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SPECIAL FEATURES OF THE INTERACTION OF GRAPHITIZED CARBON MATERIALS WITH GASES IN THE 700-2500° TEMPERATURE REGION

I. A. Yavorskiy and M. D. Malanov

The interaction of graphitized carbon materials with CO_2, H_2O, and O_2 at temperatures up to 2500° is studied. It is shown that the density of graphitized carbon materials has an influence on the reaction rate, due to differences in the structure of the materials. Anomalous patterns in the change in the reaction rate of carbon with CO_2, H_2, and O_2 on temperature are revealed. It is established that the concentration of oxidizer does not have a noticeable effect on the degree of abnormality of the rates of these reactions.

Reaction of Porous Graphites

Recently the interaction of carbon with gases has claimed considerable attention, in connection with the wide practical use of pure carbon or its compounds in various branches of modern technology. Therefore knowledge of the physicochemical constants and the oxidation mechanism is very important; this is especially true in high-temperature regions, where the accumulated experimental material is comparatively limited and contradictory.

Thus, during investigation of the rate of reaction of carbon with CO_2, O_2, and H_2O Hittrin, Golovina, and Khaustovich [1-4] obtained anomalous relationships of reaction rate and temperature only in

CO_2 and H_2O media. The experiments were conducted with spherical specimens (ø = 15 mm) made of electrode carbon. A high-frequency generator was used for heating; the reacting gases were not preheated. In all experiments the flow rate was maintained constant (0.6 m/s).

Khaustovich [5] connects the appearance of anomalous parameters in a medium of CO_2 with reaction inside the pores.

Mosse [6] studied the process of secondary interaction of the products of combustion with coke carbon in a flow with an oxidizer deficiency. It is proposed that the reaction of carbon proceeds basically with carbon dioxide. The temperature range was 1000 to 1750°. Kinetic equations of the process were obtained and the fact was established that the maximum reaction rate appears at ~1600°; however, no explanation of the nature of the maximum is given.

The research in the works by Revzin [7] was conducted by a procedure analogous to that in [6]; the study yielded kinetic equations of the process. An anomalous dependence of reaction rate on temperature was also detected. The author submits the hypothesis that the cause of the observed anomaly is connected with a change in the carbon lattice of the coke during the reaction at a given experimental temperature. Thus a purely chemical cause for the appearance of abnormality is proposed.

A more detailed analysis of the mechanism of carbon interaction with gases is given in the work by Letorte [8]. The author connects the obtained values of reaction rate in an oxygen medium with a change in the ratio of the effective number of encounters of oxidizer to the total number of collisions per unit surface in a unit time. The law which is obtained is explained by the change in the mobility of carbon atoms in a solid body. With a growth of temperature (up to 1900°K) the activity of surface atoms of carbon grows and the conditions for chemical interaction with the oxidizer are improved, but at the same time the surface mobility of carbon atoms also grows. With a further increase in temperature the mobility becomes so great that recombination occurs more quickly than secondary collision of an oxidizer atom. As a result the fraction of effective collisions of molecules which accomplish a chemical reaction is reduced. Thus, the anomaly is explained by the change in properties of the solid body with an increase in temperature.

Processing the experimental data by the authors of [1-4], Ong [9] attempted to explain the cause of the anomalous change in the reaction rate as a function of temperature.

In this work we present experimental data which make it possible to obtain new information about the special features of the reaction of porous materials in different gas media in a broad temperature range.

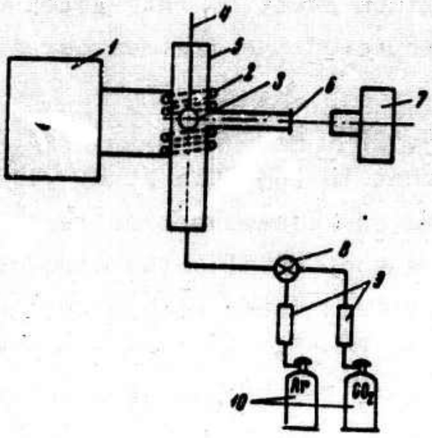

Fig. 1. Diagram of experimental installation: 1 - high-frequency generator, 2 - inductor, 3 - test specimen, 4 - graphite rod, 5 - quartz reaction tube, 6 - tube coated with optical glass for temperature measurements with a pyrometer, 7 - FEP-4 pyrometer, 8 - gas distribution valve, 9 - rotameter, 10 - gas bottles.

The experimental installation (Fig. 1) consisted of a quartz reaction chamber 35 mm in diameter and 300 mm in length. The test specimen was placed inside this tube on a graphite rod; the specimen had the form of a sphere 15 mm in diameter (or a 4 × 15 × 20-mm plate). The specimen was heated by high-frequency currents (1.5 MHz) from an 8 kW HF-generator by a means of a solenoid located outside the reaction tube. The oxidizer gas for the reaction (air, CO_2, water vapor) was fed into the lower end of the tube. The flow rate of gas was measured by the rotameter and that of vapor was measured by weighing the water arriving in the evaporator.

The specimens were prepared from graphitized carbon materials with a density ranging from 1.55 to 1.85 g/cm^3 and from pyrographite. Their weight was determined before and after the experiments on analytical balances; determination accuracy was up to $2 \cdot 10^{-4}$ g. Reaction time was determined with a timer to an accuracy of 0.1 s, and the temperature was measured by a FEP-4 photoelectric pyrometer with recording of the readings on tape. Variations in temperature in the course of the experiment did not exceed ±10°. Specimen dimensions were determined with a comparator or a micrometer.

The experimental procedure was as follows: after being placed in the reaction tube, the test specimen was heated in a current of argon up to the temperature to be studied. Then switching from the inert gas to the oxidizer was carried out by means of a special gas distributor; the switch was made in tenths of a second. The flow rate of oxidizer was regulated preliminarily and was maintained constant throughout the experiment. The same switching device was used to feed inert gas in place of the oxidizer after completion of the experiment. The HF-generator was switched on simultaneously. After the specimen was cooled to room temperature in an inert medium it was removed from the reaction chamber for weighing and for other measurements.

The gaseous medium was not preheated. In all experiments the flow rate was constant and equaled 0.6 m/s. In all experiments we determined the average weighted rate per unit of average external (geometric) surface of the specimen (g/cm^2•s). In order to reduce the effect of possible changes in the surface structure, the experiments were conducted only with new specimens. The degree of specimen burnup was maintained within the limits of 10%.

In order to clarify the effect of the temperature of the reacting gas on the reaction rate, we conducted special experiments in a resistance heater which was preheated up to the experimental temperature.

It was established that under these relatively small flow rates (0.6 m/s) the thermal boundary layer is many times greater than the value of mean free path of reacting gases. Therefore each molecule of the oxidizer could be heated up to the temperature of the specimen surface even in the limits of the laminar boundary layer. No noticeable difference was detected in the reaction rate with heating of the blast in a resistance furnace and with high-frequency heating of the specimen without preliminary heating of the oxidizer.

During the experiments we noted a certain increase in specimen surface temperature during exothermic reactions and a reduction of temperature during endothermic reactions. As the working (calculated) temperature we took the temperature which was actually established after the introduction of the oxidizer (average temperature on the pyrometer tape).

No special determinations were made of the degree of diffusion hindrance; this phenomenon does not lead to an anomalous change in reaction rate with a growth in temperature. During diffusion hindrance the reaction rate is increased in accordance with the law of growth of diffusion coefficient of the reacting gas as a function of temperature.

Results of experiments and discussion. Figure 2 shows averaged curves of the change in the weighted reaction rate (K_s) as a function of temperature for three different gaseous media: a mixture of 5.5% O_2 and 94.5% N_2, 100% CO_2, and 100% H_2O. The experiments were conducted with spheres made of graphite with a specific weight of 1.85 g/cm^3 at a gas flow rate of 0.6 m/s. As is evident from the figure, at 1550-1700° a maximum is achieved in all gaseous media, including the oxygen medium. At a higher temperature the reaction rate diminishes, reaching a minimum at 2000°.

In order to establish the influence of physical factors on the reaction rate, we conducted a series of experiments with four different flow rates (Fig. 3).

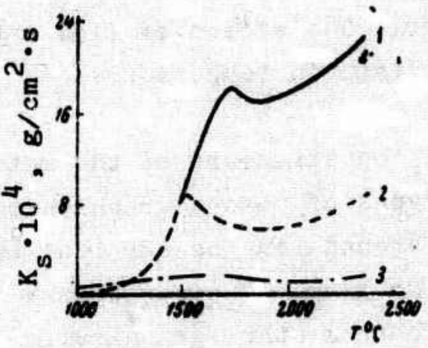

Fig. 2.

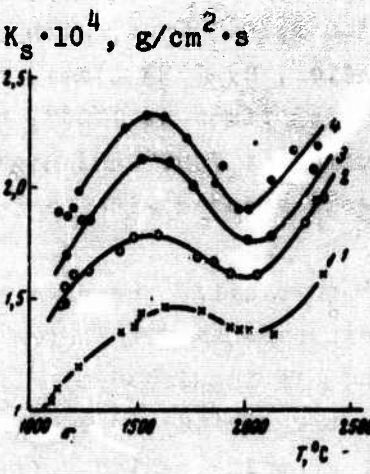

Fig. 3.

Fig. 2. Reaction rate as a function of temperature for a sphere in different media: 1 – H_2O, 2 – CO_2, 3 – 5.5% O_2 + 94.5% N_2.

Fig. 3. Reaction rate as a function of the temperature of the sphere at different flow rates, m/s: 1 – 0.56, 2 – 1.19, 3 – 1.53, 4 – 1.86.

From the data given it is clear that the anomaly in the change of reaction rate is a function of temperature is manifested quite clearly at all the investigated oxidizer supply rates.

If we take the ratio of rates at the points of the maximum and minimum of the curve, i.e. K_{max}/K_{min}, as the characteristic degree of abnormality, the degree of anomaly increases with an increase in the rate of oxidizer supply. Thus, at a flow rate of 0.56 m/s this ratio of reaction rates comprises 1.07, while at a flow rate of 1.86 m/s it equals 1.21.

It should be noted that either a transient or a diffusion process regime took place over the entire investigated temperature region. Even at temperatures of 1100-1500° the process was influenced significantly by the flow rate, which indicates the presence of noteworthy diffusion hindrance.

Comparison of data from Fig. 3 at different temperatures shows that the oxidizer flow rate exerts a different influence on the magnitude of the reaction rate. Thus, with an increase in flow rate from 0.56 to 1.86 m/s, i.e., by 3.33 times, the ratio of reaction rates is increased by 1.63 times at 1100°, by 1.69-1.64 times at 1500-1600°, and by 1.42 times at 2000° and higher. The effect of flow rate on the reaction rate is reduced with an increase in temperature.

In order to clarify the role of the structure of the material, we carried out experiments with three types of porous graphite and pyrographites, distinguished by differences in the apparent specific weight within the limits $\gamma = 1.55\text{-}2.08$ g/cm^3. Comparisons were also made with pyrographite, which differs from other graphites in the absence of pores and a higher specific weight.

In order to obtain comparable data, the only medium used in all the experiments was carbon dioxide at a constant flow rate of 2.16 m/s. Since it was not possible to obtain specimens in the form of spheres of a given size from pyrographite, the entire series of experiments was conducted with specimens in the form of 4 × 15 × 20-mm plates. In this way we eliminated any influence of specimen shape, which is important in the presence of diffusion hindrance.

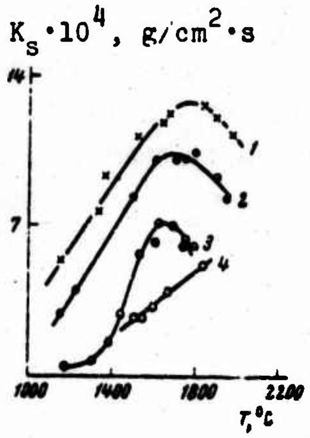

Fig. 4. Reaction rate as a function of the temperature of the sphere for materials with different densities, g/cm^3: 1 - 1.65, 2 - 1.55, 3 - 1.80, 4 - 2.08.

As is evident from the curves on Fig. 4, only the experiments with pyrographite display no anomaly. It should be noted that the appearance of anomaly cannot be explained by the presence of pores in the material alone. From Fig. 4 it is also clear that the reaction of pyrographite proceeded in a region which is close to the kinetic, while that of porous graphites occured in a transition region with significant diffusion hindrance (a sharp change in the slope of curves of reaction rate with approach to the maximum).

Therefore one would expect that the curves for pyrographite would also display a maximum, but in a region of higher temperatures, corresponding to the noticeable diffusion hindrance of the chemical reactions. One might assume that with the use of a more active oxidizer (oxygen) anomaly might also occur in temperature regions below 1900-2000° for some lots of pyrographite.

Noncoincidence of specific reaction rates in absolute magnitude for porous materials even in the high-temperature region, where the diffusion regime of the process is achieved, is apparently due to the different structural and reaction properties of the investigated materials; these differences have an essential effect on the reaction rate in this temperature region. From the given curves it also follows that there is no law of change of reaction rate as a function of density of the material.

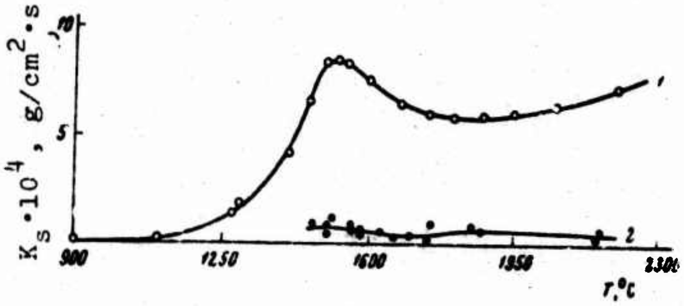

Fig. 5. Evaluation of the effect of entrainment on reaction rate: 1 – total reaction rate, 2 – magnitude of entrainment.

A characteristic feature of material with medium density (1.65 g/cm^3) is a presence of pores of predominately small dimension (finely dispersed filler). In the process of complete combustion specimens of this graphite remain comparatively smooth, while specimens of the other two types of graphite became rough and displayed granular crumbling. Crumbling of unreacted material was particularly apparent during reaction with CO_2. Figure 5 shows data on the reaction rate at a flow rate of 0.6 m/s, with consideration of entrainment.

As is evident, the entrainment of material amounts to a significant quantity. These data show that a purely diffusion combustion regime is not achieved in the entire investigated temperature range (up to 1900°).

The fact that the material crumbles in the form of individual grains indicates that the more active portion of the graphite – the binder – burns up first; the filler grains, being less reactive, are only partially burned and are separated from the specimen with little change in their dimensions. The comparatively "smooth" surface of specimens after oxidation of graphite with a density of 1.65 g/cm^3 can apparently be explained by the fact that the small grains of filler are able to burn simultaneously with the binder directly on the surface of the specimen.

Change in reaction rate as a function of oxygen concentration at different temperatures.

T °C	O_2, %	$K \cdot 10^4$ g/cm$^2 \cdot$ s	T °C	O_2, %	$K \cdot 10^4$ g/cm$^2 \cdot$ s	T °C	O_2, %	$K \cdot 10^4$ g/cm$^2 \cdot$ s
1200	4,6	1,23	1600	4,6	1,50	2100	4,6	1,35
	2,1	4,45		21	7,30		21	6,90
	30	6,30		30	10,70		30	10,20
	45	9,15		45	16,0		45	15,20

The effect of oxidizer concentration was studied by varying it within the limits 4.6 to 45% O_2 (table) mixed with nitrogen at a constant flow rate.

A continuous relationship, $K_s = f(T)$, was constructed for a concentration of 4.6% O_2, while the values of the reaction rate were found for the remaining three concentrations at only three temperatures – 1200, 1600, and 2000°. The 1200° temperature corresponds to the regime up to the beginning of an anomalous shape of the curve; 1600° corresponds to a maximum reaction rate and 2000°, to the minimum rate.

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Change in reaction rate as a function of oxygen concentration at different temperatures.

T °C	O_2, %	$K \cdot 10^4$ g/cm^2·s	T °C	O_2, %	$K \cdot 10^4$ g/cm^2·s	T °C	O_2, %	$K \cdot 10^4$ g/cm^2·s
1200	4,6	1,23	1600	4,6	1,50	2100	4,6	1,35
	2,1	4,45		21	7,30		21	6,90
	30	6,30		30	10,70		30	10,20
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The reliability of the data is confirmed by the good repeatability of the experiments. A characteristic feature is the fact that the dependence of reaction rate on oxidizer concentration is linear over the entire investigated temperature range and corresponds to the first order of reaction. An increase in oxygen concentration by 10 times leads to approximately the same increase in reaction rate both in the temperature region corresponding to the maximum reaction rate (1600°) and in that corresponding to the minimum rate (2100°). Consequently, a change in oxidizer concentration in wide limits does not have a noticeable influence on the anomalous nature of the reaction.

Conclusions

1. An anomaly exists in the rate of reaction of graphitized carbon materials not only with CO_2 and H_2O, but also with O_2.

2. The anomaly is intensified with an increase in the oxygen flow rate.

3. In a medium of carbon dioxide, individual graphite materials (examples of four types of graphite) may not give an anomalous change in the reaction rate as a function of temperature.

4. The effect of the density of the graphitized carbon material on reaction rate varies owing to differences in the structure of the material.

5. The concentration of oxidizer does not have a noticeable influence on the degree to which anomalies appear in the reaction rate as a function of temperature.

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