THE OXIDATION OF CARBON BY NITROUS OXIDE.

By R. F. Strickland-Constable.

Received 15th August, 1938.

The results here described have already been discussed from the theoretical standpoint in a recent paper by the writer.¹

Shah² finds that the gaseous product of the combustion of charcoal in N_2O is mainly CO_2 with a little CO, and that no NO is formed. He also finds that freshly out-gassed charcoal always "fixes" a part of the oxygen of the nitrous oxide in the form of a solid carbon-oxygen complex, so that the gaseous products, CO and CO_2 have a smaller, oxygen content than the initial N_2O .* (The nitrogen of the N_2O is not, however, "fixed" in this way, but is returned to the gas phase.)

He also states that the reaction is bimolecular, but publishes no data in support of this assertion. In the present work for a charcoal whose surface had, by repeated oxidation, attained a state of constancy, the reaction was not found to be bimolecular; but with a freshly outgassed

* This "fixed " oxygen will hereafter be referred to generally as "The Surface Oxides."

¹ Strickland-Constable, Trans. Faraday Soc., 1938, 34, 1074.

² Madhavlal Sukhlal Shah, J.C.S., 1929, 2661.

charcoal the reaction might simulate second order behaviour, owing to the fact that in this condition the reaction gives a rapidly decreasing first order "constant."

Experimental Details.

The apparatus consisted of a silica bulb (volume 170 c.c.) with a long neck of about 4 mm. internal diameter. This was connected by a buttjoint and capillary glass tubing (Int. Diam. 1 mm.) to a manometer and also to a two-way tap. This tap led in one direction to the N₂O storage, and in the other to the Töpler pump, and vacuum pumps. Evacuation was by means of a three-stage mercury vapour pump, backed by a mechanical pump.

The \bar{N}_2O used was taken from a commercial cylinder, dried over P_2O_5 , redistilled with the aid of liquid air to free from permanent gases and

stored over mercury. No difference in behaviour was however observed whether the N_2O was redistilled or not.

The charcoal used was a sample of highly activated coconut charcoal originally prepared for gas-mask purposes. (This same charcoal was used by J. D. Lambert ³ in his work on the oxidation of carbon by oxygen.)

The silica bulb was heated in an electric furnace, the temperature being measured by a thermo-couple, whose hot junction was placed adjacent to the silica bulb in the heated air space of the furnace. The temperature was hand-controlled.

Samples of gas for analysis were extracted from the bulb by the Töpler pump. Analyses were performed either in an apparatus designed by Dr. B. Lambert, or else in a standard Bone and Wheeler apparatus. In each of these the CO_2 was absorbed in alkali, and the CO in the usual cuprammonium solution. Since N_2O is soluble in aqueous solutions, analyses were only performed on the final product of a completed reaction from which all N_2O had been removed by the reaction.

General Procedure.

Two grams of charcoal were placed in the silica bulb, which was then evacuated while being heated slowly from room temperature to 500° C. at which temperature it was maintained for two hours, likewise under vacuum. After this preliminary treatment the bulb was charged with N₂O and an experiment performed which showed that the charcoal reacts with N₂O at a convenient rate for study at 400° C. After this at no stage was the sample ever again exposed to the air.

The subsequent runs were then performed according to the following general procedure : The bulb was brought to the reaction temperature,

³ J. D. Lambert, Trans. Faraday Soc., 1936, 32, 452.

T_{ℓ}	AB	T.T	Ŧ.	Т
			_	.

Time. t (mins.).	Pressure. p (mm.).	k.					
Run 8.	Run 8. (Temp. 400° C.)						
0	1051						
4	108	0.0122					
II	112	0.0110					
20	117	0.0124					
30	122	0.0126					
50	130	0.0126					
90	141	0.0125					
122	147	0.0128					
165	1511	0.0127					
300	$155\frac{1}{2}$						
æ	158	I —					
Run 66.	(Temp. /	405° C.)					
0	238	I —					
I	246	0.069					
2	253	0.066					
4	265 1	0.065					
12	301	0.062					
221	328	0.062					
30	340	0.063					
35 1	346	0.065					
51	354	0.067					
260	358						
Run 126	. (Temp	. 404° C.)					
о	474						
2	493	0.040					
5	516	0.038					
10	549	0.032					
20	604	0.039					
30	640	0.039					
40	668	0.041					
50	686	0.042					
140	715						
		1					

1375

and then evacuated for 10 minutes. A charge of N₂O (usually from 100 to 400 mm.) was admitted and the pressure p_0 read as rapidly as possible. The temperature of the bulb being maintained constant to within about $\pm 2^{\circ}$ C. the pressure on the manometer was read at suitable intervals. At the end of a run when the pressure had ceased to rise, a sample could be removed for analysis.

The results of three runs at different initial pressures are shown in Table I.* The end-point of each, approximately 50 per cent., is consistent with the formation of pure CO₂ according to the equation :

$$2N_2O + C = CO_2 + 2N_2$$

and in agreement with the results of actual analyses given below. (The formation of CO without any CO₂ would result in an end-point of 100 per cent.).

That the reactions are accurately first order is seen from the values of k.

Samples of Charcoal.

During the experiments to be described, three different samples of charcoal were used :

> Lot I Runs 4 to 30. Lot II Runs 31 to 41. Lot III Runs 42 to 127.

The absolute rates of reaction of the three samples were not quite the same, although all were from the same bottle. It is possible that this difference in rate depended on the different amounts of moisture absorbed by the samples during weighing, and on the exact temperatures at which this moisture was removed during the evacuation and heating. Apart, however, from the absolute values of the rates of reaction the samples behaved identically.

The samples were weighed undried in air and each weighed approximately 2 grams.

Behaviour with Fresh Charcoal Samples.

When a fresh sample of charcoal was used, the rate of successive runs fell off from run to run, to attain a constant value only after half a dozen runs or more had taken place, after which the rate was reasonably reproducible.

During the first few runs with a fresh sample of charcoal, there also occurred a considerable formation of surface oxides, and as a result the end-point of the first few runs was considerably less than the end-point of 50 per cent. found in later runs.

* The following symbols will be used throughout this paper :

p = absolute pressure in mm. of mercury in the reaction bulb. p_0 and p_1 are the values of p at the beginning and at the end of a run. "Per cent. increase" is equal to $\frac{(p - p_0) \times 100}{p_0}$, *i.e.* it is the increase in pressure expressed as a percentage of the initial pressure.

t = time in minutes.

- k =first order reaction constant, given by $k = \frac{1}{t} \log_{\theta} \frac{p_{f} p_{0}}{p_{f} p}$.
- "End-point" of a run this is the per cent. increase at the end of a completed run.

† The value of "k" would of course be expected to fall off slightly from run to run as the actual mass of carbon was diminished by burning away. This effect was, however, too slight for any correction to be necessary, since in any case only small groups of consecutive runs were ever treated as comparable.

R. F. STRICKLAND-CONSTABLE

These effects are illustrated in Table II. Run 4 was the first run with Charcoal Lot I. (Runs 7, 10 and 11 are not included since the necessary data were not recorded.) It will be seen that the per cent. increase in 20 minutes falls from 16.5 in the first run down to a steady value of about 7 The endin runs 9 and 12. point of the first run was only 40 per cent., but by run 8 the charcoal had become relatively "saturated " with oxygen, and the end-point had risen to 50

TABLE II.

Runs at 400° C.

D		Per Cent.	D. 1 D	
Kun.	P0-	In 20 Min.	In 30 Min.	End-Point.
4 5 6 8 9	425 391 391 	$ \begin{array}{r} 16.5 \\ 12.5 \\ 8.9 \\ \\ 7.2 \\ 7.3 \\ \end{array} $	21·2 16·9 10·8 10·2	40·5 43·2 50·0
12	391	7.3	10.2	

per cent. near which figure it remained in all succeeding runs.

Order of the Reaction and Effect of Varying the Initial Pressure.

Numerous runs, with initial pressures of from 100 to 500 mm were calculated and all were found to give good first order reaction constants. Three examples are given in Table I, having initial pressures of approx. 100, 200 and 500 mm. respectively, and it will be seen that the values of k are indeed constant. And in fact the general conclusion was drawn that the course of all runs involving N₂O and charcoal are accurately first order.

Now, for a strictly first order reaction in which the rate is always proportional to the instantaneous pressure of the reactant, the reaction

TABLE III.

Run.	Þo.	k.

Runs at 400° C.

7	105	0.0124
8	105	0.0129
9	390	0.0081
10	54	0.0125
II	158	0.0102
12	391	0.0077
13	415	0.0069
14	100	0.0100

Runs at 450° C.

52 429 0.73 53 447 0.73 54 112 0.98 55 365 0.85 57 76 1.14 58 68 1.05 59 492 0.69	52 53 54 55 57 58 59	
---	--	--

constant k should not only be constant throughout the course of any one run, but should also be independent of the initial pressure of the reactant.

This latter condition was therefore investigated in a series of consecutive runs at varying initial pressures (p_0) and for two temperatures 400° and 450° C. (See Table III.) The values of k given in the table were calculated on an assumed end-point of 50 per cent., although most of the runs were not actually completed. It is seen that k is not quite independent of the initial pressure : the runs at low initial pressures (100 mm.) show a higher value for kthan the runs at higher pressures (400 mm.). This is difficult to correlate with the fact that the course of each individual run is strictly first order. It is of interest, however, that this phenomenon was also observed by Lambert³ for the reaction of oxygen with charcoal, graphite and diamond.

From the data of the above runs the order of the reaction was also calculated on the basis of the initial rates only and according to the equation

Initial Rate = Constant $\times p_0^n$

where n is the required "Order of reaction with regard to Initial Concentration." On this basis the order of reaction for the runs at 400° C. was approximately 0.7 and for those at 450° C. 0.8.

1377

Summing up, therefore, the reaction is exactly first order with regard to the course of any single run, and is of about 0.75 order with regard to variations in initial pressure. These two statements are incompatible with any mechanism which makes the rate of reaction solely proportional to $[N_2O]^z$ where x is a constant.

The effect of the presence of excess of reaction products on the rate of reaction was next investigated (Table IVA). In these experiments a charge of N_2O was allowed to react completely to form a certain pressure of products; a further charge of N_2O was then let into the bulb in addition to the products, and a run was performed: the reaction constant was then calculated as usual as

$$k = \frac{1}{t} \log_e \frac{p_f - p_0}{p_f - p},$$

TABLE IV.

Run.	Initial Press	k.
	N ₂ O.	Added Gas.

A. ADDED INITIAL PRODUCT.

Runs at 400° C.

15b 16 17 18	193 192 100 100	153 	0.0085 0.0096 0.0092 0.0092
72	105	519	0∙044
73	100	—	0∙068

Runs at 450° C.

56	82	532	0.31
57	86		1.14
58	68		1.05
60	124	515	0.25
61	163	—	0.77
62	87		0.94
63	133	131	0.42
64	134	325	0.32

B. ADDED NITROGEN.

Runs at 400° C.

74 75 76 77 78	89 107 107 1 102 1 108		0.054 0.047 0.062 0.064 0.053
Runs at	450° C.		
79	95	- 1	0.42
80	67		0.49
81	138	442	0.12
82	227		0.46
83	181	374	0.26
N 0		. 1	

except that p_0 is here equal to — the total initial charge of Products + Nitrous Oxide.

It is seen that at 400° C., there is on the whole a slight retardation of the reaction when added product is present, though the effect is not very pronounced. At 450° C., however, added product has a much larger retarding effect.

Experiments were also performed in which nitrogen was added in the place of "product" (Table IVB). It will be seen that N_2 has a similar effect at both temperatures.

Since the retarding effect of N_2 can only be physical in nature, it must be assumed that the retardation due to products is also purely physical. The surface of charcoal must be very intricate and be covered with cracks and pores: if there is a certain amount of inert gas present the reacting gas may not be able to diffuse through this sufficiently rapidly, and the least accessible parts of the surface may be unable to take part in the reaction. The higher the pressure of inert gas present and the higher the absolute speed of the reaction the greater will be this effect, and the smaller the fraction of the total surface which is able to react.

It is, therefore, suggested that all the deviations from first order behaviour recorded above can be attributed to this diffusion effect; apart from this secondary disturbing factor, the interaction of

 N_2O and charcoal can be regarded as strictly first order.

1379

Temperature Coefficient.

A series of 11 runs was performed with Charcoal Lot I to determine the effect of temperature on the rate of reaction. Fig. 1 shows the ressult

in the form of $Log_{10} k$ against $I/T_{abs.}$ The points fall reasonably well on a straight line corresponding to an energy of activation of 30,000 calories, which is close to that of 29,000 found by Lambert³ for oxygen and this charcoal.

Analysis of the Product.

As already explained the yield of oxygen in

the gaseous product from the first few runs with a fresh charcoal may be expected to be less than 100 per cent.

TABLE V.--ANALYSES AND YIELDS OF PRO-DUCTS. (CARBON, LOT III.)

			Anal. Product.		
Run.	₽ 0·	End-Point.	CO2 Per Cent.	CO Per Cent.	O ₂ Yield Per Cent.
67 69 85 87 114	261 256 178 311 307	50·8 50·5 53·6 51·1 50·7	31 31 311/2 311/2 321/2 321/2	0 12 0 1 0	93 <u>1</u> 94 97 97 98

pure CO₂ and N₂ with very little CO.

CO and N₂O.

It appeared somewhat surprising that N₂O containing 1 atom of oxygen, should give a product, CO_2 , containing two. The probability of two N_0O molecules simultaneously hitting one carbon atom is too small for such a mechanism to be possible. The reaction might however take place in two stages, in the first of which N_2O reacts to give CO, which latter is then oxidised in a second and independent gaseous reaction to CO₂, by a further molecule of N₂O. If this be the mechanism then CO should be readily oxidisable by N_2O , and this possibility was, therefore, experimentally investigated (see Table VI).

In these runs CO and N₂O were admitted to the reaction bulb (containing Charcoal Lot III) to the pressures shown in columns 3 and 2. The run was allowed to go to completion and the end-point, shown in the next column, was determined. The end-point is Rise in pressure during run

Initial Pressure N₂O The last column gives the mm. of CO surviving at the end of the run. calculated as follows from the end-point :





Shah, however (Table III, p. 2682

of his paper),² found that even in the 15th run of a series the yield was only 80 per cent.

During the long series of runs performed with charcoal Lot III analyses of the final products were, therefore, made from time to Table V shows that time. there is a definite slight increase in yield of O_2 with the age of the charcoal. After 72 runs the yield has risen to 98 per cent. The product in all the above cases analysed to nearly

The two possible reactions are

(1)
$$2N_2O + C \rightarrow CO_2 + 2N_2$$
.
(2) $N_2O + CO \rightarrow CO_2 + N_2$.

If the whole of the N_2O reacted by (1) the end-point would be 50 per cent., and if by (2) there would be no change in pressure. Therefore, it is possible

TABLE VI.

(Temp. 405° C.)

Run.	N ₂ O mm.	CO mm.	End-Point.	CO Surviving mm.
93	202	327	13.6	180 49 121 10 4 26 103 236 6 15 1 2
97	282	203	22.7	
100	96	197	10.4	
102	414	214	25.4	
112	188	52	37.3	
116	60	54	27.0	
117	340	300	21.0	
118	203	396	10.6	
119	20	10	40	
120	21	21	37	

to deduce from the end-point actually obtained how much N_sO has reacted according to either equation. In the case of the first four runs this method of calculation was checked by analysis of the product, and good agreement obtained.

It is seen that in fact CO is rapidly oxidised by N_2O in the presence of carbon. Thus, in runs 102 and 112 nearly the whole of the CO was oxidised, and it may perhaps be concluded that this will always be the case when the initial N_2O concentration is equal to at least twice the CO concentration.

These results therefore appear not to be inconsistent with gested above. The next experi-

the two stage oxidation mechanism suggested above. The next ex ment leads, however, to a different idea as to the mechanism.

A single run was now performed which showed that N_2O will not react with CO at these temperatures in the absence of carbon. Run 176: Temperature 442° C. (*i.e.* about 40° higher than the runs described above). 304 mm. CO and 302 mm. N_2O admitted to the bulb from which the charcoal had been removed. After 84 minutes there was no change in pressure. Analysis of the product showed CO₂ less than $\frac{1}{2}$ per cent.

This may be contrasted with the results of the runs shown in Table VI. For instance, in Run 97, 154 mm. of CO were oxidised, the run being virtually completed in thirty minutes : in Run 102, 204 mm. of CO were oxidised in approximately forty minutes. It is to be concluded, therefore, that at these temperatures N_2O will oxidise CO only in the presence of charcoal.

The simplest way of accounting for these facts is to suppose that some solid Intermediate Oxide is formed from the interaction of N_2O and the carbon surface, and that this solid oxide is then capable of oxidising the gaseous CO. This idea is developed further in the paper already referred to.¹

Carbon Monoxide and the Surface Oxides.

It might at first sight appear that this Intermediate Oxide would be identical with the Surface Oxides already referred to. It was, however, next shown that CO will not react with the main bulk of the Surface Oxides.

Runs were performed in which CO was admitted to the bulb containing Charcoal Lot III, which, owing to many previous oxidation runs, was fully charged with Surface Oxides. That the surface was so charged may be seen from the results of the "Outgassing of Charcoal Lot III," described below, which immediately succeeded the present experiments. During the Outgassing, oxides were evolved equivalent to a pressure of 365 mm. of oxygen in the silica bulb at 400° C.

The results are shown in Table VII. For the sake of comparison, two of the runs from Table VI with CO and N_2O in the presence of charcoal are included. In the last column is shown the amount of CO₂ formed from

the oxidation of the CO. In those runs (97 and 102) in which N₂O is also present, the amount of CO₂ refers only to that formed from CO oxidation and not to that from the burn-

ing of the carbon with the N_2O . Before each run with CO alone, a run with pure N₂O was performed to assure complete oxidation of the carbon surface.

In those runs in which CO alone was present only a negligible pressure of CO₂ was formed.* It may safely be concluded, therefore, that the Surface Oxides which are stable at the reaction temperature and which survive the end of the oxidation process, will not appreciably oxidise CO. These oxides are, therefore, conveni-

TABLE VII.

Runs at 403° C.

Run.	Initial Pressures.		Time	CO ₂ formed
	со	N ₂ O	(min.)	(mm.).
		j]	
91	355		70	7
97	203	282	~30	154
102	214	414	~40	204
122	431		180	$21\frac{1}{2}$
125	41		240	71
127	46		600	81

ently referred to as The Stable Oxides. The Intermediate Oxide postulated above must therefore be assumed to be so unstable as not to remain on the carbon surface for more than a short time after removal of the N₂O which gave rise to it. It may therefore be referred to as The Labile Oxide.

Out-Gassing of Charcoal Lot III. After Run 127, the silica bulb

Volume of Gas Evolved c.c. at N.T.P. Temp. °C. CO2. CO. Total. 8.0 Up to 600 3.9 11.9 600 to 750 6·0 24.4 30.4 . • 750 to 900 13.2 13.2 41.8 55.8 Total 14

TABLE VIII.

containing the charcoal was heated up slowly to 600° C. then to 750° C., and finally to 900° C., and at each temperature the evolved gases were pumped off, and The quantities analysed. and analyses of the gases evolved are shown in Table The total oxides VIII.† evolved correspond to 35 c.c. of oxygen; and since there was about 1.4 g. of charcoal in the bulb, this would be equivalent to 25 c.c. of

Therefore in this sample, one atom in forty is oxygen, oxygen per gram. and the empirical composition is $C_{40}O_1$.

Schilow's Oxides.

Schilow and his co-workers 5 report the existence of acid and basic oxides on the surface of carbon which has been heated in oxygen at various temperatures. Charcoal Lot I, after having served for 30 Runs with pure N_2O , was therefore examined to see if it would combine with acids and alkalis in the manner of the charcoals treated by Schilow. After 30 runs there is every reason to suppose that Surface Oxides would have been

* No change of total pressure was recorded in any of these runs; it must be concluded, therefore, that the small quantities of CO2 produced must have resulted from the oxidation of CO by surface oxides and not from the reaction

 $2 \text{ CO} = \text{C} + \text{CO}_2$. † Other workers have repeatedly shown that CO₂ and CO are not sorbed by charcoal at 400° C. (See Shah,² p. 2672, and Rhead and Wheeler,⁴ p. 467). This is mentioned to avoid any misapprehension as to the origin of the \overline{CO}_2 and CO in the present experiment, which are of course derived from the decomposition of solid oxides formed originally by the interaction of N₂O and solid carbon. ⁴ Rhead and Wheeler, J.C.S., 1913, Tr., 1, 461. ⁵ Schilow, Kolloid Z., 1930, 52, 107; Z. physik. Chem., 1930, 149, 211.

formed, comparable in quantity to those found on Lot III (in which case 25 c.c. of oxygen were "fixed" per gram.).

0.5 g. of Charcoal Lot I was violently shaken for $\frac{1}{2}$ hour in a mechanical shaker with 25 c.c. of N/50 NaOH solution. The soda was then decanted from the charcoal, and a measured portion titrated with N/50 HCl using phenol phthalein as indicator; 18 per cent. of the soda had been absorbed by the charcoal.

In the same way a further 0.5 g. of the same charcoal was shaken with 25 c.c. N/50 HCl, and the amount of acid which had combined with the charcoal was determined by titration against N/50 NaOH using phenol phthalein; $22\frac{1}{2}$ per cent. of the acid had been absorbed by the charcoal.

Schilow reported similar results with a charcoal treated at 450° C., and in his experiments the amounts of acid and alkali absorbed were of the same order of magnitude.

The volume of O_2 to which the basicity of this charcoal is chemically equivalent was calculated; the basicity of I g. of the charcoal is equivalent to about II c.c. of N/50 acid, which is chemically equivalent to 2.5 c.c. of gaseous O_2 at N.T.P. The acidity of the charcoal is likewise equivalent to about 2 c.c. O_2 . The data, therefore, of this single experiment tend to show that a not very large proportion of the whole of the Surface Oxides has these acidic-basic properties.

Discussion of Certain of the Experimental Results.

In the course of the paper already referred to,¹ mechanisms are put forward for the oxidation of C by N_2O and for the oxidation of CO by N_2O in the presence of C: these mechanisms are shown schematically below:

Stage I: (common to both reactions):

 N_2O gas + C solid = Solid Intermediate Oxide + N_2 gas (a rapid reaction compared to the second stage reactions).

Stage II:



(both of these are slow first order reactions).

In order to account for the fact that the interaction of N_2O and carbon is of the first order, one of the two stages of the reaction must be far more rapid than the other, and it is natural to assume that the first stage is the rapid one from a consideration of the nature of the two stages. For, during the combustion of C it may be supposed that the surface C atoms are progressively removed, and must leave behind free valencies. These free valencies (which can be compared to free radicals), will then react with gaseous N_2O , to give the Intermediate Oxide. Stage I, therefore, involves the decomposition of the N_2O molecule, and the combination of the O with a free C valence (the latter probably a strongly exothermic process). In stage 2 a further molecule of N_2O is decomposed, and the resulting O must combine with the C atom of the Intermediate Oxide, which no longer has any free valence; the bonds, which hold the C atoms in the lattice, must also be broken (this latter part being a strongly endothermic process). These considerations point clearly to the second stage being a slow one compared to the first.

Recently a considerable amount of data has been published concerning the surface area of the crystalline particles of activated carbons (see, for instance, Berl⁶). These data tend to show that, as a whole, activated charcoals have a crystal surface area of between 1000 and 2000 sq. metres per gram, corresponding to an extremely small crystal containing only some hundreds of C atoms. The rate of a first order heterogeneous reaction is sometimes assumed to be given by an expression such as :

Number of gram-moles reacting per second = $(\alpha s)ne^{-E/\mathbf{R}T}$ where E = activation energy, s = total area of crystal surface, α = fraction of total surface which takes part in the reaction, n = number of grammoles of gas hitting one square centimeter of surface in one second.

 (αs) is therefore that part of the total area of the solid which takes part in the reaction. Inserting in this formula data for Charcoal Lot I (k = 0.01 in minutes per 2 g. charcoal at 400° C., activation energy 30,000 calories), (αs) is found to be of the order of $\frac{1}{2}$ sq. metre, for I g. of charcoal. If we take 1500 sq. metres as an average value for s, we obtain $\alpha = 1/3000$. This calculation, therefore, leads to the conclusion that 1/3000th only of the total surface takes part in the reaction. Without attaching too much significance to this type of calculation, we may conclude that the Labile Oxides cover at least 1/3000th part of the whole surface.

It is also of interest to consider what fraction of the total surface can be covered by the Stable Oxides. It has already been shown above that Stable Oxides corresponding to I atom of O per 40 atoms of C can be fixed on the surface of a thoroughly oxidised charcoal. Assuming that one atom of O is held by one surface C atom, that the C crystal contains 450 atoms (corresponding to a surface area of about 1500 sq. metres), and that it is of average shape, then approximately I atom in 25 on the surface of the C attaches an O atom. Even in a carbon largely "saturated "with surface oxides, therefore, the actual proportion of O atoms in the surface is very small. This is very different from the picture frequently drawn of the carbon surface completely covered with sorbed O atoms; the general conclusion to be drawn is that only very few points on the surface of the carbon are available at any one time for the attachment of O atoms for the formation of either Stable or Labile Oxides.

The rôle played by the Stable Oxides is also of great importance. Rhead and Wheeler ⁴ concluded that the Stable Oxides serve as *inter-mediate* compounds in the oxidation of C by O, and are continually formed and decomposed again during the reaction. Other writers have taken an opposite view : in particular, Barrer⁷ maintains that, in the oxidation of diamond, the Stable Oxides are bye-products, and in fact retard the reaction. The latter view is supported by the present work. The mechanism here proposed involves definite intermediate compounds which are distinct from the Stable Oxides : the formation of Stable Surface Oxides is regarded as an alternative reaction, and not as a step in the main reaction.

> ⁶ E. Berl., *Trans Faraday Soc.*, 1938, **34**, 1040. ⁷ Barrer, *J.C.S.*, 1936, 1261.

Summary of Experimental Results.

The experimental work described in this paper may be summarised as follows :

1. Nitrous Oxide reacts with charcoal at 400° C. in two ways :

(a) As the main reaction the charcoal is oxidised to give CO_2 and N_2 (there being usually also produced a very small amount of CO).

(b) Concurrently the N_2O acts on the carbon surface to give the solid Surface Oxides. This is a subsidiary reaction, and the possibility of its occurrence depends largely on the amount of oxides already formed.

2. The main reaction between charcoal and $\mathrm{N}_2\mathrm{O}$ is predominantly of the first order.

3. The reaction is retarded both by excess "Products" and also by added N, especially when the absolute rate of the reaction is high.

4. The heat of activation of the main reaction is about 30,000 cal.

5. CO is shown to react rapidly with N_2O at 400° C. in the presence of charcoal, but not at all in its absence.

6. CO is hardly at all oxidised by the Stable Surface Oxides.

7. Acidic-basic oxides of the type discovered by Schilow are shown to be present, although of the total surface oxides only a small proportion belong to this type.

The writer wishes to express his special thanks to Prof. C. N. Hinshelwood for his advice and help throughout the work described in this paper.

The work described above was carried out as part of the programme of the Fuel Research Board and is published by permission of Dr. F. S. Sinnatt, Director of Fuel Research.

Oxford.