

PROGRESS IN NUCLEAR ENERGY

SERIES IV

**TECHNOLOGY,
ENGINEERING
AND
SAFETY**

VOLUME 2

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CHEMICAL STUDIES OF CARBON DIOXIDE AND GRAPHITE UNDER REACTOR CONDITIONS

By *A. R. ANDERSON, †H. W. DAVIDSON, ‡R. LIND, §D. R. STRANKS,
||C. TYZACK and ¶J. WRIGHT

1. The first stage of the development of nuclear power in the United Kingdom has been based on the use of graphite as moderator and carbon dioxide gas as coolant. In the designs of Calder Hall and of the first reactors for the Central Electricity Authority these two components are in contact with the reactor core. Many chemical studies have been undertaken to determine the behaviour of these materials under operating conditions, the probable limits set by compatibility, and possible methods of extending those limits. The present paper brings together details of five such studies.

2. Part I is concerned with the chemical behaviour in the absence of radiation and at temperatures below those at which gasification of the carbon is significant. Part II describes techniques for protecting reactor grade graphite from attack by carbon dioxide at higher temperatures and gives the results of tests of these protected graphites under radiation. Part III deals with the effect of radiation on the graphite-CO₂ system and describes some experiments in a model channel designed to simulate reactor operating conditions. In Part IV results obtained during the start-up of the Calder Hall reactors are given. The work described in Part V on exchange reactions between C¹⁴O and CO₂ was not originally conceived as part of this programme, but the results provide valuable background information assisting the interpretation of the radiation-induced reaction between graphite and carbon dioxide.

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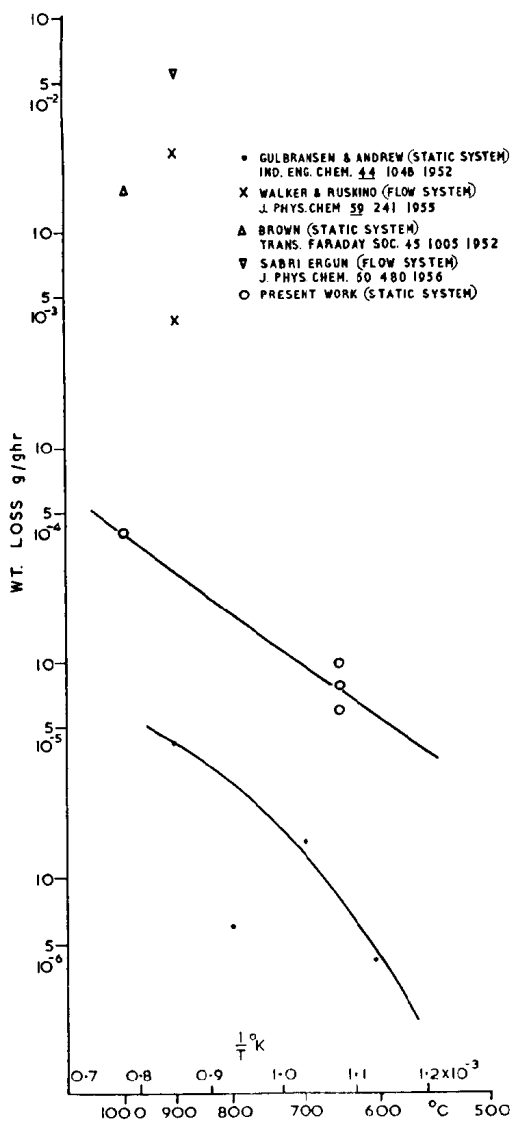


FIG. 1. Reaction of graphite with carbon dioxide. Rates selected from literature

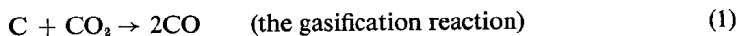
PART I

*THE REACTION OF GRAPHITE WITH CARBON DIOXIDE
AT TEMPERATURES NEAR 500°C

By T. B. COPESTAKE, H. W. DAVIDSON and B. L. TONGE

Introduction

3. Investigations of the reaction between carbon and carbon dioxide have generally been confined to the temperature region where the overall reaction can be written:



It has been shown that the first step in this reaction is the formation of a surface oxide^(1, 2, 3)

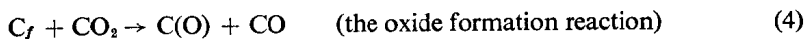


which subsequently decomposes removing a carbon atom from the solid:



Using C^{14}O_2 Bonner and Turkevich⁽⁴⁾ showed that surface oxide formation was a faster reaction than the oxide decomposition. Sabri Ergun⁽⁵⁾ interpreted the results for a variety of carbons in terms of the existence of different numbers of "active sites" on the surface, and obtained values for the equilibrium constant for reaction (2) and the rate constant for reaction (3). It has been our object to investigate the properties of these active sites and surface oxides on amorphous carbon and graphite.

4. Fig. 1 shows a selection of gasification rates for graphite taken from the literature and from our own gravimetric measurements. It is clearly difficult to extrapolate these results to 500°C. The results of the present work are consistent with the view that at temperatures near 500°C the available measurements can be interpreted in terms of the formation of a surface oxide. According to this view, carbon dioxide decomposes on the carbon surface and deposits an oxygen atom on an "active site". The reaction thus results in the formation of an oxidized "active site" and the evolution of carbon monoxide:



where C_f represents an "active" carbon atom and C(O) an oxidized "active site".

5. The gasification and the oxide formation reactions can be distinguished as follows:

(a) Reaction (1) involves a volume change of the system, but reaction (4) does not. However, the measurement of gasification rates by volume changes may be masked by the adsorption or desorption of carbon monoxide, carbon dioxide and other gases.

(b) In a closed system the progress of reaction (1) will be limited by the equation $K = (\text{CO})^2/(\text{CO}_2)$. Fig. 2 illustrates values of the composition of carbon monoxide: carbon dioxide mixtures which are in equilibrium with graphite. This equilibrium composition will be independent of the amounts of carbon and gas present and should be only slightly affected by the amount and the

*Communication from the staff of the Research Laboratories of the General Electric Company Limited, Wembley, England.

kind of gas which is adsorbed on the graphite. On the other hand, if oxide formation occurs to the exclusion of gasification, then the gas composition will be controlled by the following equilibrium:

$$K = \frac{[C(O)] \cdot [CO]}{[C_f] \cdot [CO_2]} \quad (5)$$

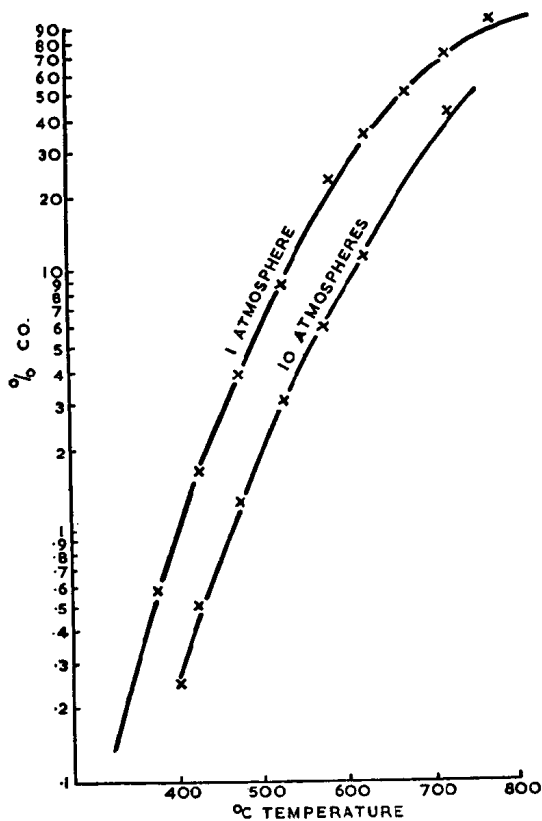


FIG. 2. Concentration of CO at equilibrium in the system C—CO—CO₂ (Calculated from selected values of physical thermo-dynamic properties of hydrocarbons and related compounds
American Petroleum Inst. Pro. 44, Carnegie Press, Pittsburgh)

where $[C_f]$ and $[C(O)]$ refer to the surface concentrations of the free and oxidized sites. If $C_f + C(O) = T$ (where T is the maximum number of possible active sites), and if carbon monoxide will reduce an oxidized site back to its original active state, it then can be shown (Appendix I) that the equilibrium value of the gas composition will depend on the ratio of gas to graphite in the system. More precisely, the gas composition will depend on the value of T and on the way in which it is apportioned between free and oxidized sites. In fact, the gas composition is more sensitive to variations of the gas:graphite ratio the lower the degree of oxidation of the surface and the lower the gas to graphite ratio. For a given value of this ratio the concentration should be independent of the pressure.

- (c) If gasification takes place, then repeated applications of carbon dioxide to graphite in an evacuated closed system will always result in the evolution of the same total amount of carbon monoxide. If, on the other hand, oxide formation takes place to the exclusion of gasification, the equilibrium (5) permits a forecast of the gas composition under these circumstances. Repeated applications of CO_2 to the graphite will result in a progressively higher degree of oxidation of the graphite surface. According to the equilibrium (5), therefore, the final carbon monoxide concentration will fall steadily for each application. In the same way, if fresh carbon monoxide is repeatedly applied to a graphite surface, the carbon dioxide concentration will follow a similar sequence.
- (d) It is not clear how the extent of the gasification reaction will depend on the gas content of the carbon. In the case of the oxide formation the gas content of the carbon will play an important and predictable role. In particular, if it is assumed that a large proportion of the gas content of carbon and graphite is associated with surface oxide, then it is reasonable to expect that a graphite of high gas content will evolve only a little carbon monoxide when exposed to carbon dioxide but a large amount of carbon dioxide when exposed to carbon monoxide. In fact, a carbon monoxide treatment at 500°C should reduce the gas content of graphite.

Experimental

6. *Materials*—Amorphous carbon and nuclear grade graphite were used in the investigation. The amorphous carbon was prepared from ground petroleum coke (about 30% less than 200 mesh) hot pressed with 20% of pitch and calcined at 1000°C . Carbon dioxide was obtained from solid carbon dioxide by repeated vacuum distillation in a liquid air trap. Carbon monoxide was obtained either from commercially available cylinders or by reacting degassed formic acid with sulphuric acid.

7. *Analysis*—Gaseous reaction products were analysed by several methods. Samples containing 1 to 10% CO_2 in CO were examined by the modified Haldane gas analysis system⁽⁶⁾. Samples containing 0.1 to 5% CO in CO_2 were analysed by circulating the gases through a liquid air trap and measuring pressure changes with the aid of a modified McLeod gauge. The carbon monoxide was subsequently oxidized on hot copper oxide and the resulting CO_2 was frozen, re-evaporated and remeasured. This apparatus also provided an estimate of gases other than CO and CO_2 , so that experiments could be rejected if leakage had occurred in the reaction systems. A simple apparatus depending on the measurement of pressure with a Pirani gauge was used for the determination of gas not condensable at liquid air temperature (usually CO). This was effective when the percentage of this constituent was very low (down to 10 ppm). A later form of this apparatus incorporated a hot oxide-covered copper wire to permit a direct determination of carbon monoxide. An infra-red gas analyser of the Luft type (made by the Infra Red Development Company Limited) was also used to determine CO particularly when continuous readings were required.

8. *The measurement of gas content*—The gas contents of the carbons were determined by heating cylindrical specimens (approximately 3 cm \times 1 cm dia.) to about 1300°C in a quartz tube with an eddy current generator. The evolved gas was pumped away rapidly by means of two mercury diffusion pumps, a three-stage pump backing a high-speed single-stage version. The gas was collected in an evacuated reservoir where the pressure could be measured with a McLeod gauge. Entrained air was removed prior to the measurements by evacuating to a pressure of less than 10^{-5} mm Hg with the carbon cold.

9. *The volumetric apparatus* comprised a quartz vessel fitted with a gas burette and connected to another similar vessel by a U-tube manometer. Volume changes as small as $2\mu\text{l}$. could be estimated on the Haldane burette which was sealed with mercury. The pressure of the gas in the test bulb (which held the graphite specimen) was equalized with that in the compensating bulb before carrying out a volume measurement. The sensitivity necessary for the pressure adjustments was obtained by observing the reflection of a stylus in the surface of the mercury in the U-tube manometer. The test and reference bulbs fitted into holes in a large copper block which itself occupied the central position of a vertical tube furnace and ensured an adequate temperature distribution. A platinum resistance thermometer controller maintained the operating temperature. The burette and manometer were immersed in a thermostat bath.

10. *Gas circulation apparatus*—About 200 g of carbon were held in a vertical quartz tube heated in a furnace, the temperature being controlled to $\pm 3^\circ\text{C}$ by means of a platinum resistance thermometer controller. The apparatus could be thoroughly evacuated and then filled with gas. The gas was circulated through the bed of carbon and then through the infra-red gas analyser by means of a totally enclosed diaphragm pump. The leakage rate into the entire system did not exceed 10^{-6} l. $\mu\text{Hg}/\text{sec}$.

11. *Experiments with rotating discs*—In order to investigate the effect of the flow rate of carbon dioxide over the graphite, an apparatus was constructed in which a graphite disc (5 mm thick and 10 cm dia.) could be rotated in an atmosphere of carbon dioxide. A split annular graphite disc with its plane parallel to the first disc was heated to 500°C by means of a current of about 100 A. The rotating disc was mounted on the shaft of a sealed rotor taken from a therapeutic X-ray tube and would revolve at 3000 r.p.m. The discs were mounted in a brass vessel closed with an O-ring seal. The temperature of the rotating disc could be measured photometrically by observation through a window in the top of the case and was found to be about 350°C when the stationary disc was at 500°C and 5 mm from the rotating disc.

12. *Lamp experiments*—The lamps were of two types. Standard commercial carbon filament lamps (ungettered) were equipped with break seals and pumping stems. They were degassed at about 300°C with a mercury diffusion pump and were then filled at room temperature with carbon dioxide to a pressure of one atmosphere. The current and voltage were measured periodically and the temperature distribution was observed by a specially developed technique relying on infra-red photography. In a later development, lamps with graphite strip filaments ($1.5\text{ mm} \times 0.5\text{ mm} \times 15\text{ cm}$) were constructed by joining copper leads to the graphite with flame-sprayed copper. The leads were cold welded through two glass-to-copper seals at either end of a Pyrex glass tube which was again provided with a break seal and pumping stem.

13. *Gravimetric experiments*—A quartz spring balance capable of weighing to 0.5 mg was used to determine changes in weight of carbon specimens weighing about 1 g. The apparatus consisted of a quartz tube mounted vertically in a furnace. The spring was suspended from the top and the carbon specimens, attached to the bottom of the spring by long quartz fibres, hung down into the centre of a furnace. The all-glass apparatus could be thoroughly evacuated before filling with carbon dioxide.

14. *Experiments with quartz bulbs*—The quartz bulbs were of about 80 cc capacity and held about 10 g of carbon. They were evacuated, filled with gas and sealed. The gas could be removed for analysis at the end of the experiment by means of a break seal. These vessels were suspended in a large furnace controlled to $\pm 10^\circ\text{C}$ by a bimetallic strip controller.

15. *Surface oxide determinations*—By passing a stream of carbon monoxide over carbon heated to 500°C , it was possible to determine the surface oxide content of

the sample by estimating the carbon dioxide produced. Carbon monoxide from a cylinder was passed through a furnace heated to 1000°C and packed with platinum wire to convert any oxygen to carbon dioxide. This was removed by two liquid air traps and the oxygen-free gas then passed to the furnace at 500°C containing the carbon specimen and out through two bubblers containing $0.1N$ baryta. Provision was made for sweeping the bubblers with nitrogen during filling with baryta and titration with standard potassium hydrogen phthalate. The carbon specimen could be moved into and out of the hot zone of the furnace magnetically, thus enabling "blank" runs to be performed without opening the apparatus. There was provision for evacuating the apparatus with a mercury pump and the carbon was degassed at

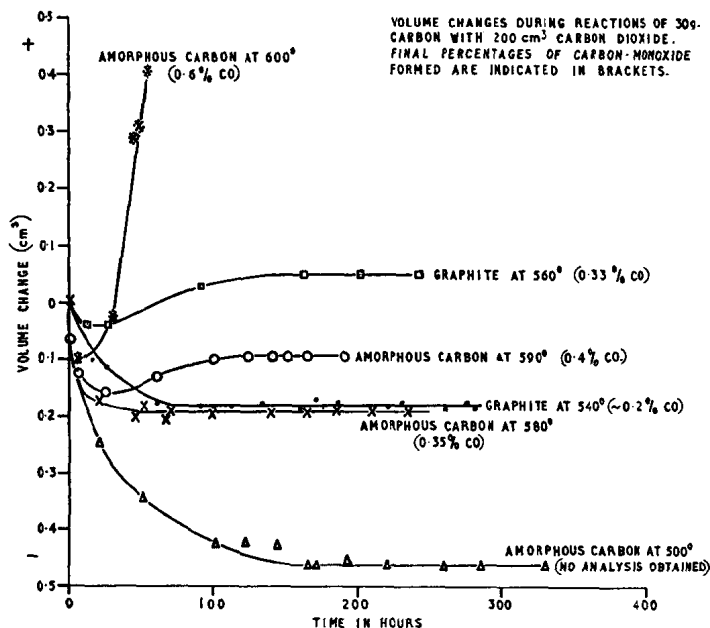


FIG. 3. Volume changes in the system carbon: carbon dioxide

500°C for about 8 hours before passing carbon monoxide. The weight of the specimen was 1 to 10 g depending on the expected oxygen content. Runs lasting several days were usually necessary before no further carbon dioxide was evolved.

Results

16. Fig. 3 shows the results of measurements on amorphous carbon and graphite in the volumetric apparatus. An initial volume decrease is apparent at all temperatures and this must be the result of adsorption. When this transient condition has been passed no continuous increase in volume can be measured. The final carbon monoxide concentration in the gas falls short of that predicted for the gasification reaction on thermodynamic grounds. Gasification, if it takes place, will therefore still be proceeding at a finite rate. To a first approximation this rate will correspond to the carbon monoxide build-up averaged over the time of the experiment and will then result in a volume increase which can be readily measured by the apparatus. It might, however, be argued that the carbon monoxide has been built up by means of the gasification process but that this process is inhibited by the presence of carbon monoxide. This is, however, considered unlikely as it has been found that there is

no such retardation arising from the presence of carbon monoxide at a temperature of 600°C when gasification is indeed observable. Further, experiments with the gas circulation apparatus (Fig. 4) have demonstrated that the rate of carbon monoxide build-up does indeed decrease. The deceleration is not a unique function of the carbon monoxide concentration, but depends also on the degree of oxidation of the carbon surface.

17. Results similar to those described have also been obtained with pure graphite as starting material. In this case gasification became noticeable at a temperature of about 625°C. Amorphous carbon and graphite, therefore, both begin to gasify at a similar temperature.

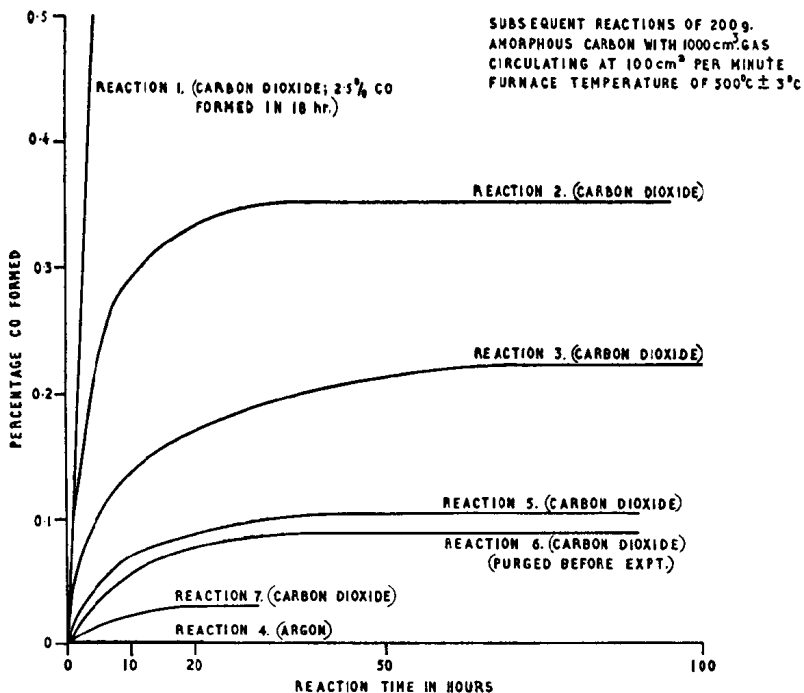


FIG. 4. Carbon monoxide evolved from amorphous carbon at 500°C in circulating carbon dioxide

18. Fig. 4 shows the results of measurements on amorphous carbon in a circulating current of carbon dioxide. It is clear that the production of carbon monoxide diminished as successive atmospheres of fresh carbon dioxide were admitted to the carbon and that the reaction was not inhibited in a way which depended on the carbon monoxide concentration alone. The gas composition reached a steady limiting value except in the first experiment where the values were too large to measure continuously. These observations are consistent with the view that the surface is being progressively oxidized and the final gas concentrations are in qualitative agreement with the requirements of equation (5).

19. It might be argued that a measurement as sensitive as that of the infra-red analyser could be misleading in view of the high inherent gas content of amorphous carbon and graphite (*cf.* Fig. 5). The carbon monoxide measured represents only

a fraction of the potential carbon monoxide content. Large errors are, therefore, possible if any gas liberation occurs during the experiment. To show that the results are not misleading, the system was thoroughly evacuated and filled with pure argon. The results are shown as run 4 in Fig. 4 and demonstrate that no carbon monoxide arises from desorption. The experiment was bracketed by runs 3 and 5 which exhibited carbon monoxide evolution characteristic of oxide formation.

20. Table 1 summarizes a set of experiments in another similar gas circulation apparatus. The material was a graphite regraphitized at 2800°C and cooled in a stream of argon. It is clear from experiments (1), (2) and (3) that this material exhibits no measurable reaction with carbon dioxide at temperatures below 625°C. The onset of the reaction at 625°C appears to have produced "active sites" since carbon monoxide evolution is now observed at 575°C and 600°C (runs 5 and 6) in

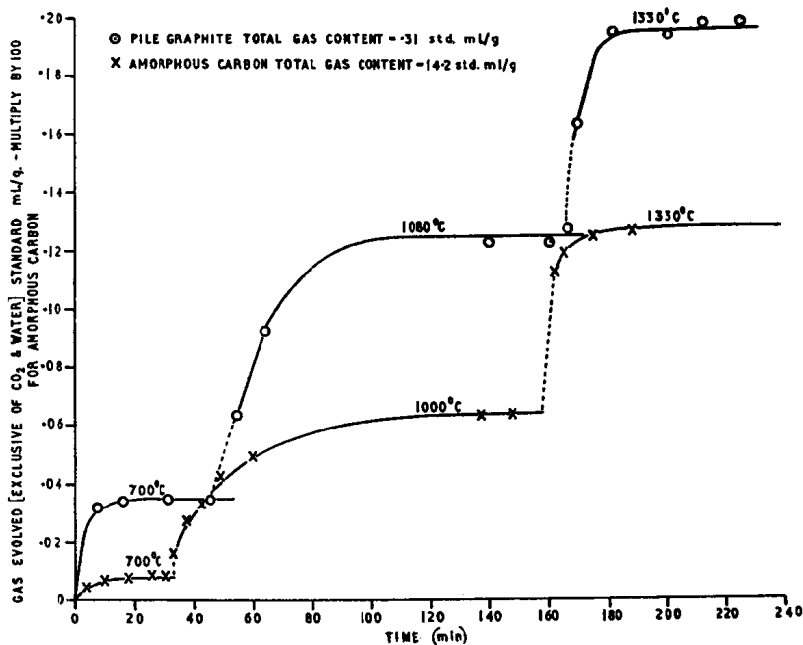


Fig. 5. Gas evolution from pile grade graphite and amorphous carbon

subsequent experiments. The carbon dioxide was replaced by carbon monoxide and the evolution of carbon dioxide in experiments 7 to 11 is recorded. No comparable pressure changes could be observed on the mercury manometer attached to the system in spite of the relatively large concentrations of carbon dioxide produced.

21. Inspection of Table 1 reveals that appreciably more surface oxide is being reduced in runs 7 to 11 than was deposited on the graphite in experiments 4, 5 and 6. It must, therefore, be assumed that the high temperature treatment was ineffective in removing all the surface oxide. The fact that the gas content of the re-graphitized material as measured by high vacuum treatment at 1300°C is negligible (Table 3) merely means that this process does not account for all the oxide on the graphite.

22. The sequence of analyses in experiments 7 to 11 is comparable to those shown in Fig. 3. Clearly the gas is tending to reach equilibrium with the surface, which is progressively reduced after each admission of fresh gas.

23. Table 2 presents the results of an investigation during which graphite samples were exposed to carbon dioxide or carbon monoxide sealed in quartz vessels. Experiments 1 to 10 show that the carbon monoxide concentrations tend to build up to higher limiting values, the higher the degassing temperature of the graphite. According to the present viewpoint, pretreatment at temperatures up to 1750°C would be expected to decompose the oxidized sites with the simultaneous creation of active sites. Subsequent exposure to carbon dioxide would, therefore, result in larger concentrations of carbon monoxide, as are indeed found. Eventually, heat treatment at graphitizing temperatures results in the destruction of the active sites and consequent loss in reactivity as shown in experiments 11 and 12.

24. Experiments 1, 2 and 3 of Table 2 demonstrate the effect of varying the gas to graphite ratio which has been achieved by altering the pressure. The results indicate that the carbon monoxide concentration falls as the gas to graphite ratio rises in accordance with the theory (*cf.* Appendix I).

TABLE 1

The Behaviour of Graphite in Recirculated Gases

Material: 200 g graphite regraphitized in argon at 2800°C
 Volume of system: 1 l.
 Gas pressure: 1 atmosphere
 Gas flow rate: 100 ml. (N.T.P.) min

No. of expt.	Gas	Temp. of graphite °C	Gas composition (% v/v)	Time (hr)	Gas composition (% v/v)	Time (hr)
1	CO ₂	450	10 ⁻² CO	80	10 ⁻² CO	140
2	CO ₂	500	10 ⁻² CO	80	10 ⁻² CO	140
3	CO ₂	575	10 ⁻² CO	80	10 ⁻² CO	140
4	CO ₂	625	1.1 CO	80	1.9 CO	140
5	CO ₂	575	0.25 CO	80	0.45 CO	140
6	CO ₂	600	0.45 CO	80	0.80 CO	140
7	CO	550	10 CO ₂	96		
8	CO	550	8.5 CO ₂	70	8.9 CO ₂	96
9	CO	550	5.0 CO ₂	96	4.8 CO ₂	146
10	CO	550	2.2 CO ₂	90	2.3 CO ₂	134
11	CO	550			1.5 CO ₂	115

25. Experiments 3, 4 and 13 to 16 demonstrate the effect of successive applications of carbon dioxide, carbon monoxide and carbon dioxide to a graphite. It can be seen that the carbon monoxide treatment raises the reactivity of the graphite during the subsequent exposure to carbon dioxide. Since the carbon monoxide would produce a reduced and "active" surface, this is again in accordance with the theory. The magnitude of the effect on the reactivity can be qualitatively predicted as outlined in Appendix I and in Fig. 35. Assuming reasonable values for the various constants, it appears that a threefold increase in the ratio of occupied to free sites would produce an effect similar to that found.

26. Experiments 17 to 22 demonstrate the same effect for the converse treatment, namely, the successive application of carbon monoxide, carbon dioxide and carbon monoxide to a degassed graphite. Comparison of experiments 13 to 14 and 17 to

TABLE 2
Effect of Degassing and Re-graphitization on Reaction of Pile Grade Graphite with CO₂ at 500°C

No. of expt.	Treatment	Wt. of carbon (g)	Vol. of bulb (ml.)	Pressure at room temp. (cm Hg)	Reaction with	Time (hr)	Vol. % CO	Vol. % CO ₂	ml. (N.T.P.) of reaction product
1	Degassed 500°C	10	80	5	CO ₂	168	0.19		
2	"	10.05	83	10	CO ₂	168	0.14		
3	"	11.09	83	25	CO ₂	168	0.057		
4	"	11.64	86	25	CO ₂	168	0.09		
5	"	7.5	68	25	CO ₂	65	0.015		0.0032
6	"	7.5	81	25	CO ₂	120	0.025		0.0064
7	" 1400°C			25	CO ₂	195	0.09		
8	"	11.25	87	25	CO ₂	425	0.10		0.027
9	" 1780°C			25	CO ₂	195	0.13		
10	"	11.7	82	25	CO ₂	425	0.22		0.056
11	Re-graphitized	7.9	79	25	CO ₂	65	0.005		0.0012
12	"	7.9	73	25	CO ₂	120	0.005		0.0012
The effect of alternate oxidation and reduction at 500°C									
3	Degassed 500°C	11.09	83	25	CO ₂	168	0.06		0.015
4	"	11.64	86	25	CO ₂	168	0.09		0.024
13	" cold	11.09	83	25	CO	89		93.2	24
14	"	11.64	86	25	CO	89		76.7	20
15	"	11.09	83	25	CO ₂	91			0.035
16	"	11.64	86	25	CO ₂	91			0.027
17	" 1400°C	11.19	81	25	CO	89		6.8	1.7
18	"	10.28	79	25	CO	89		7.8	2.0
19	" cold	11.19	81	25	CO ₂	89	0.3		0.075
20	"	10.28	79	25	CO ₂	89	0.2		0.049
21	"	11.19	81	25	CO	89		20.5	5.15
22	"	10.28	79	25	CO	89		50.0	12.2