

THE REACTION OF GRAPHITE "WEAR DUST" WITH CARBON DIOXIDE AND OXYGEN AT LOW PRESSURES

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SOMMAIRE

Les techniques de spectrométrie de masse sont utilisées pour étudier la réaction du graphite *Wear dust* sur le gaz carbonique à des pressions de départ de 2,7 à 16 microns de mercure, et sur l'oxygène à des pressions de départ de 30 à 35 microns de mercure. La sensibilité du système de mesure est assez grande pour permettre l'étude des réactions du gaz carbonique et de l'oxygène à des températures aussi faibles que 350 et 150 °C respectivement.

Pour le gaz carbonique, on a trouvé que la réaction est d'ordre un en ce qui concerne la consommation du gaz carbonique, à toutes les températures étudiées. Le taux de production d'oxyde de carbone est presque le double du taux de consommation de gaz carbonique. L'écart constaté est attribué à la chimisorption d'une petite quantité d'oxyde de carbone au cours de la réaction.

On a trouvé que la réaction sur l'oxygène est d'ordre un en ce qui concerne la consommation d'oxygène à une température de 500 °C; cependant, à 200 °C, on a noté un effet de diminution de la constante de vitesse effective en raison de la formation d'une grande quantité de complexe superficiel stable. Le complexe superficiel a une énergie d'activation de désorption variable. Les réactions du graphite *Wear dust* sont catalysées par le fer introduit dans le matériau pendant le processus de broyage. Un mécanisme est proposé pour expliquer l'activité catalytique du fer.

Introduction.

The carbon «wear dust» produced by the fine grinding of graphite (1) is an interesting material to use for the study of the reaction of carbon with oxidizing gases because of its high reactivity. In order to study the reaction of carbon with carbon dioxide and oxygen with particular emphasis on the role of any surface oxide intermediates, certain factors must be considered. Since the surface complex is unstable at high temperatures, the reactions should be carried out at temperatures as low as possible in order to maximize the probability of surface oxide formation. The amount of gas necessary to completely cover a carbon surface is relatively small [approximately 10 micromoles per square meter for carbon monoxide as the adsorbate (2)]. Therefore, the relative change in pressure resulting from the formation

of a given amount of surface complex can be maximized by operating at low pressures. A sufficient number of the reaction variables have to be measured to be able to compute a complete material balance throughout the progress of the reaction. Furthermore, the measuring system has to be sensitive enough to detect small amounts of reaction in order to minimize the effect of changing surface area during the course of the reaction.

For this investigation, the reaction of carbon with carbon dioxide was followed in the temperature range of 400° to 700 °C and at initial pressures ranging from 2,7 to 16 microns of mercury. The reaction of carbon with oxygen was followed in the temperature range of 200 to 500 °C at initial pressures of 30 to 35 microns of mercury.

Apparatus and Experimental Procedure.

Figure 1 shows a schematic picture of the low pressure reactor. The tubing in the system is 1 1/4

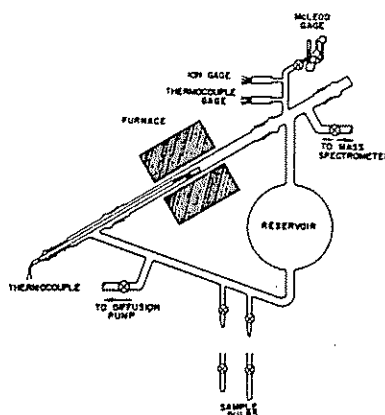


Fig. 1. — Low Pressure Reactor.

inches in diameter; the volume of the system is 16,6 liters. The fused silica reactor tube is set at an

angle of 45° so that thermal convection will aid in the mixing of the reacting gases. The system can be evacuated to pressures of 10^{-5} mm Hg using an oil diffusion pump.

There are three pressure measuring devices — an ionization gauge, a thermocouple gauge, and a McLeod gauge. Since the mass spectrometer measures partial pressure of all gases present, it also can be used as a pressure measuring device.

The carbon sample is placed in a 1×5 cm fused silica tube sealed at one end. The sample container can be lowered into the reaction tube through a sample port in the upper part of the apparatus. The sample container rests on a fused silica tube, which extends upwards from the bottom of the reaction tube. This support tube also contains a chromal-alumel thermocouple. The cap for the upper port in the reactor contains a Pyrex optical-flat window through which the sample can be observed.

The sample is heated by a 1 kw tube furnace which surrounds the reaction tube. The furnace is $8 \frac{3}{4}$ inches long. The temperature of the furnace, as indicated by the thermocouple in the sample support tube, is regulated by an automatic controller-recorder.

The mass spectrometer has been modified so that the reactor can be directly connected to the inlet leak of the spectrometer analyzing tube. Under the conditions used in this investigation, the spectrometer bled off less than two per cent of the total gas present during the course of a run.

A programmed magnetic field controller was constructed to enable the mass spectrometer to sequentially monitor the mass 44 (CO_2^+), the mass 32 (O_2^+) and the mass 28 (CO^+) ion beam every 15 seconds.

In order to determine the time constant of the analyzing system, the reactor was filled with carbon monoxide to a pressure of 8 microns of mercury; and a 5% increment of carbon dioxide was admitted into the reactor. By adjusting the mass spectrometer to monitor mass 44 (CO_2^+), the time taken for the 44 peak to reach a steady state gives an idea of the rate of diffusion and mixing of the gases in the reactor. It was found that the initial response of the spectrometer was practically instantaneous, with a steady state value obtained within 5 seconds.

The carbon used for this investigation was a highly ground sample of SP-1 spectrographic graphite (*). The spectrographic graphite was ground (**) for 16 hours in a vacuum ball mill in order to increase its surface area, as described by WALKER and SEELEY (1). After grinding, the area of the graphite wear dust was $560 \text{ m}^2/\text{g}$. The grinding process introduced ca 5 per cent iron into the sample.

(*) The unground SP-1 sample was supplied by the National Carbon Company.

(**) The SP-1 sample was ground through the courtesy of Mr. S. B. Seeley of the Joseph Dixon Crucible Company.

The carbon sample was heated to a temperature of 850°C in vacuo for 3 hours prior to each run. This pretreatment insured that the gases evolved upon the heating of the sample at the end of each run were a result of the reaction and not the past history of the carbon.

Results and Discussion.

The Carbon-Carbon Dioxide Reaction. — Figure 2 illustrates the type of information obtained from the reaction of carbon with carbon dioxide. The

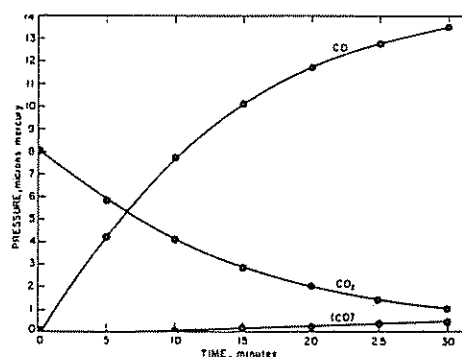
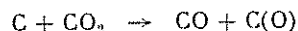


Fig. 2. — Carbon-Carbon Dioxide Reaction at Temperature of 500°C .

reaction was found to be first order with respect to carbon dioxide consumption throughout the range of temperatures and pressures investigated. The rate of carbon monoxide formation was slightly less than twice the rate of carbon dioxide consumption. This departure from a two to one ratio involves a small amount of carbon monoxide « tied » to the surface of the carbon sample. This complexed carbon monoxide could be recovered by heating the carbon in vacuo at higher temperatures after the run. However, only a negligible amount of this complex could be removed at outgassing temperatures below ca 600°C . At the end of a run (for a particular starting pressure of carbon dioxide) the amount of complex existing was found to increase to a maximum with increasing reaction temperature up to 600°C and then to decrease with further increase in reaction temperature.

The carbon monoxide surface complex could be formed as a product of the carbon dioxide reaction



or it could be due to the chemisorption of carbon monoxide on the surface of the sample,



Here C(O) represents a complex formed upon reaction of carbon dioxide, while (CO) represents chemisorbed carbon monoxide. By exposing the carbon surface to carbon monoxide, chemisorption can be studied. It was found that the amount of carbon monoxide chemisorbed increased to a maximum around 600 °C. Table I shows the amount of carbon monoxide chemisorbed at 600 °C. for various pressures and lengths of time. A semi-log plot of per cent of surface covered versus log of adsorption pressure for an equilibrium time of 30 minutes gives a straight line, which is characteristic of the Temkin isotherm⁽³⁾. A coverage of 0,125 per cent of the surface in three days for a carbon monoxide pressure of 24 microns indicates that only a small fraction of the total surface will chemisorb carbon monoxide. The relatively small difference between the amount of surface coverage at a pressure of 2,7 microns of carbon monoxide for 30 minutes and a 24 micron pressure of carbon monoxide for 3 days indicates that the majority of this small area is rapidly saturated with chemisorbed carbon monoxide. The chemisorbed carbon monoxide could be recovered by heating the carbon to temperatures greater than 600 °C.

TABLE I

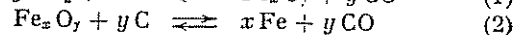
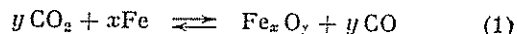
Per cent of wear dust surface covered with chemisorbed carbon monoxide at 600 °C.

Time	Pressure, (microns of CO).		
	2,7	8	24
30 mn	0,054	0,065	0,074
3 days	—	—	0,125

Since the chemisorbed carbon monoxide exhibits the same characteristics as the complex formed during the carbon dioxide reaction, it appears that the complex is chemisorbed carbon monoxide. This chemisorption is a side reaction and does not play a role in the mechanism of the conversion of carbon dioxide to carbon monoxide.

It is recalled that, as a result of the grinding process, the carbon sample used in this investigation contained ca 5 per cent iron. A ground sample from which the majority of the iron was removed did not chemisorb any measurable amount of carbon monoxide. Also the iron had a very strong catalytic effect on the reactivity of the carbon. The « iron-free » sample had to be heated ca 300 °C higher than the « iron-containing » sample in order to obtain a comparable reactivity. Although the experimental data indicate that the carbon dioxide is converted to carbon monoxide with no measurable build-up of any intermediate products, the great difference in reactivity between the original « iron-containing » sample and the « iron-free » sample indicates that the iron must play an important role in the reaction mechanism.

A possible mechanism by which the iron could catalyze the reaction would be



The equilibrium ratio of carbon dioxide to carbon monoxide of step one is pressure independent and is approximately one for the range of temperatures used in this investigation. Step two is a pressure dependent reaction; operation at low pressures of carbon monoxide favors the reduction of the iron. If the rate of the forward reaction in step two is sufficiently fast to prevent a significant build-up of iron oxide, the rate of the back reaction in step one would be small. Under these conditions, only the forward reactions of step one and two would play an important role in the over-all reaction scheme.

The Carbon-Oxygen Reaction. — The carbon-oxygen reaction was carried out in the same manner as the carbon-carbon dioxide reaction; however, the mass spectrometer was set to monitor the mass 32 (O_2^+) ion beam, as well as the mass 44 (CO_2^+) and mass 28 (CO^+) ion beams. Since oxygen is much more reactive to carbon than is carbon dioxide, the reaction can be easily studied at temperatures as low as 200 °C.

Figures 3 and 4 show the type of information obtained from the reaction of ground SP-1 graphite

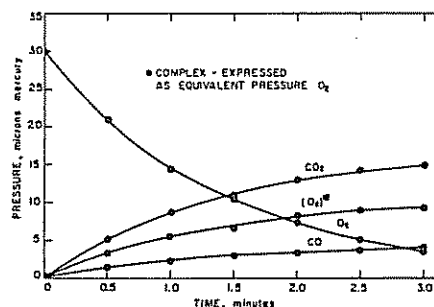


Fig. 3. — Carbon-Oxygen Reaction at Temperature of 200 °C.

with oxygen at 200 and 500 °C, respectively. As in the case of the carbon dioxide reaction, the amount

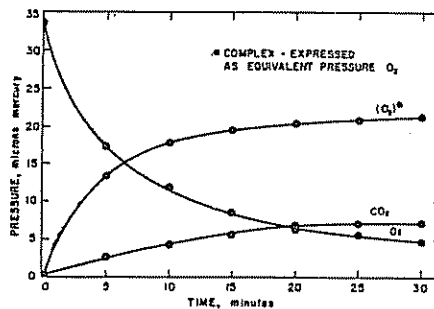


Fig. 4. — Carbon-Oxygen Reaction at Temperature of 500 °C.

of oxygen « tied » to the surface is determined by making a material balance. At the 200 °C reaction temperature, carbon dioxide is the only gaseous product; most of the reacting oxygen forms some type of complex. At the 500 °C reaction temperature carbon dioxide, carbon monoxide, and surface complex are formed. Figures 5 and 6 show relationship between the logarithm of the oxygen pressure and

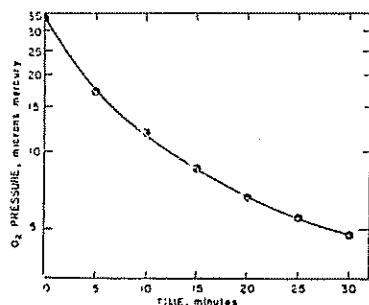


Fig. 5. — Deviation from First Order Relationship of Oxygen Consumption at Reaction Temperature of 200 °C.

time for the reactions at both temperatures. From these plots, it is seen that the reaction is first order with respect to oxygen at 500 °C but not at 200 °C. At 200 °C the effective rate constant of oxygen consumption decreases as the reaction proceeds.

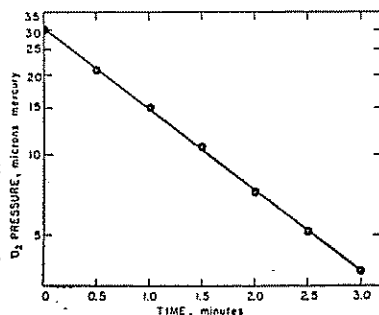


Fig. 6. — First Order Relationship of Oxygen Consumption at Reaction Temperature of 500 °C.

If further reactions are carried out at 200 °C without outgassing the sample between runs, the rate constant of oxygen consumption slowly approaches the rate constant that an uncatalyzed sample (« iron-free ») of ground SP-1 graphite would have at the same temperature. Also the rate constant of carbon dioxide formation will increase and approach the value found for an uncatalyzed sample.

This decrease of the rate constant of oxygen consumption to a limiting value equal to that of an uncatalyzed sample and the increase in the rate constant of carbon dioxide production during the course of a reaction indicate that two competing reactions are taking place at 200 °C. This leads to a

rate expression of the form

$$-\frac{dP_{O_2}}{dt} = k_1 P_{O_2} (1 - \theta) + k_2 P_{O_2}$$

where k_1 is the true rate constant of the active surface, k_2 is the rate constant of the less active (« iron-free ») surface, and θ is the fraction of the active surface that is covered by the complex. It can be seen from this equation that as the active surface is covered by complex the first term of the rate equation will become small and the over-all rate will approach that of the « iron-free » carbon.

The activation energy of desorption of the complex depends upon the extent to which the surface is covered (4). At each temperature, a certain characteristic proportion of the complex formed will be stable. Thus, at higher reaction temperatures, the amount of stable complex will be smaller and more of the reacting oxygen will appear in the form of gaseous products. The carbon monoxide-carbon dioxide product ratio is dependent upon the relative stability of the complexes formed.

Some idea of the nature of the surface complexes can be obtained from the outgassing process at the completion of a reaction. Figure 7 shows for the

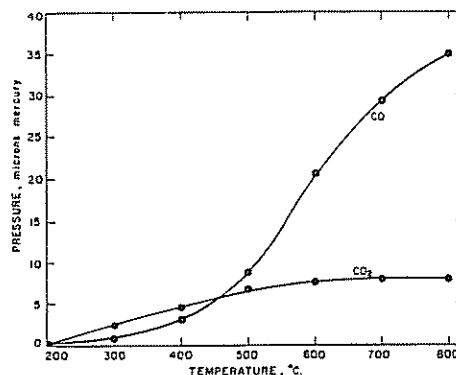


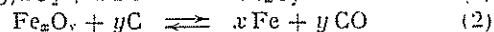
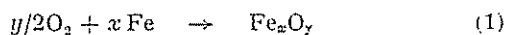
Fig. 7. — Decomposition of surface Complex Formed during 200 °C. Oxygen Reaction.

reaction at 200 °C the amount of carbon monoxide and carbon dioxide produced from the decomposition of the surface complex as the temperature of the carbon is increased. The temperature of the carbon was raised in 100 °C increments, with the sample held at each temperature until the rate of complex removal was negligible. At reaction temperatures of 200 °C, all of the carbon monoxide complex which is formed is stable; the carbon dioxide complex is less stable and partially decomposes which results in carbon dioxide being produced during the reaction. Upon heating the carbon in vacuo after a reaction at 200 °C, the carbon dioxide complex continues to decompose until the temperature range of 500 to

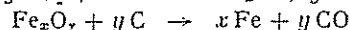
600 °C is reached. Above this temperature, no further carbon dioxide is produced, indicating that the carbon dioxide complex is completely unstable at higher temperatures. The rate of decomposition of the carbon monoxide forming-complex is not equal to that of the carbon dioxide forming-complex until a temperature of 300 °C is reached. Above this temperature, the rate of decomposition of carbon monoxide forming-complex increases rapidly, which ultimately results in several times more carbon monoxide than carbon dioxide being recovered. The carbon monoxide complex is much more stable than the carbon dioxide complex. The large evolution of carbon monoxide in the 600 °C region indicates that there may be more than one form of carbon monoxide producing-complex.

In the reaction of uncatalyzed ground SP-1 graphite with oxygen, much less complex is formed per unit oxygen consumption than in the reaction with catalyzed ground SP-1 graphite. The thermal decomposition of this complex also exhibits the pattern of varying activation energy with coverage; however, the large increase of carbon monoxide evolution in the 500-600 °C region is absent.

If the role of the iron in the over-all reaction is taken to be the same in the oxygen reaction as in the carbon dioxide reaction, the following mechanism can be postulated

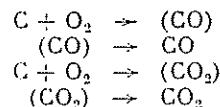


Step 2 in this mechanism is a reversible reaction; however, at the low pressures used in this investigation the reduction of the iron is favored. In the reaction with carbon dioxide, the oxidation of the iron by carbon dioxide was the rate controlling step, resulting in a negligible amount of complex (eg., Fe_xO_y) being present during the reaction.



Because of the greater reactivity of oxygen with carbon than carbon dioxide with carbon, the former reaction can be carried out at much lower temperatures. At these low temperatures, the rate of oxidation of the iron is initially much faster than the rate of its reduction by carbon. This results in the formation of large amounts of iron oxide and a slowing down of the reaction as the amount of available iron decreases.

The fact that the rate constant at 200 °C of the iron-containing sample approached the rate constant of the « iron-free » sample for the oxygen reaction indicates that reactions other than the oxidation and reduction of iron are taking place. The carbon is also being directly oxidized by the oxygen,



where (CO_2) and (CO) represent complex forming carbon dioxide and carbon monoxide, respectively.

At 200 °C the iron oxide is not reduced to any great extent, and also the carbon monoxide forming complex is stable. Therefore, carbon dioxide is the only gaseous product. At 500 °C the rate of the iron oxide reduction is sufficiently fast to prevent lowering of the effective rate constant due to the $(1 - \theta)$ term in the rate equation. Also at 500 °C the carbon dioxide complex is almost completely unstable resulting in the production of large amounts of carbon dioxide, while the carbon monoxide complex is partially unstable resulting in the production of some carbon monoxide. The catalytic effect of the iron on the oxygen reaction is much smaller at 500 °C than at 200 °C. This indicates that the activation energy of the direct oxidation of carbon is higher than the activation energy of the oxidation of the iron in this system; thus the effect of iron catalysis is diminished at higher temperatures.

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- (4) *Ibid*, 103-106.

DISCUSSION

H. Hering. — Could F. J. VASTOLA not have resorted to more efficient means for removing the iron contamination?

F. J. Vastola. — For this investigation, it was desired to observe the difference between large and small amounts of iron on the reaction rate, no attempt was made to reduce the concentration of the iron to levels lower than 0.1 %.