a*) the gas will be easily removed as such by evacuation, in case (*b*) it will resist removal by pumping and will be recovered unchanged by heating in a vacuum, whilst in case (*c*) it will not be removed unchanged by such treatment. Accordingly, at 0°, the first four gases afford instances of adsorption by charcoal, and the other two of sorption.

The tendency of all recent work is to show that oxygen is held in charcoal owing to surface combination. This view is strongly supported by the evidence adduced in the present paper, *viz.*, (1) at low temperatures nitric oxide is reduced by charcoal, its oxygen is fixed, as in the experiments with oxygen alone, and a further quantity of nitric oxide reacts with this fixed gas and the charcoal, giving carbon dioxide and nitrogen; (2) the reaction between charcoal and nitrous oxide at 470° proceeds with evolution of nitrogen and fixation of oxygen.

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