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I hereby recommend that the thesis prepared under my supervision by FRED KISSLINGER

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be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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THE ROLE OF ENERGIZERS IN PACK CARBURIZING

A dissertation submitted to the

Graduate School of Arts and Sciences
of the University of Cincinnati

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INTRODUCTION

Carburizing, or cementation, is a process in which the carbon content of an iron or steel object is increased without melting the object. The process consists of heating the iron or steel object to a suitable temperature and holding it at this temperature in contact with a suitable carburizing agent for a sufficient length of time to allow carbon to enter the surface and diffuse into the object.

The carburizing agent may be solid, liquid or gaseous. Graphite, charred vegetable or animal matter, coke or almost any form of solid carbon may be used as a solid carburizing agent. Liquid carburizing agents are compounds such as sodium and potassium cyanides and calcium cyanamid. Gaseous carburizing agents are compounds such as carbon monoxide and the volatile hydrocarbons. The carburizing temperature used commercially is usually between 1500° F and 1750° F. The carburizing time varies considerably from about 30 minutes or more for liquid carburizing up to 8 hours or more for gas and solid, or pack, carburizing.

The carburizing process has been known and used for a very long time. Giolitti (1)* gives an excellent review of much of the early work on carburizing. Vannuccio Biringuccio in 1540 and George Agricola in 1556 describe the first pro-

* The figures in parentheses refer to the bibliography.

cess recorded. This consisted of heating iron objects in a bath of molten cast iron. Carburizing with solid agents was probably used in the sixteenth century to obtain a case on iron objects. In the seventeenth century carburization of iron bars for the purpose of producing blister steel developed.

Reaumur, 1720-22, reported the first scientific study of carburization. His investigation led him to conclude: 1. the best results were produced with a wood charcoal base to which other substances were added; 2. the transformation of iron into steel begins at the surface and proceeds inward; 3. the transformation was effected by sulphur and volatile salts entering the iron. Reaumur described various carburizing compounds and the equipment to be used in great detail. This ended the monopoly of those few people who knew the then secret details of this art. This stimulated the manufacture of blister steel and led to many attempts to improve the process.

Scientific investigations were conducted to determine the mechanism of the action of solid carburizing agents. In 1841, Leplay advanced the theory that the carbon reacted with the oxygen of the air to form carbon dioxide which was reduced by the carbon to carbon monoxide. The carbon monoxide then transferred carbon to the iron or steel and formed more carbon dioxide which repeated the cycle. While this theory of the action of solid carbon is the accepted theory today,

it was not widely accepted in Leplay's time because many investigators thought that there was no good reason for eliminating the possibility of solution and diffusion of carbon into the steel by simple contact between the steel and carbon.

Caron, in 1860, concluded from the results of his investigations that the action of solid carbon was due to formation of cyanogen or volatile cyanides. These compounds, according to Caron, resulted from the reaction of the ashes of the charcoal (or salts added to the charcoal) with nitrogen. Caron later proposed a carburizing compound of three parts charcoal and one part barium carbonate.

Marguerite, in 1864, disagreed with Caron's cyanide theory and tried to show that iron is carburized by direct contact between carbon and iron. Marguerite also carburized iron with pure carbon monoxide in order to disprove Caron's assertion that carbon monoxide was not capable of carburizing. Cailletet, in 1865, found no cyanogen or cyanides in the analyses of gases taken from carburizing boxes. Charpy confirmed this in 1909 by showing that there were no cyanides in either the carburizing compound or gases contained in carburizing boxes. This disproved the cyanide theory but did not settle the question of whether carbon acted directly on the steel or whether a gas, carbon monoxide, acted as a carrier.

Mannesmann, 1879, studied this question and came to

the conclusion that while the gases inside a carburizing box may carburize under special conditions they are too dilute inside a carburizing box to have any appreciable carburizing action in commercial practice and that the action of solid carbon in the commercial process was solution and diffusion of carbon into the steel by direct contact. Roberts-Austen came to the same conclusion in 1890.

Guillet, 1904, showed that carbon did not carburize iron in a vacuum and decided that carbon monoxide acted as a carrier. He also believed that carburizing compounds energized with barium carbonate formed barium cyanide and the ashes of the wood charcoal formed potassium cyanide and that these cyanides also acted as carriers. As mentioned previously, Charpy's work later led to discarding the cyanide theory. Ledebur challenged the conclusions of Guillet and attempted to show that the intervention of a gas was not necessary during pack carburizing.

Giolitti and collaborators published the results of their studies between 1908 and 1912. Giolitti concluded that carbon may diffuse into iron by contact but that this action is slow and of such intensity that it has no practical significance. From a study of carbon distribution in the case of carburized parts he concluded that carbon monoxide diffused into the steel and deposited its carbon where the carbon concentration of the steel is lower than that at

the surface. The carbon dioxide formed during this reaction could diffuse back toward the surface and pick up carbon from the higher carbon steel surface and then carry it into the interior of the object. Giolitti believed that the equilibrium studies of Schenck supported this mechanism.

In his book, Giolitti drew a number of conclusions from the information available up to 1912. These conclusions were:

1. The direct action of carbon on iron is, at best, very slight.
2. The action of carburizing compounds composed of charcoal and alkali or alkaline earth carbonates is not due to the formation of cyanogen or volatile cyanides but to the formation of carbon monoxide resulting from the reaction of carbon and the carbon dioxide released by the carbonates.
3. Carbon monoxide carburizes by acting directly on the steel.
4. The action of carbon monoxide is greatest in the presence of carbon and this action predominates over all other mechanisms of carburizing in carburizing compounds in which carbon monoxide can be formed.

The simple carbon dioxide evolution theory, the second of Giolitti's conclusions given above, had been and is still accepted by many as the explanation of the energizer action

of certain carbonates. In more recent years the energizing action of carbonates has been the subject of a number of investigations and the mechanism of this action is not yet a settled question. Some of the papers of special interest will be reviewed briefly.

Takahashi (2),(3) investigated the carburizing reactions and his results led him to conclude that the diffusion of carbon monoxide and carbon dioxide in steel, as postulated by Giolitti, was not likely and that the probable mechanism of the carbon penetration into steel was the deposition of nascent carbon atoms on the surface and diffusion of this carbon into the steel. He also showed that carbon monoxide precipitates carbon in the presence of carbonates. His final conclusion was that the carbonates accelerate the precipitation of carbon on the steel surface and this carbon being very fine dissolved in the austenite and diffused inward. The carbon precipitation resulted from reactions similar to those given for barium carbonate:

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (1)$$

$$BaO + 2CO \longrightarrow BaCO_3 + C \qquad (2)$$

Papers by Ragatz and Kowalke (4) and by Enos (5) cast doubt on the previous theories. These investigators showed that a number of compounds, other than carbonates, are equally good energizers. For example, sodium carbonate, bicarbonate, hydroxide, acetate, oxalate, cyanide, chromate and tungstate all gave approximately the same activity when used as

energizers. This led Ragatz and Kowalke to conclude that the energizing action was due to the sodium in these compounds since the carburizing compounds used in these experiments were made up in such a way that the weight ratio between sodium and carbon was the same in each instance. These investigators proposed a theory in which the energizer acted as a catalyst for the reaction

$$CO_2 + C \rightleftharpoons 2CO \qquad (3)$$

This provided a high carbon monoxide concentration in the gas phase which increased the degree of carburization. The mechanism, as given by Ragatz and Kowalke, whereby sodium and barium carbonates catalyzed reaction (3) consisted of a series of cyclic reactions. For sodium carbonate the following reactions occurred at the gas-carbon interface:

$$Na_2CO_3 + C \longrightarrow Na_2O + 2CO \qquad (4)$$

$$Na_2O + C \longrightarrow 2Na + CO \qquad (5)$$

The sodium from reaction (5) volatilized and reacted with carbon dioxide in the gas phase:

$$2Na + CO_2 \longrightarrow Na_2O + CO \qquad (6)$$

$$Na_2O + CO_2 \longrightarrow Na_2CO_3 \qquad (7)$$

The sodium carbonate from reaction (7) dropped back on the carbon and repeated the cycle, Barium carbonate reacted according to the following reactions:

$$BaCO_3 + C \longrightarrow BaO + 2CO \qquad (8)$$

$$BaO + CO_2 \longrightarrow BaCO_3 \qquad (9)$$

Mahin (6) has supported the simple carbon dioxide evolution theory. He believes that the gradual evolution of carbon dioxide by the carbonate flushes the nitrogen from the carburizing box and that this action is responsible for a high carbon monoxide concentration which would give more intense carburization. He pointed out that the good energizers reported by Ragatz and Kowalke were capable of giving off oxygen or carbon dioxide while the poor energizers contained no available oxygen. He also reported some experiments which showed that calcium oxide and barium oxide were capable of picking up carbon dioxide at low temperatures during heating. He claimed that this carbon dioxide would be released later at higher temperatures. The fact that barium oxide and barium carbonate showed equal activity had led Enos to believe that the evolution of CO_2 was not the real function of the energizer.

Fong and Ragatz (7) showed that the carbon dioxide given off by barium carbonate and sodium carbonate in a carburizing compound is not given off gradually and progressively during carburization. Their results indicate that the evolution of carbon dioxide ceases shortly after reaching the carburizing temperature. They concluded that sodium and barium carbonates can react with carbon at temperatures below the minimum temperature at which the respective carbonate can dissociate in the presence of carbon. They also showed that barium hydroxide and sodium hydroxide were converted to

carbonates when heated with carbon to relatively low temperatures (up to 750° C for sodium hydroxide and up to 850° C for barium hydroxide) but the carbon dioxide absorbed was evolved rapidly upon further heating. They propose the following reaction between sodium carbonate and carbon:

$$Na_2CO_3 + 2C \longrightarrow 2Na + 3CO \qquad (10)$$

This reaction together with reactions (6) and (7) were said to be responsible for the energizing action. Reactions (8) and (9) were given for barium carbonate.

Object of this investigation:

It is generally accepted that carbon monoxide is the active carburizing agent during pack carburizing and that certain carbonates increase the carburizing action when added to the carburizing compound. As can be seen from the above review of the investigations on this subject, there is still some question about the mechanism of the energizer action. The present investigation was intended to yield further information on this subject. Specifically, the object is to study the effect of barium carbonate on two reactions occurring during pack carburizing.

Carbon dioxide and carbon react to form carbon monoxide according to the reversible reaction

$$CO_2 + C \text{ (solid)} \rightleftharpoons 2CO \qquad (11)$$

Since this reaction occurs at the carbon-gas interface and since the carbon monoxide is the carburizing agent, the

carbon monoxide formed in reaction (11) must diffuse through the gas phase to the steel surface where it gives up part of its carbon according to another reversible reaction which we shall write as

$$2CO \rightleftharpoons CO_2 + C \text{ (dissolved in austenite)} \qquad (12)$$

These two reactions, (11) and (12), are the reactions under consideration. The experiments reported in this paper carried out these reactions separately under such conditions that each occurred in the absence of the other. In this way the effect of barium carbonate on each reaction has been determined.

APPARATUS

The apparatus used to study the two carburizing reactions is shown in Figure 1. This apparatus consists of a vacuum pump A and calcium chloride drying tower B. The vacuum pump served to remove water from the system at the start of each experiment and the drying tower prevented the moisture from going through the pump.

The gas entering the system, either air or carbon dioxide, passed through two drying towers, either C and D or E and F depending upon which reaction was being studied. Towers C and E contained anhydrous calcium chloride while towers D and F contained magnesium perchlorate.

G and H are two electrically heated tube furnaces. Fused quartz tubes were used in each furnace. These tubes were 30 inches long and were 1 inch inside diameter. The ends of the furnace tubes were closed by rubber stoppers through which thermocouple wires and alundum tubes entered the furnaces. The alundum tubes carried the gas into and out of the furnaces. They were 5/16 inch outside diameter and had a 3/32 inch bore.

J is a capillary tube flow meter. The manometer of the flow meter was filled with mineral oil. This flow meter was merely used to indicate the instantaneous flow rate and served as a guide in regulating and controlling the flow rate. All the flow rates reported in this work were deter-

mined by measuring the time required for a definite volume of gas to pass through the wet test meter, S.

The gas was analyzed by the absorption bulbs K, L, N and Q and the hot copper oxide tube M. The gas analysis will be described in more detail in a separate section.

R is a drying tower filled with magnesium perchlorate which prevented water from diffusing back into the system from the wet test meter S. The gas left the system through the trap T and the sulfuric acid bubbler U.

The various parts of the apparatus were connected together with glass tubing and thick-walled rubber tubing was used to make connections.

A number of by-passes are shown in Figure 1. When using furnace G it was possible to send the gas directly to the absorption bulbs without going through furnace H. The capillary tube flow meter was equipped with a by-pass which was used while the system was being evacuated. A by-pass was also necessary for the absorption bulbs and copper oxide tube.

Pressures were measured by the manometers shown in Figure 1. P_4, the manometer on the wet test meter S, was filled with water. All the other manometers were filled with mercury. The pressure inside the two furnaces was indicated by the manometers P_1 and P_2. These two manometers were connected to the furnaces through mercury traps and stopcocks. P_3, the only closed manometer, indicated the

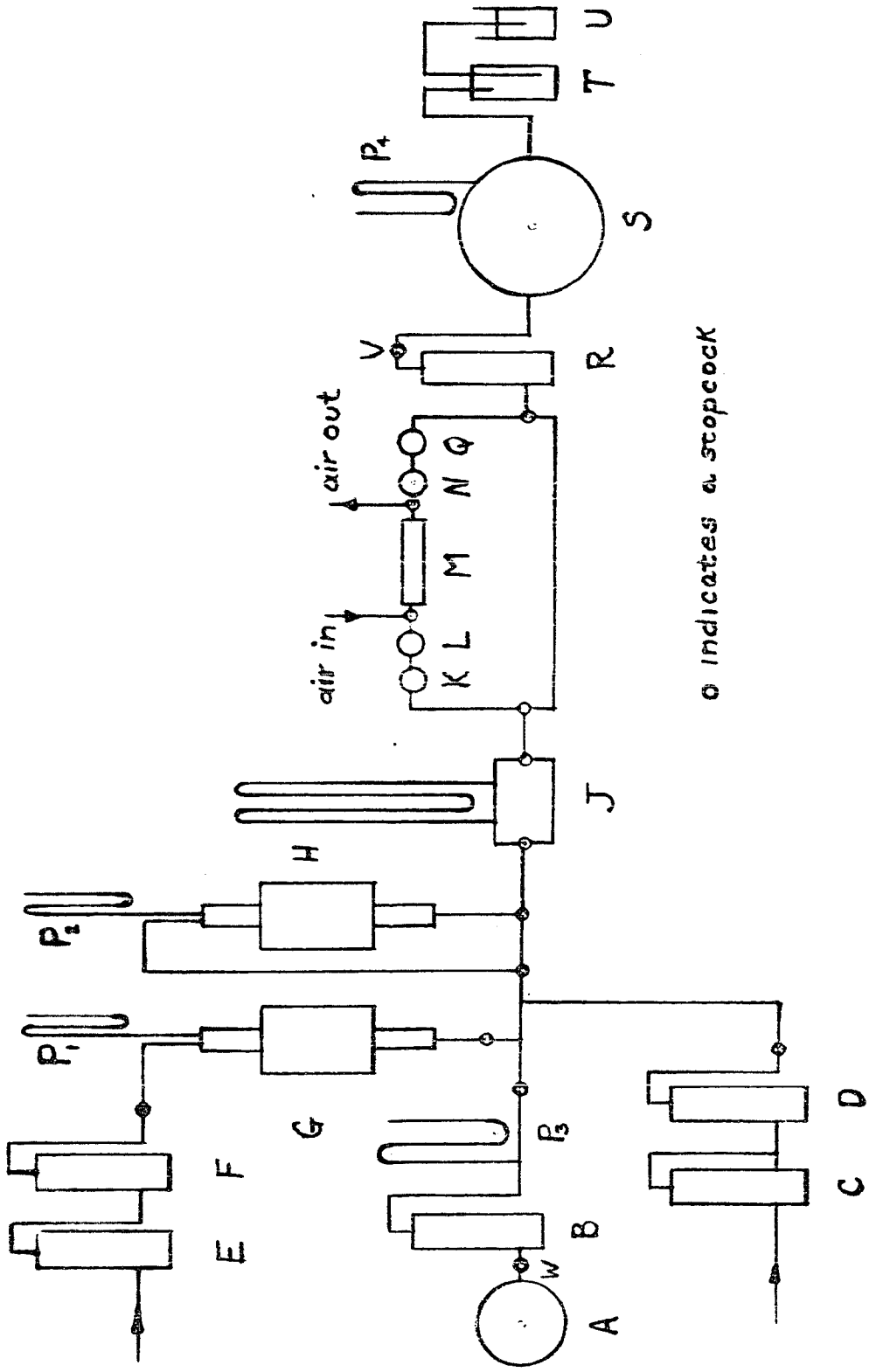

FIGURE 1

pressure in the system while the system was being evacuated. The pressure of the gas in the wet test meter was measured by the manometer P_4. In all the experiments reported in this study the sulfuric acid bubbler was adjusted to keep P_4 at 0.4 inches of water pressure.

The arrangement of charcoal, thermocouple and alundum tubes inside the furnaces for each part of this study is shown in Figure 2. The gas entered through the upper alundum tube which extended down to the surface of the charcoal. After passing through the bed of charcoal the gas left the furnace through the lower alundum tube. The lower alundum tube was fitted with an alundum disc which supported the charcoal. The hot junction of the thermocouple was placed in the charcoal just above the gas outlet in the center of the disc.

The temperature was measured by chromel-alumel thermocouples and a potentiometer. Since chromel-alumel thermocouples are unreliable in a reducing atmosphere, the temperature of the furnace was controlled by a control thermocouple placed outside the furnace tube as shown in Figure 2. At the start of each experiment, while the system was evacuated, the furnace was brought up to temperature and the controller was set to produce the desired temperature according to the thermocouple inside the furnace. The controller then maintained this temperature during the remain-

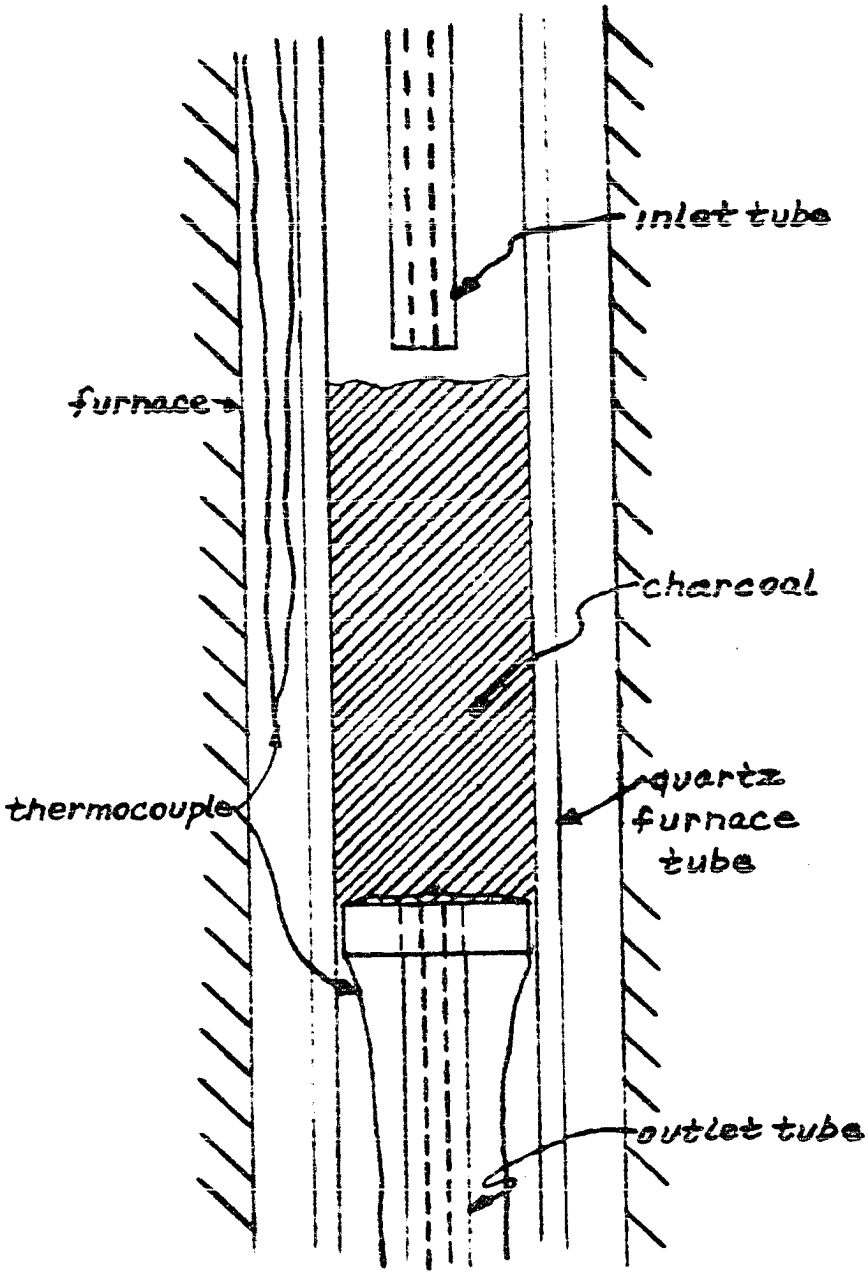

FIGURE 2

der of the experiment.

Except as noted, a calibrated thermocouple was used inside the furnace for each experiment. The affected portion of the thermocouple was cut off after the experiment and the thermocouple was recalibrated for subsequent experiments. All the thermocouples were calibrated against one reference thermocouple. Calibrations were made by placing the hot junctions of the two thermocouples inside a hole in a nickel block.

In the study of the reaction between carbon monoxide and austenite, ingot iron samples were carburized in furnace H by a carburizing atmosphere generated by passing air through a bed of hot charcoal in furnace G. After trying various methods of suspending the sample from the gas-inlet tube it was realized that some method for obtaining very intimate contact between gas and sample was necessary. The arrangement shown in Figure 3 was finally accepted as satisfactory. As will be seen by the results, hypereutectoid cases could be produced in four and one-half hours. When samples were suspended inside the furnace about one-half inch below the inlet tube a very light hypoeutectoid case was produced by the same atmosphere in the same time and at the same temperature.

The samples shown in Figure 3 were cylindrical pieces of ingot iron about 0.45 inches in diameter and 0.85 inches

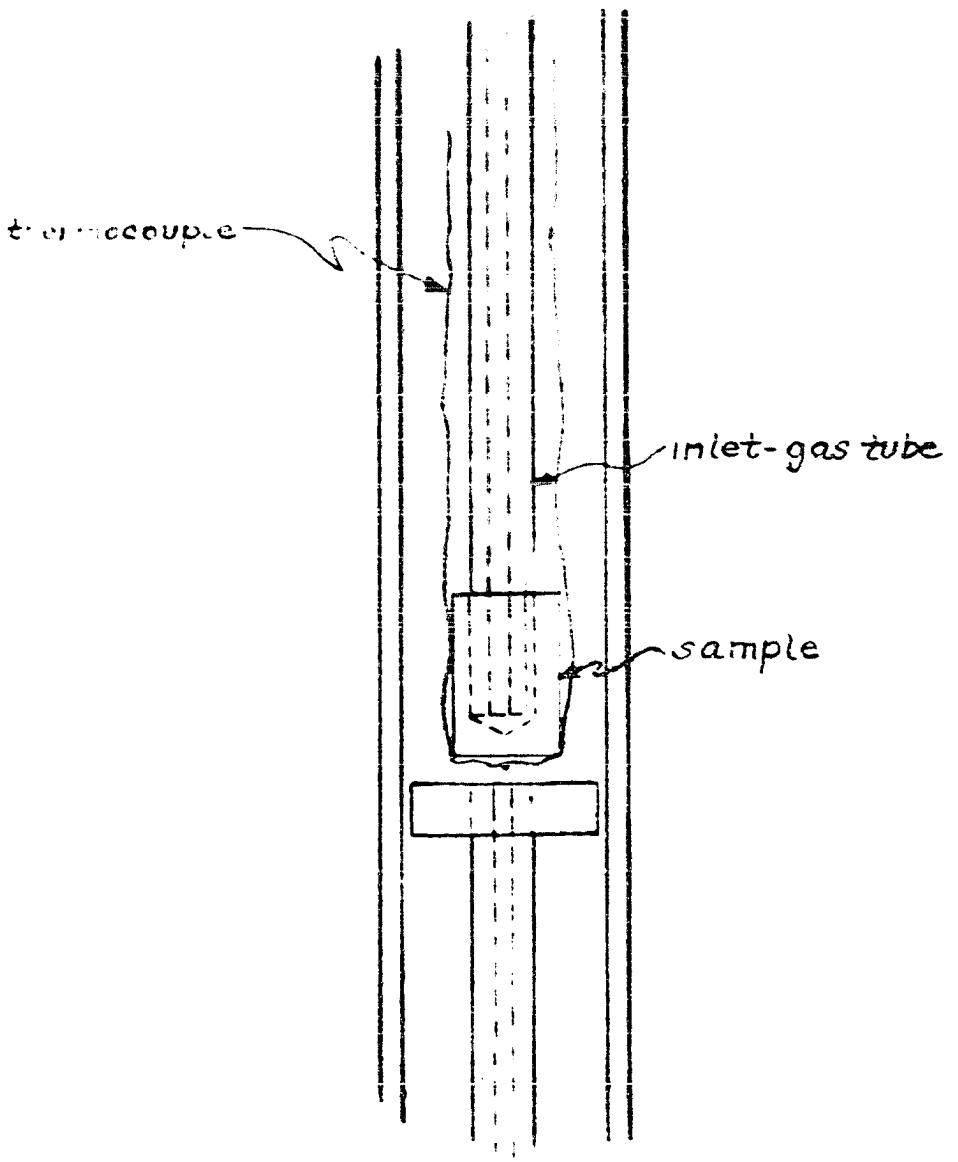

FIGURE 3

long. A 5/16 inch hole was drilled into the samples. The samples were turned down and drilled on a lathe. These samples were placed over the gas-inlet tube as shown.

A flat side was ground on the inlet tube to provide a channel for the gas. The gas-inlet tube measured 0.313 inches (5/16 inch) outside diameter. After grinding the flat on one side of the tube it measured 0.294 inches across at the flat. With this arrangement all the gas was forced over the surface of the sample at a relatively high velocity.

In order to determine the effect of barium carbonate on the reaction, samples were carburized with and without barium carbonate at the base of the hole. In this way the samples could be carburized with the gas alone or with the gas in the presence of barium carbonate. No solid carbon was present in either case.

The thermocouple was used as a stirrup to prevent the samples from falling off the alundum tube at the carburizing temperature. The gas-outlet tube, fitted with a disc, was placed under the samples as an additional precaution.

GAS ANALYSIS

The gas analyses were first attempted with an Orsat gas analyzer, Unitized, Technical Time-Saver model. The carbon dioxide was absorbed in potassium hydroxide. A number of procedures were possible for determining the carbon monoxide. It could be absorbed in acid cuprous chloride but this absorption was very slow for the high carbon monoxide contents encountered in this work. Since the absorption capacity of acid cuprous chloride is rather low (8), this procedure was soon abandoned.

The other two procedures involved oxidizing the carbon monoxide to carbon dioxide and absorbing it in a potassium hydroxide solution. In the first of these, copper oxide at 310° C was the oxidizing agent. In the other method, the carbon monoxide was mixed with oxygen and a slow combustion was effected by passing the mixture over a glowing platinum coil. Analyses by these two oxidation methods did not check each other nor could check analyses be obtained with either method. Marshall and Chipman (9) encountered some of the above troubles and believed that carbon monoxide in such high concentrations can be absorbed to some extent in the potassium hydroxide solution.

The method finally adopted was a dry method. This eliminated errors due to the solubility of the various constituents of the gas in any solutions. The arrangement of the

apparatus is shown in Figure 1. The gas was analyzed by the four absorption bulbs, the hot copper oxide tube and the wet test meter. The copper oxide tube was constructed from a one-inch inside diameter fused quartz tube, 28 inches long. An 11 inch section in the center of the tube was electrically heated. The heated portion of the tube was filled with copper chips which were then oxidized by heating the tube and passing air through the chips. The ends of the tube were closed by rubber stoppers fitted with three-way stopcocks.

As mentioned above in connection with the Orsat analysis, carbon monoxide is oxidized to carbon dioxide by copper oxide. This oxidation (10) will occur at 300° C. Copper oxide will oxidize hydrogen to water at 250° C. A temperature of 310° C is recommended for the Orsat apparatus when both are present. At this temperature the reaction is too slow to suit the purposes of this investigation. Therefore, the copper oxide tube was heated to 600° C in order to increase the rate of reaction.

Bulbs K and N (see Figure 1) were filled with magnesium perchlorate and bulbs L and Q were filled with Ascarite. Water was absorbed in bulb K and carbon dioxide in bulb L. The remainder of the gas passed through the hot copper oxide tube where the carbon monoxide and hydrogen were oxidized. The hydrogen was then absorbed as water in bulb N and the carbon monoxide absorbed as carbon dioxide in bulb Q.

The analysis of the gas was conducted as follows: The copper was oxidized prior to each analysis by passing air through the hot tube. The bulbs were replaced by pieces of capillary tubing and the air was flushed from the copper oxide tube. The gas was then changed to the by-pass while bulbs K and L were put in the train in place of one of the pieces of capillary tubing. These two bulbs and the copper oxide tube were flushed. Then bulbs N and Q were put in the train and the final flushing took place. Since the carbon monoxide content of the gases was always high, bulb Q had to absorb an appreciable amount of carbon dioxide. If this bulb were permitted to absorb too much carbon dioxide, it became very hot and the spent Ascarite "caked up". When this occurred it offered too much resistance to the passage of gas and interfered with the flow rate. For this reason bulbs N and Q were inserted during the final flushing period only. For this reason, too, bulbs Q and L were cleaned and refilled frequently.

After flushing, the gas was sent through the by-pass and the copper oxide tube was closed while the bulbs were weighed. Bulb Q became rather warm during the flushing and analysis and it was allowed to cool to room temperature before the bulbs were weighed. The weighed bulbs were put back in the train and a sample of the gas was allowed to pass through them. Any unabsorbed gas was measured by the wet test meter. The bulbs were reweighed to complete the

analysis.

The unabsorbed gas should have been nitrogen. It will be referred to as "inert gas". The volume of inert gas as measured by the wet test meter was corrected for the vapor pressure of water in the meter and referred to standard conditions (temperature of the meter and barometric pressure were recorded). The volume of gas at standard conditions, equivalent to the weight change for each bulb, was also calculated and then the volumetric per cent of each constituent was determined.

Sources of error in gas analyses:

The bulbs were weighed on an analytical balance capable of weighing to one-tenth milligram. An absorption bulb was used as a counterpoise on the other balance pan.

The smallest amount of carbon dioxide, resulting from the oxidation of carbon monoxide, which was weighed in bulb Q, was larger than 0.5 grams. This weight could be determined with a small percentage of error. However, as mentioned above, bulb Q limited the size of the sample because it would interfere with the flow rate if it picked up too much carbon dioxide.

The weight change for bulb K was always small and sometimes it amounted to only a few tenths of a milligram. Since it was necessary to handle the bulbs, such small weight changes could produce 100 per cent error. While the actual

per cent water given in the analyses may be in error, these values are significant because they show the water content to be low.

Errors due to small weight changes were also produced by low hydrogen and carbon dioxide concentrations. When air was passed through energized hardwood charcoal 10-20 milligrams was the usual weight change due to hydrogen while the weight change produced by the carbon dioxide was 1.5-3 milligrams. When carbon dioxide was passed through sugar charcoal, or energized sugar charcoal, the resulting gas showed less hydrogen and the usual weight change due to the hydrogen was 0.5-1 milligrams. In this case the carbon dioxide was greater and the smallest amount of carbon dioxide weighed was 21.3 milligrams. The largest amount of carbon dioxide weighed in these experiments was about 250 milligrams.

The smallest division on the wet test meter corresponds to 0.001 cubic feet. An attempt was made to estimate to the nearest tenth of one of these divisions. When using air, 0.0300 cubic feet of inert gas, nitrogen, was allowed to pass through the wet test meter during an analysis. In this way a gas sample of approximately the same size, 1.1 liters, was always analyzed. When using carbon dioxide as the initial gas, the usual reading on the wet test meter was 0.0001-0.0003 cubic feet and due to the higher carbon monoxide content of this gas 0.5 liter samples were analyzed. An error

of 0.0001 cubic feet in reading the meter was equivalent to about 0.6 per cent of a 0.5 liter sample. The inert gas in these experiments was one per cent or less and therefore, these values may be in error. The values indicate that the amount of inert gas in these experiments was small.

MATERIALS

Two different charcoals were used in these experiments. Chemically pure sugar charcoal was obtained for use in the study of the effect of barium carbonate on the rate of the reaction between carbon dioxide and solid carbon. This charcoal was obtained as a fine powder while a granular product was desired to permit free passage of the gas. In order to lump up this charcoal, 100 grams of the charcoal were mixed with 100 grams of sugar and 50 cc. concentrated sulfuric acid were added to char the sugar. The mixture was then heated to about 760° C (1400° F) in a covered alundum crucible to drive off the acid. It was then ground and screened. The particles passing through a 3 mesh screen and retained on a 28 mesh screen were then heated to 1290° C (2350° F). This procedure was adopted because it gave a granular product which was fairly strong. It was found that the original powdered charcoal contained 3.00 per cent ash and the final product contained 3.94 per cent ash. Spectrographic analysis of the ash showed the following elements to be present: Mg, Al, Si, Fe Na and Ca. No K, Sr or Ba was detected in the ash.

The second charcoal, used to generate the carburizing atmosphere in the experiments on the study of the reaction between steel and carbon monoxide, was a hardwood charcoal. It was Tec-Char grade 4 manufactured by the Tennessee East-

man Corporation. This charcoal was ground and screened. The charcoal passing through an 8 mesh screen and retained on a 28 mesh screen was used.

These granular charcoals did not mix well with barium carbonate. In order to insure a uniform distribution of the barium carbonate, it was precipitated on the charcoal. Barium hydroxide was dissolved in water and this solution was added to the charcoal. The volume of solution was just sufficient to wet all the charcoal. Carbon dioxide was then added until all the hydroxide was converted to carbonate. The energized charcoal was dried at 120° C (250° F).

The ingot iron samples were made from $\frac{1}{2}$ inch rods. This material had the following analysis:

Carbon	0.010 % by weight
Manganese	0.013 %
Silicon	0.001 %
Sulfur	0.022 %
Phosphorus	0.005 %

The carbon dioxide used in these experiments was taken from one 50 pound cylinder. Orsat analyses showed that more than 99.8 per cent of the gas was absorbed by the potassium hydroxide solution, indicating less than 0.2 per cent impurities.

RESULTS

Part I.- The effect of barium carbonate on the reaction between austenite and a carbon monoxide-carbon dioxide carburizing atmosphere.

Reaction (12), the reaction between austenite and carbon monoxide, was studied by carburizing ingot iron samples with a gas composed of carbon monoxide, carbon dioxide and nitrogen. The carburizing atmosphere was generated in furnace G (see Figure 1). Thirty grams of energized hardwood charcoal was placed in furnace G as shown in Figure 2. The sample was placed in furnace H as shown in Figure 3.

At the start of the experiment the system was closed and evacuated up to stopcock V (see Figure 1), while the furnaces were heated up to temperature. During this period a great deal of moisture was given up by the charcoal and was pumped out of the system by the time the furnaces reached temperature and the actual carburizing started. As a test for the presence of moisture in the system, stopcock W was closed and the pressure in the system as indicated by P_3 was observed. If all the moisture were not removed the pressure increased rather rapidly.

The temperature of furnace G was controlled by a thermocouple outside the tube as described above while the temperature of furnace H was adjusted to the proper value by

setting the rheostat on the furnace and allowing it to reach a steady thermal state with its surroundings. After the temperature of each furnace was adjusted to the same value and all moisture was removed from the system the carburizing period started. About two hours were consumed during the heating period.

In some of the early experiments carbon dioxide was used to generate the carburizing atmosphere but it was found that the flow rate would not remain constant, especially at the higher rates, and constant attention was necessary to maintain a fairly constant flow rate. When it was found that the flow rate remained more nearly constant when air was used it was decided to use air instead of carbon dioxide for these experiments. The first source of air was a blower. This blower was also the source of air for the gas furnaces in the laboratory and some difficulty was experienced in maintaining a constant flow rate when the gas furnaces were placed in use. Later it was found that air taken from a compressed air line maintained at twelve pounds gage pressure gave a flow rate which remained practically constant and required little or no attention. This source of air was used in some of the experiments as indicated.

The gas entered the system through the drying towers E and F, passed down through the hot energized charcoal and then over to furnace H where it carburized the ingot iron sample. After leaving furnace H the gas passed through the

flow meter, wet test meter and out of the system. At the end of the carburization period the furnaces were turned off and allowed to cool.

The results of the early experiments are shown in Table I. The ingot iron samples have been described above. Barium carbonate was placed in some of the samples and tapped very lightly with the end of a pencil to spread it over the bottom of the hole.

The flow rates given in Table I are the overall average flow rates as calculated by dividing the total dry volume of gas at standard conditions by the carburizing time. The volume of gas passing through the system registered on the wet test meter. This volume was corrected for the vapor pressure of water and reduced to standard conditions. The volume of gas absorbed during any analyses was added and this total volume was used to calculate the flow rate in liters per hour. The source of air in these experiments was the blower mentioned above.

The case depths were measured on the sectioned and polished samples at the base of the hole. The case depths were measured by projecting the samples at 100 diameters onto the ground glass focusing screen of a Bausch and Lomb metallograph. The case depths were measured to the base of the eutectoid zone.

In these experiments the thermocouples had not been calibrated and had been used more than once.

Table I

Effect of Barium Carbonate on the Reaction Between Iron and Carbon Monoxide at 950° C.

Sample[1]	Carburizing[2] Compound	Time, hr.	Flow Rate, L/hr.	Case Depth, mm.	Type Case[3]
1	I	5.0	4.51	0.40	E
2x	I	4.5	4.45	0.94	C
3	II	4.5	3.27	0.00	0.6 - 0.7% carbon
4	II	4.5	3.80	0.73	C
5	II	5.0	7.52	0.60	E
6	II	4.5	11.9	0.68	E
7	II	4.5	13.7	0.87	E
8	II	4.5	15.4	0.68	E
9x	II	5.5	4.27	1.28	C
10x	II	4.5	5.34	0.83	C
11x	II	4.5	11.6	1.04	C
12x	II	4.5	16.4	0.90	C
13[4]	I	4.7	4.04	0.68	C
14x	I	4.8	4.35	0.93	C

1. Those samples marked "x" had barium carbonate at the base of the hole.
2. These hardwood charcoal compounds generated the carburizing atmosphere. Compound I had 10% barium carbonate added; compound II had 2% barium carbonate.
3. Samples marked "E" had eutectoid cases; samples marked "C" showed excess cementite.
4. Carbon dioxide was used to generate a pure carbon monoxide-carbon dioxide gas for samples 13 and 14.

It is generally believed that carbon monoxide alone is a poor carburizing agent. However, it has been shown (11) that the carburizing action of carbon monoxide depends on the velocity with which the gas passes over the steel surface. It will be seen by sample 13 in Table I that a carbon monoxide-carbon dioxide atmosphere produced a hypereutectoid case in 4.7 hours at 950° C (1742° F). This would certainly seem to indicate that under special conditions where very intimate contact between steel and carbon monoxide is possible the carburizing action can be rather intense. Samples 4-8 also indicate that appreciable case depths and rather high carbon contents may be obtained even when the carbon monoxide is diluted with 65 per cent nitrogen.

The data in Table I indicate that the presence of barium carbonate has a favorable effect on the reaction between carbon monoxide and austenite. Comparison of samples 13 and 14 shows that a deeper case was obtained when barium carbonate was present. In this instance, however, sample 14 had a slight advantage since it was carburized slightly longer (5 min.) and the flow rate was greater. With samples 1 and 2, sample 1 had the advantage and still the sample with the barium carbonate formed the deeper case. In addition to the deeper case, sample 2 had a higher surface carbon content as indicated by the presence of excess cementite in the case.

Samples 3-12 were carburized over a range of flow rates

since it was difficult to reproduce a given flow rate. Except for samples 5 and 9 the carburizing time was 4.5 hours in each case. A better correlation between flow rate and case depth had been expected. However, one striking difference is immediately apparent between samples with and those without barium carbonate present. In each experiment where barium carbonate was present a hypereutectoid case was produced; whereas, when barium carbonate was not present a eutectoid case was produced. Samples 3 and 4 were the two exceptions. Sample 3 had a hypoeutectoid case while sample 4 had a hypereutectoid case. No barium carbonate was present in either run. Another difference between samples with and without barium carbonate present was the extent of the case up the side of the samples. This will be discussed and illustrated in connection with the next set of experiments.

The appearance of the samples in these experiments seemed to indicate that the outside surface was oxidized during the heating period, reduced during the carburizing period and then oxidized again during the cooling period. There was no apparent sign of oxidation inside the hole. Later it was found that if furnace H were closed off from the rest of the system during the heating period, after it had been evacuated, and if it were again closed off from the system immediately after the carburizing period this oxidation did not occur and the samples came out with a bright metallic surface.

Table II

Gas Analyses

Sample[1]	Per Cent by Volume % inert	% CO	% CO_2	% H_2O	% H_2	K'_{11}
1	66.9	31.5	0.41	0.30	0.88	24.2
2	66.6	30.6	1.05	0.73	1.82	8.8
3	64.6	33.1	0.52	0.02	1.83	20.4
3	67.3	31.5	0.52	0.00	0.64	18.4
4	64.5	31.3	2.87	0.15	1.21	3.3
4	63.7	29.9	4.22	0.48	1.61	2.1
5	65.1	32.9	0.62	0.00	1.40	17.7
5	65.4	33.3	0.44	0.00	0.97	25.2
5	65.3	33.2	0.36	0.00	1.15	30.6
6	65.6	33.0	0.30	0.03	0.95	36.7
7	63.4	35.3	0.36	0.05	0.85	34.8
8	65.3	33.1	0.40	0.16	1.11	28.4
8	66.5	32.2	0.24	0.00	1.17	44.5
8	62.3	36.1	0.20	0.00	1.34	67.7
9	62.6	35.4	0.35	0.07	1.72	37.6
9	64.4	33.2	0.36	0.14	1.98	30.5
10	66.0	31.6	0.70	0.08	1.62	14.1
10	64.6	33.5	0.43	0.08	1.58	25.9
11	65.8	33.0	0.23	0.00	1.08	46.3
12	65.5	33.6	0.25	0.07	0.65	46.4
12	66.0	33.2	0.25	0.02	0.58	45.5
13	2.13	94.0	3.23	0.01	0.74	27.4
14	2.20	95.9	1.62	0.24	0.05	56.7

1. Number of sample refers to ingot iron samples in Table I. These analyses were conducted during the carburizing period of the given samples.

Gas analyses were made during these experiments. The gas analyses are tabulated in Table II. The equilibrium constant for reaction (11) is:

$$K_{11} = \frac{(CO)^2}{(CO_2)} P$$

where (CO) is the volume fraction of carbon monoxide, (CO_2) is the volume fraction of carbon dioxide and P is the total pressure.

Since equilibrium was not obtained in the experiments, an equilibrium constant may not be calculated. However, the values for carbon monoxide, carbon dioxide and pressure were substituted in the equation for K_{11} and the calculated result is given in Table II as K'_{11}. This may serve to indicate the degree of approach to equilibrium. At 950° C (1742° F) the value of K_{11} should be 76.7 (12).

The values of K'_{11} listed in Table II led to the conclusion that the gas had precipitated carbon inside furnace H and formed carbon dioxide by reversing reaction (11). The equilibrium constant for the reaction increases with increase in temperature. This means that a carbon monoxide-carbon dioxide atmosphere in equilibrium with solid carbon will contain more carbon monoxide at a high temperature than at a lower temperature. It also means that if the equilibrium gas mixture at the elevated temperature is cooled to a lower temperature it will have a tendency to form carbon dioxide

and precipitate carbon. After leaving the sample the gas was free to circulate inside furnace H (see Figure 3) before reaching the outlet tube. Therefore, while the sample was at the same temperature as the charcoal in the other furnace and there should be no tendency to deposit carbon on the sample there was a tendency for the gas to precipitate carbon in the cooler portions of the furnace and carbon was found on the thermocouple wires in the cooler sections of the furnace. Since the composition of the gas had changed before it was analyzed, no definite conclusions can be drawn from the data in Table II.

A better correlation between flow rate and case depth was desired than that shown in Table I. Therefore, a new set of experiments was performed using an improved experimental technique. For these new experiments air was taken from the compressed air line in order to obtain a constant flow rate. A new calibrated thermocouple was used in each furnace for each experiment. Furnace H was closed off from the rest of the system during the heating and cooling periods to prevent the oxidation mentioned above and the samples came out clean and bright. The hardwood charcoal used to generate the carburizing atmosphere was energized with 10 per cent barium carbonate. Forty grams of the energized charcoal was used in each experiment.

The results of this set of experiments are shown in Table III. These samples were carburized 4.5 hours at 925° C

Table III

Effect of Barium Carbonate on the Reaction Between Iron and Carbon Monoxide at 925° C.

Sample	Flow Rate, L/hr.	Case Depths in mm. Base Eut.	Base Hypereut.	Side Wall Eut.	Side Wall Hypereut.
Samples with no barium carbonate present:					
15	2.90	0.53	0.19	0.24	0.00
16	3.09	0.19	0.00	0.00	0.00
17	5.19	0.53	0.25	0.33	0.00
18	8.03	0.54	0.21	0.00	0.00
19	8.11	0.56	0.20	0.54	0.19
20	8.32	0.62	0.27	0.11	0.00
21	9.95	0.67	0.25	0.75	0.25
Samples with barium carbonate present:					
22	3.01	0.60	0.00	0.51	0.00
23	5.43	0.62	0.22	0.60	0.17
24	7.86	0.64	0.26	0.62	0.23
25	10.0	0.68	0.28	0.70	0.27
26	10.1	0.66	0.35	0.73	0.31

Table IV

Gas Analyses

Flow Rate, L/hr.	Per Cent by Volume % CO	% CO_2	% H_2O	% H_2	% inert	K'_{11}
2.88	32.9	0.14	0.10	2.99	63.9	73.8
5.41	33.7	0.11	0.12	0.98	65.2	95.5
5.49	31.9	0.12	0.07	2.50	65.5	83.7
7.53	33.7	0.12	0.09	1.56	64.6	95.0
8.13	32.6	0.08	0.07	0.85	66.3	133.0
8.53	32.7	0.07	0.06	0.84	66.3	154.0
10.0	33.0	0.07	0.03	0.30	66.6	158.0

(1697° F). The case depths were measured by the same method as was used with the first set of samples. The eutectoid case depth given in Table III refers to the distance from the surface to the base of the eutectoid zone and therefore, includes the hypereutectoid zone. The hypereutectoid case depths alone were also measured. Table III gives these case depths as measured at the base of the hole and on the sides of these samples. The case in the side wall was measured near the base where it was of maximum depth. The relationship between the case depth and flow rate is shown in Figures 4-7.

Hypereutectoid cases were produced on all the samples except samples 16 and 22 which were carburized at the lowest flow rate. Examination of the data shows that there is a definite trend toward deeper cases in the presence of barium carbonate, confirming the results of the first set of experiments. When barium carbonate was placed at the bottom of the samples the case extended to the top of the samples. For example, sample 22 showed an eutectoid case throughout the length of the side wall. On the other hand, in the samples with no barium carbonate present the hypereutectoid or eutectoid case did not extend to the top of the sample except in one instance: sample 19 had a eutectoid case throughout the side wall but the hypereutectoid case did not extend to the top of the sample. Figure 9 shows sample 15 and the extent of the eutectoid case is marked.

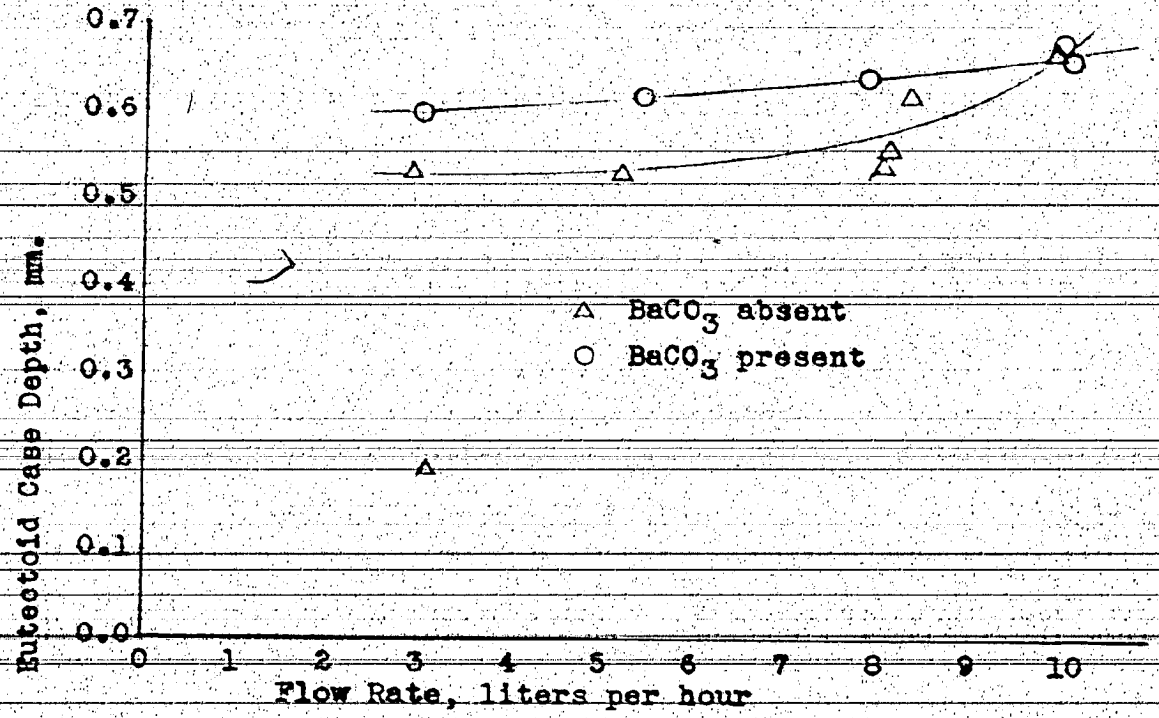

Figure 4. Effect of barium carbonate on reaction between carbon monoxide and steel. Case depths at base of hole.

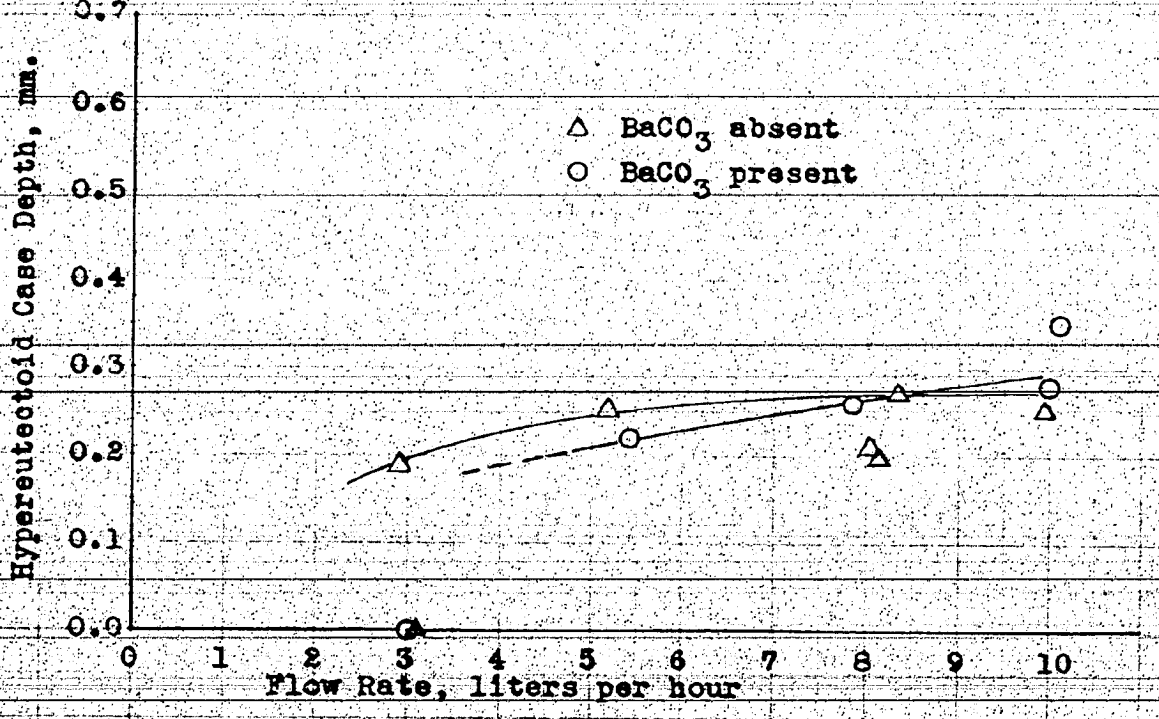

Figure 5. Effect of barium carbonate on reaction between carbon monoxide and steel. Case depths at base of hole.

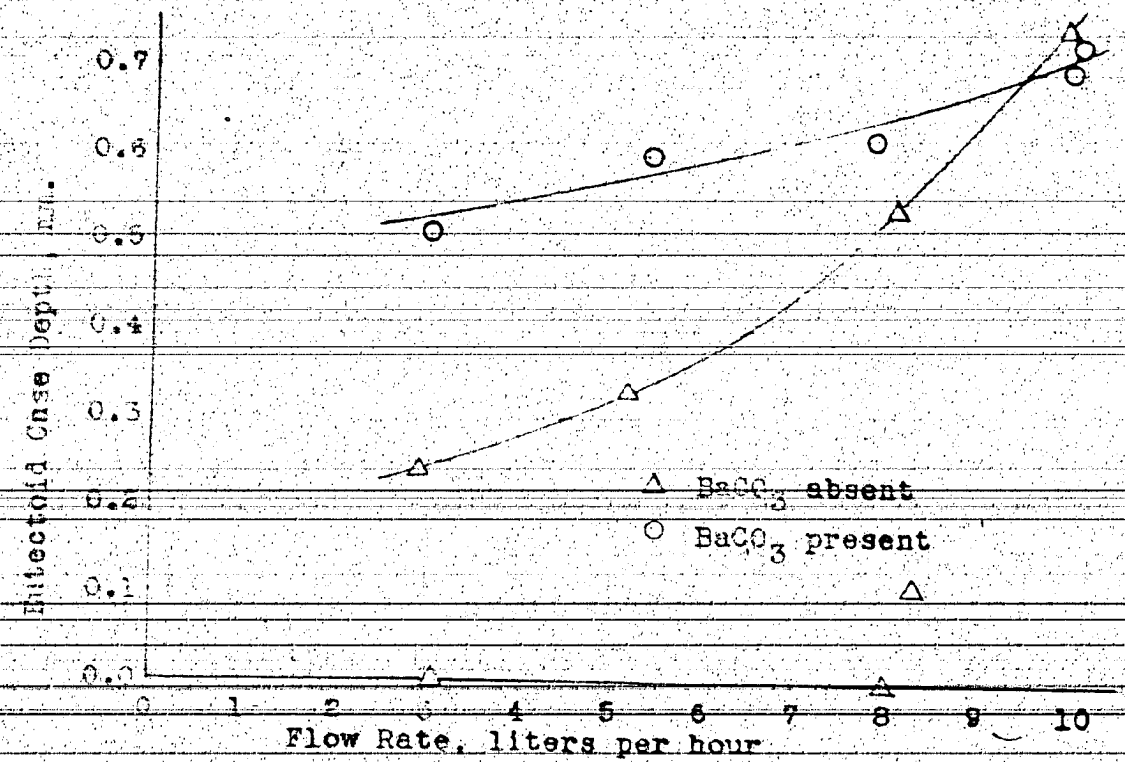

Figure 6. Effect of barium carbonate on reaction between carbon monoxide and steel. Case depths in side wall.

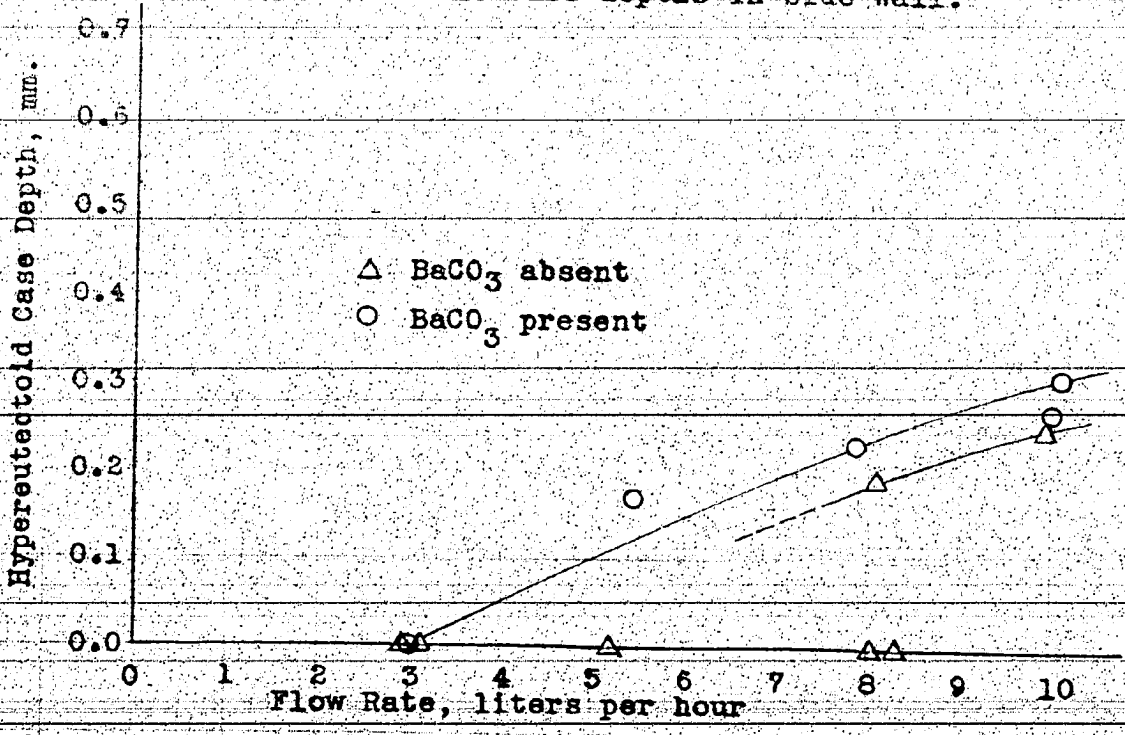

Figure 7. Effect of barium carbonate on reaction between carbon monoxide and steel. Case depths in side wall.

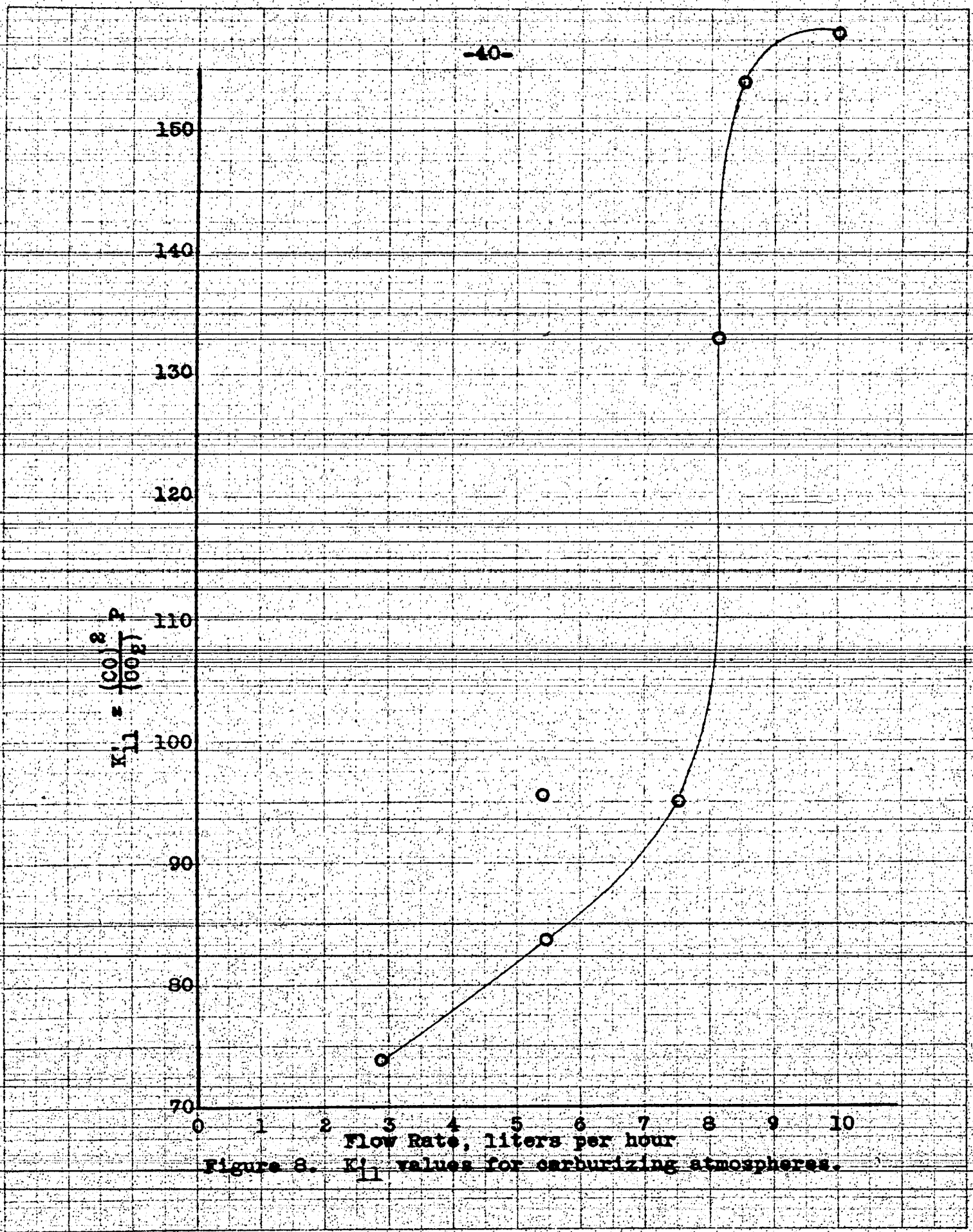

Figure 8. K'_{11} values for carburizing atmospheres.

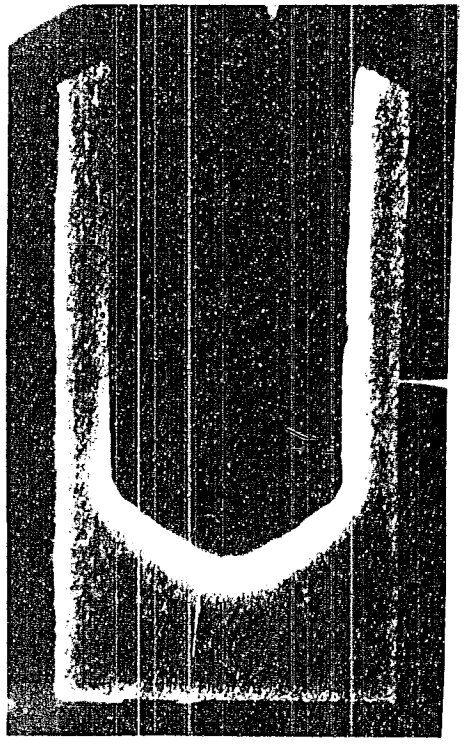

Figure 9. Sample 15 with the extent of the eutectoid case indicated by pointer at right. X 4.

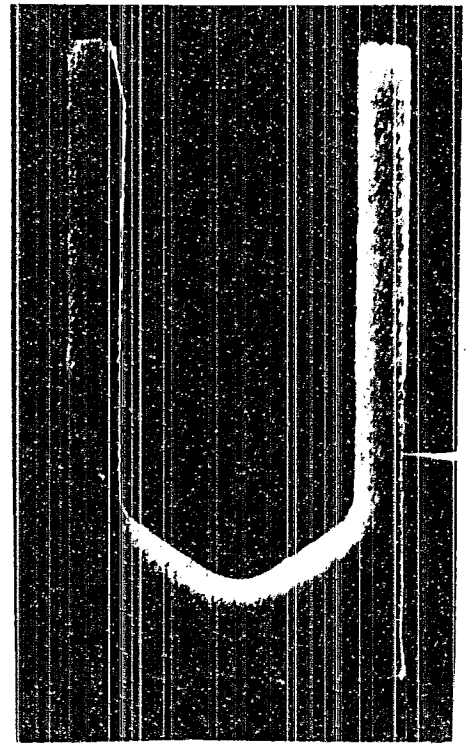

Figure 10. Sample 17 with the extent of the eutectoid case indicated by pointer at right. X 4.

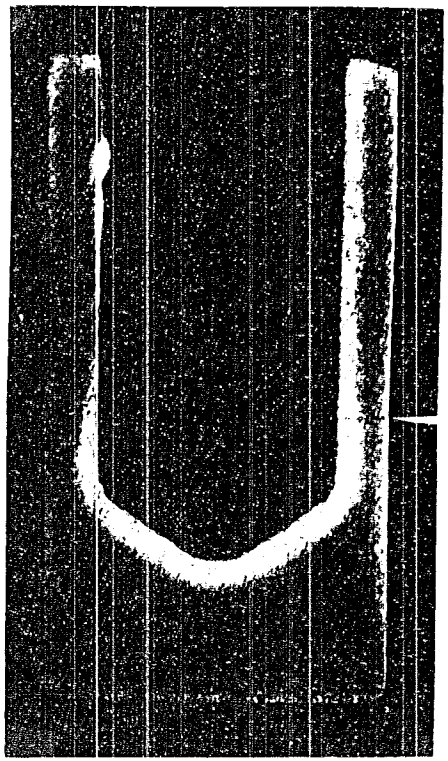

Figure 11. Sample 19 with the extent of the hypereutectoid case indicated by pointer at right. Eutectoid case extends to top of sample. X 4.

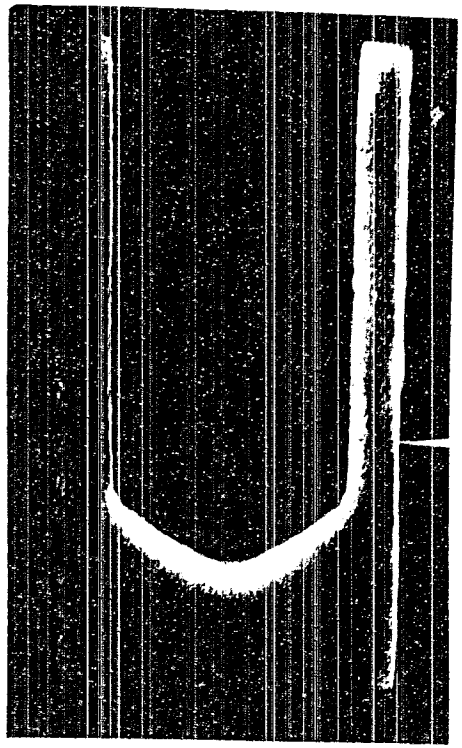

Figure 12. Sample 20 with the extent of the eutectoid case indicated by pointer at right. X 4.

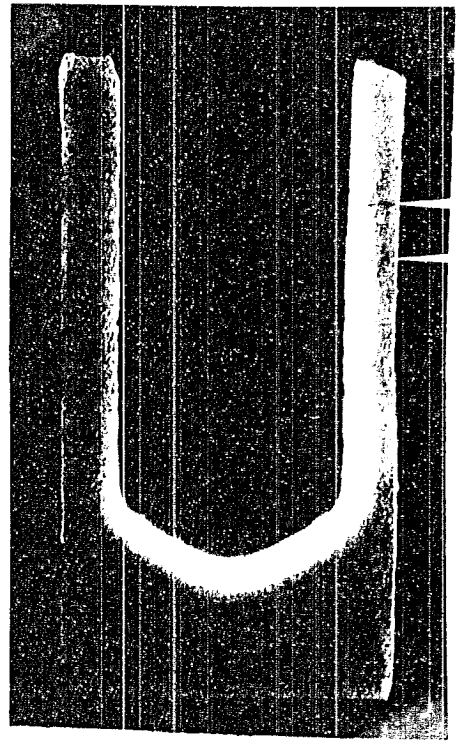

Figure 13. Sample 21 with the extent of the hypereutectoid and eutectoid cases indicated at right. Lower pointer indicates extent of hypereutectoid case; upper pointer indicates extent of eutectoid case. X 4.

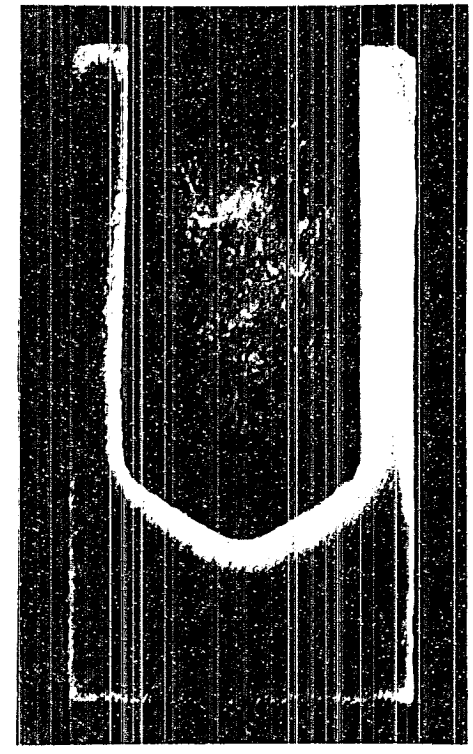

Figure 14. Sample 24 showing case in right side wall of sample. Hypereutectoid case extends to top of sample. X 4.

Figures 10-13 show the extent of the cases in the other samples where no barium carbonate was present. Figure 14 shows a sample to which barium carbonate was added.

After the last set of samples was carburized a separate set of experiments was conducted to determine the gas analyses at various flow rates. The gas was sent directly to the absorption bulbs after leaving the charcoal and was not reheated in furnace H. These analyses represent the composition of the gas which carburized the samples. These analyses are given in Table IV. The value of K'_{11} as calculated from these analyses is also tabulated with the analyses and is shown graphically as a function of the flow rate in Figure 8. At 925° C (1697° F) the value for K_{11} is 55.0.

Figure 8 indicates that the gas composition was not constant for the various flow rates. A gas of practically the same composition at all flow rates was desired in order to show the effect of gas velocity on the degree of carburization. However, the effect of gas velocity has been demonstrated by Bramley and Jinkings (11). For the purpose of this work the difference in composition of the gas at the various flow rates does not affect the conclusions to be drawn from the experiments since it is believed that identical conditions existed for the samples at any given flow rate except for the addition of barium carbonate to some of the samples.

It is evident from the results tabulated in Table IV

and shown graphically in Figure 8 that the gas composition was such that K'_{11} was greater than the accepted value of K_{11}. This means that either the carbon monoxide was too high or the carbon dioxide was too low to satisfy the equilibrium conditions for reaction (11). If we assume that the oxygen in the air reacts to form carbon dioxide and that this carbon dioxide reacts with more carbon according to reaction (11) these results are difficult to explain because the carbon monoxide concentration would not be expected to exceed the equilibrium value. Since K'_{11} tends to approach the value of K_{11} as the flow rate decreases the system appears to approach equilibrium for reaction (11). It may be that reactions such as (8) and (9), given by Ragatz and Kowalke, are responsible for the unusual conditions observed in these experiments as the flow rate is increased.

Part II.- The effect of barium carbonate on the rate of reaction between carbon dioxide and charcoal.

The procedure for these experiments was similar to that given in Part I. Twenty grams of sugar charcoal, or energized sugar charcoal, was placed in furnace H (see Figures 1 and 2). Furnace G was closed off from the rest of the sys-

tem during these experiments. The system was evacuated, as before, while the furnace was brought up to temperature. The temperature was maintained constant in these experiments by the controller. The control thermocouple was placed outside the furnace tube and the controller was adjusted as before. After the heating period carbon dioxide was admitted to the system. The gas entered the system through drying towers C and D, moved up to the top of furnace H, down through the bed of charcoal, through the capillary tube flow meter, drying tower, wet test meter and out of the system through the trap and bubbler. After adjusting the flow rate to the desired value, a sample of the gas was analyzed by the procedure described in the section on gas analysis.

Extreme care was used in placing the charcoal in the furnace to prevent any charcoal or barium carbonate from getting into the bore of the gas-outlet tube. The hot junction of the thermocouple was formed into a rather large bead and this was placed over the opening of the tube leaving just enough space between the thermocouple and opening to allow free passage of the gas. The bore of the gas-outlet tube was kept clean by forcing high pressure air through the tube before each experiment and it was occasionally washed out with dilute hydrochloric acid.

The results of these experiments are shown in Table V. The flow rates were determined, again, by the time taken for a definite volume of gas to pass through the wet test meter

Table V

Effect of Barium Carbonate on the Rate of Reaction Between Carbon Dioxide and Carbon an 925° C.

Flow Rate, L/hr.	Gas Analyses: Per Cent by Volume % CO	% CO_2	% H_2O	% H_2	% inert	K'_{11}
Sugar charcoal:						
0.53	88.6	9.85	0.20	0.33	1.08	7.81
1.21	85.1	14.0	0.00	0.02	0.94	5.09
2.43	77.8	20.9	0.04	0.87	0.38	2.87
4.00	73.2	26.3	0.02	0.52	0.04	2.00
5.08	67.5	31.0	0.58	0.00	0.96	1.46
Sugar charcoal energized with 2% $BaCO_3$:						
0.52	92.6	5.86	0.06	0.18	1.36	14.2
1.57	89.8	8.98	0.13	0.13	0.93	8.83
2.55	84.4	13.8	0.33	0.18	1.37	5.00
3.67	79.6	18.5	0.51	0.48	1.01	3.36
5.02	77.1	21.2	0.21	0.52	0.97	2.81
Sugar charcoal energized with 10% $BaCO_3$:						
0.56	97.6	2.37	0.04	0.00	0.00	39.8
1.67	94.2	4.61	0.12	0.04	1.04	18.7
2.71	91.3	7.75	0.11	0.55	0.37	10.5
3.79	90.0	9.10	0.39	0.10	0.41	8.67
5.53	88.8	9.82	0.00	0.00	1.33	7.85

and are given as liters per hour of dry gas at standard conditions.

The values of K'_{11} were calculated and give some idea of the approach to equilibrium. The experiments were conducted at 925° C (1697° F) at which temperature the equilibrium constant, K_{11}, has a value of 55.0. A pure carbon monoxide-carbon dioxide atmosphere in equilibrium with carbon at one atmosphere pressure contains 98.4 per cent carbon monoxide.

The carbon monoxide content of the gas resulting from the reaction between the carbon dioxide and hot sugar charcoal is shown graphically as a function of the flow rate in Figure 15. These curves show that the carbon monoxide content of the gas is increased by the addition of barium carbonate to the charcoal. The addition of 10 per cent energizer produces a greater effect than the addition of 2 per cent energizer. The calculated values of K'_{11} are also shown as a function of the flow rate in Figure 16. These curves show that, again, the approach to equilibrium is greater when barium carbonate is added to the charcoal.

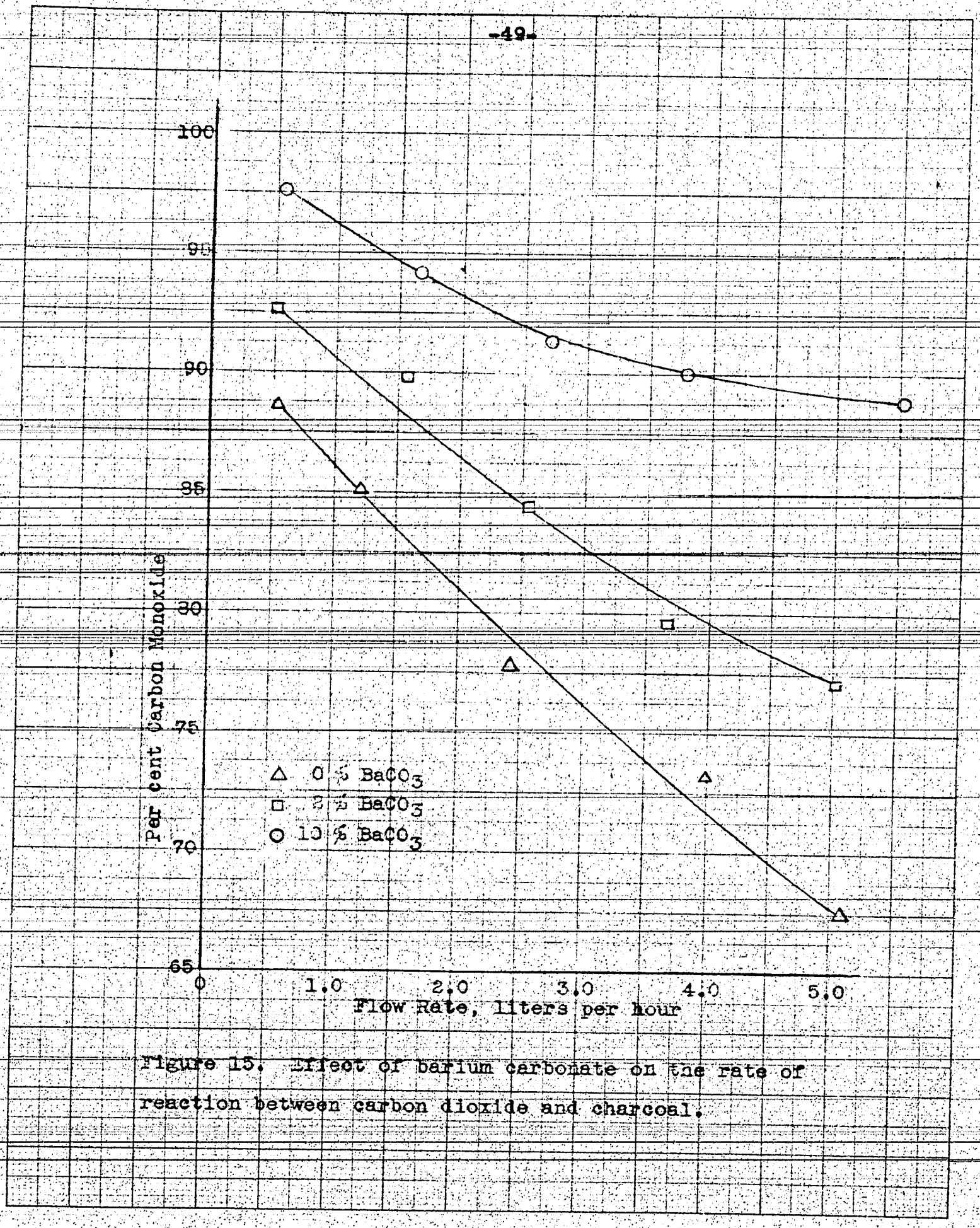

Figure 15. Effect of barium carbonate on the rate of reaction between carbon dioxide and charcoal.

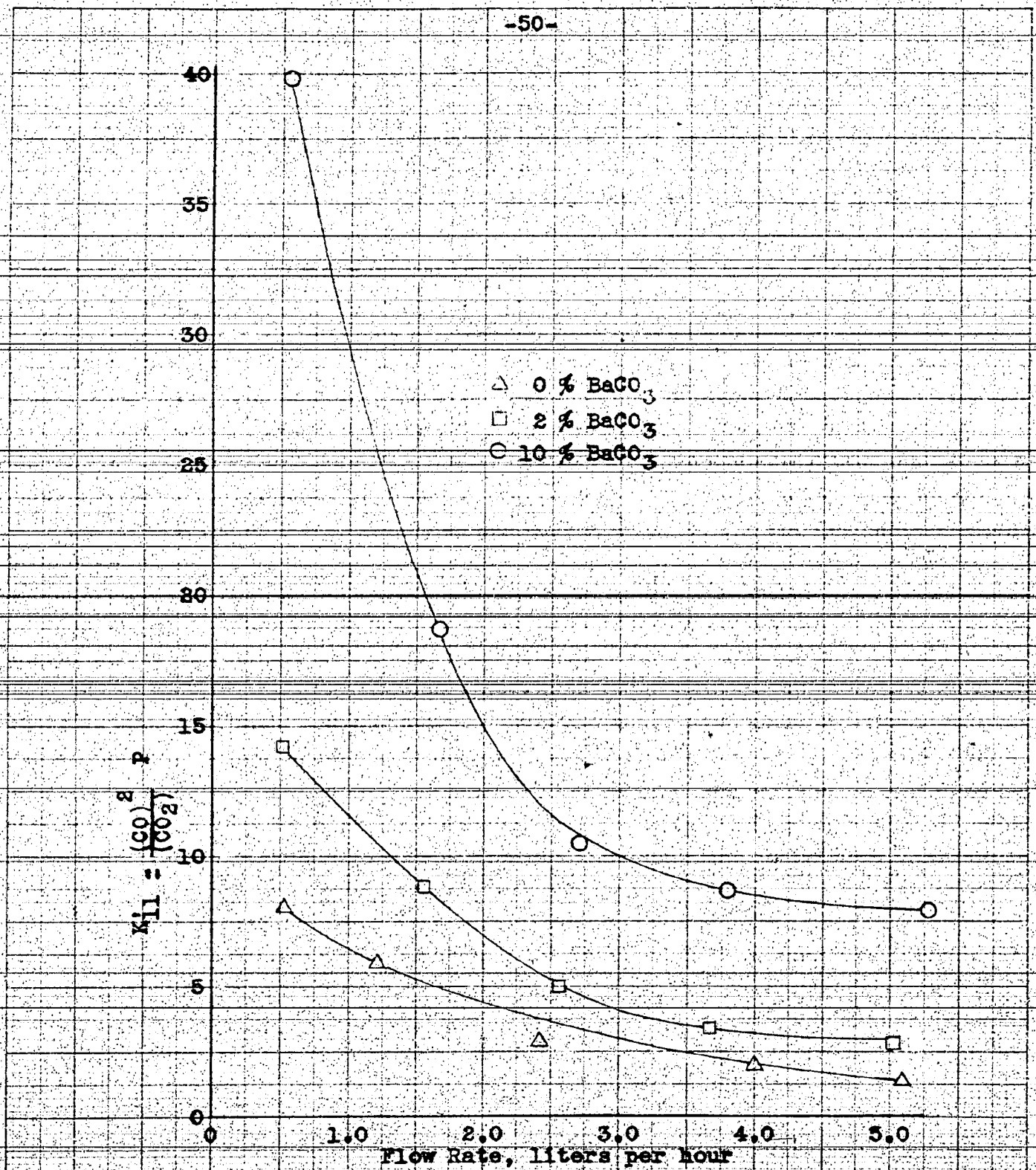

Figure 16. Effect of barium carbonate on the rate of reaction between carbon dioxide and charcoal.

DISCUSSION

During pack carburizing the steel pieces are placed in a carburizing compound which is contained in a closed carburizing box. When the box is heated to and held at the carburizing temperature, the case depths and surface carbon concentrations will be greater if an energizer has been added to the carburizing compound than if the carbon base alone (usually a mixture of hardwood charcoal and coke) were used as the carburizing compound. Why the difference?

At the present time there is some doubt about the validity of the carbon dioxide evolution theory. According to this theory the carbonate energizer slowly evolved carbon dioxide which flushes nitrogen from the carburizing box. The carbon dioxide then reacts with the charcoal to form an atmosphere of nearly pure carbon monoxide. The high carbon monoxide concentration is said to be responsible for the more intense carburizing in the energized charcoal.

It was shown (4), (5) that a carbonate was not necessary and that many other compounds show equal activity as energizers. However, this evidence was not considered sufficient to disprove the carbon dioxide evolution theory because it was pointed out that the other compounds were capable of evolving oxygen or carbon dioxide, either of which would produce carbon monoxide by reacting with carbon, and it was shown that some of these compounds could pick up car-

bon dioxide during heating and release it at elevated temperatures (6), (7). Recently (7) it has been shown that the evolution of carbon dioxide ceases soon after reaching carburizing temperature. This, too, has not been considered sufficient evidence to warrant discarding the carbon dioxide evolution theory because the early evolution of carbon dioxide would flush the nitrogen from the carburizing box and after that, evolution of more carbon dioxide would not be necessary (13).

The proponents of the carbon dioxide evolution theory imply that if an atmosphere of very high carbon monoxide content is produced inside the carburizing box the steel will be carburized well. This assumption may not be justified because Takahashe (3) showed that when carbon monoxide was passed through a carburizing compound of plain charcoal the case depth and carbon concentration of the case were not so great as those of samples carburized by energized charcoal in a closed container. When carbon monoxide was passed through the energized charcoal even deeper cases and higher carbon concentrations were produced. Apparently the existence of an atmosphere of very high carbon monoxide content does not in itself insure rapid carburizing.

Unfortunately actual gas analyses of atmospheres inside carburizing boxes are not available but since the boxes are not air tight it is not likely that analysis will show a pure carbon monoxide-carbon dioxide atmosphere. During the

heating period evolution of carbon dioxide by the energizer may flush most of the nitrogen from the box but after cessation of carbon dioxide evolution air will undoubtedly diffuse or leak into the box. This inward diffusion of air does occur through leaks in heat treating furnaces and is the reason why nitrogen cannot be used commercially as an inert atmosphere (14), (15). In the absence of gas analyses one may only speculate on the amount of air which diffuses into the box but it seems reasonable to expect an appreciable quantity to enter during the course of an eight hour carburizing period. In this connection, a discussion such as that of Grossmann (16) is misleading because it is based on the probably erroneous assumptions that the combined partial pressures of the carbon monoxide and carbon dioxide is one atmosphere and that a pure carbon monoxide-carbon dioxide atmosphere exists inside a carburizing box. Grossmann deduces the composition of the atmospheres inside carburizing boxes when energized and when unenergized charcoal is used as the carburizing compound. By means of the surface carbon content of the case and the equilibrium data on the carbon-oxygen-iron system he concludes that the surface of the steel is in equilibrium with an atmosphere of 95 per cent carbon monoxide when unenergized charcoal is used while the atmosphere contains between 96 and 97 per cent carbon monoxide when energized charcoal is used. This is, indeed, a clever means of obtaining information about the composition

of the gas contained in a carburizing box but the atmosphere need not contain such high carbon monoxide concentrations and, furthermore, the carbon monoxide may not be greater when energized charcoal is used as shown by this line of reasoning. In the first place, if air leaks into the box the combined partial pressures of the carbon monoxide and carbon dioxide will not be one atmosphere and some nitrogen will be present along with other gases. Carburizing compounds may release quantities of hydrogen and methane (17). Therefore, if the surface of the steel were in equilibrium with the surrounding atmosphere such high carbon monoxide concentrations would not exist nor are they necessary as we shall see later. In the second place, equilibrium between the steel surface and the gas may not exist, especially in the unenergized carburizing compound. The results of the present investigation show that the energizer accelerates the rate of reaction between austenite and carbon monoxide. Suppose the atmospheres are identical when energized and unenergized charcoal are used. If the energizer accelerates the rate of reaction between austenite and carbon monoxide sufficiently to attain equilibrium while the rate of reaction in the plain charcoal is too slow to attain equilibrium one would conclude, using Grossmann's line of reasoning, that the energized charcoal produced a higher carbon monoxide concentration than the plain charcoal.

In the last paragraph the atatement was made that the

carbon monoxide content of the gas inside a carburizing box need not be as high as that deduced by Grossmann. In order to explain this point it is best to mention the equilibrium studies of the carbon-oxygen-iron system (18)-(21). The various sets of data on this system are not in complete accord but this need not concern us here. These studies are concerned with reaction (12) whose equilibrium constant is:

$$CO_2 + C \text{ (dissolved in austenite)} \rightleftharpoons 2CO \qquad (12)$$

$$K_{12} = \frac{(CO)^2}{(CO_2)} P$$

where (CO) is the volume fraction of carbon monoxide, (CO_2) is the volume fraction of carbon dioxide and P is the total pressure.

It is seen that the same expression represents K_{11}. However, there is a difference between K_{11} and K_{12}. K_{11} is a function of temperature only (assuming a given form of carbon) while K_{12} is a function of temperature and carbon content of the austenite. Both the K's are independent of pressure but the actual gas compositions do change with a change in pressure. For a given total pressure, introduction of an inert gas such as nitrogen is equivalent to decreasing the pressure of a pure carbon monoxide-carbon dioxide atmosphere. In order to use the equilibrium data to deduce the gas composition inside a carburizing box it is necessary to assume equilibrium exists between the surface of the steel and the gas. It is

then necessary to know the carburizing temperature, the carbon concentration at the surface of the steel, the total pressure and the amount of nitrogen and other gases present. The values Grossmann read off the equilibrium diagram tell us that the atmospheres inside the boxes are equivalent to these carbon monoxide concentrations in a pure carbon monoxide-carbon dioxide atmosphere at one atmosphere pressure. Using the values read by Grossmann it is necessary to calculate values of K_{12}. These values are:

% CO	% CO_2	Total Press., Atm.	K_{12}
95	5	1	18.1
96	4	1	23.0
97	3	1	31.4

Suppose sufficient nitrogen and other gases are present in the box to make up 50 per cent of the gas. Equilibrium is still possible if the proper relationship exists between the carbon monoxide and carbon dioxide. This relationship must be according to the expression given for K_{12}. The K_{12} values must be the same for the same equilibrium to exist. For 50 per cent foreign gases the steel samples would be in equilibrium with the gas if the analyses were:

% N_2, etc.	% CO	% CO_2	Total Press., Atm.	K_{12}
50	48.69	1.31	1	18.1
50	48.96	1.04	1	23.0
50	49.23	0.77	1	31.4

Thus, we see that it is not necessary to have nearly pure carbon monoxide atmospheres in carburizing boxes. The carbon dioxide content is equally as important as the carbon monoxide content. It does not seem reasonable to expect as much as 95 per cent carbon monoxide in a carburizing box which is not air tight.

In this investigation hypereutectoid cases were produced by a carbon monoxide-carbon dioxide atmosphere diluted with approximately 65 per cent nitrogen. These results were obtained by using rather high gas velocities and in this respect the conditions were different from those existing in a carburizing box. However, these experiments show it is possible to obtain high carbon contents and deep cases with a diluted atmosphere in a short time. Thus, we see that deep cases are possible when an appreciable amount of nitrogen is present and Takahashi has shown that the presence of a pure carbon monoxide atmosphere in a plain charcoal compound does not give as deep a case as a less pure atmosphere when an energizer is added to the charcoal. These facts lead to the conclusion that the function of the energizer is more than that of furnishing an atmosphere of high carbon monoxide content.

In recent years there appears to be a trend toward the theory that the energizer catalyzes the reaction between carbon dioxide and carbon. Ragatz and co-workers (4), (7) have offered a rational explanation for the mechanism of this

action. In this way the energizer decreases the amount of carbon dioxide in the gas phase and enhances the carburizing ability of the gas. The function of the energizer in this catalytic theory is, in a sense, very similar to that of the energizer in the carbon dioxide evolution theory. The difference lies in the means by which the result is accomplished. The carbon dioxide evolution theory has the energizer flush nitrogen from the container with carbon dioxide and then assumes that all or most of the carbon dioxide is converted to carbon monoxide. The catalytic theory insures conversion of the carbon dioxide to carbon monoxide by having the energizer act as catalyst for the reaction between the gas and charcoal. Both these theories assume that if the gas in the carburizing box is in equilibrium with the charcoal carburization will proceed satisfactorily.

The results of this investigation support the catalytic theory in that they show that the rate of reaction between carbon dioxide and charcoal is accelerated by the presence of barium carbonate. This effect is important if the rate of carburization is such that carbon dioxide is produced by reaction (12) more rapidly than plain charcoal can convert it to carbon monoxide. The carbon monoxide content of the gas must be relatively large for the gas to have an appreciable carburizing capacity but for every carbon monoxide analysis, according to K_{12}, a corresponding maximum carbon dioxide analysis is permissible if the gas is to have the

ability to raise the carbon content of the steel surface to any given value. Thus, one function of the energizer may be to accelerate reaction (11) in order that it may "keep pace" with reaction (12). However, evidence indicates that the function of the energizer is more than maintaining a nearly pure carbon monoxide-carbon dioxide atmosphere or maintaining the proper relationship between the carbon monoxide and carbon dioxide in an atmosphere diluted with nitrogen.

A pure carbon monoxide atmosphere carburizes very slowly unless it is passed over the steel at a fairly high velocity (11). There is no reason to expect any great turbulence inside a carburizing box and, therefore, there is good reason to suspect the carburizing ability of a carbon monoxide atmosphere inside the box even though regeneration of the atmosphere is possible by the charcoal. The results of this investigation show that the presence of barium carbonate accelerates the rate of carburization by a carbon monoxide-carbon dioxide atmosphere drawn off a bed of hot charcoal. The results show that the effect of barium carbonate is more pronounced at low velocities than at the higher velocities. It should also be remembered that the gas composition was such that the "carburizing potential" was less at the lower velocities. Inside a carburizing box this effect may well be responsible for the difference in results produced by energized and unenergized charcoal.

Takahashi (3) found that a number of carbonates accel-

erated the rate of carburizing by pure carbon monoxide. In his experiments carbon was precipitated on the samples and this led him to believe that the function of the carbonate was to decompose the carbon monoxide and precipitate carbon on the steel. This carbon, being very finely divided and in intimate contact with the surface, was believed to dissolve in the austenite. The exact mechanism whereby carbon is transferred from the carbon monoxide to the austenite is a problem which deserves further study but the intermediate solid carbon phase may not be necessary. In Takahashi's experiments with pure carbon monoxide, there was a tendency for the gas to precipitate carbon and form some carbon dioxide according to the equilibrium demanded by reaction (11). However, Takahashi even claimed that certain carbonates had the ability to promote the precipitation of carbon from mixtures of carbon monoxide and carbon dioxide whose carbon monoxide partial pressure was not more than that required by equilibrium for reaction (11). In the present experiments no evidence of carbon precipitation was ever found on the ingot iron samples or on the alundum tube. It is very possible that carbon monoxide is adsorbed on the metal surface where a reaction occurs between the austenite and carbon monoxide forming cementite. The cementite could then dissolve in the austenite and diffuse inward.

Another point which should be mentioned here is the fact that the carburizing experiments in this investigation indi-

cate that the carbon monoxide is "activated" by contact with barium carbonate. The gas exhibited a prolonged carburizing activity after passing over barium carbonate. This action may be important during pack carburizing since the carbon monoxide is generated at the carbon surface in contact with the energizer and must travel through the gas phase to the steel surface.

The compositions of the carburizing atmospheres in Part I should also be mentioned. These experiments showed that the carbon monoxide concentration in a diluted atmosphere exceeded the equilibrium value for reaction (11). If this condition can exist inside a carburizing box and if the energizer is responsible for the condition it may be that an atmosphere in contact with energized charcoal is richer in carbon monoxide than when it is in contact with plain charcoal as deduced by Grossmann. This condition would be important because the atmosphere would have an increased carburizing capacity and the carburizing potential would be increased. In Part II of this investigation the carbon monoxide concentration did not exceed the equilibrium value. Air had been used in Part I while carbon dioxide was used in Part II. It is difficult to evaluate the effect of this difference and further work is necessary to clarify this matter. At equilibrium in the presence of solid carbon the gas composition should be that demanded by K_{11}.

CONCLUSIONS

1. Barium carbonate has a definite effect on the rate of reaction between austenite and a carbon monoxide-carbon dioxide carburizing atmosphere. In the presence of barium carbonate the atmosphere produced a hypereutectoid case while the same atmosphere under the same conditions in the absence of the barium carbonate produced only a eutectoid case. The presence of barium carbonate also led to greater case depths. This effect is responsible for much of the difference produced by energized and unenergized carburizing compounds.

2. A carbon monoxide-carbon dioxide carburizing atmosphere is "activated" by barium carbonate and this activity persists for some time after the gas leaves the barium carbonate. This effect is also important during pack carburizing with an energized compound.

3. Barium carbonate accelerates the rate of reaction between carbon dioxide and charcoal. The optimum amount of barium carbonate has not been determined but the addition of 10 per cent barium carbonate to the charcoal has a much greater effect than the addition of 2 per cent. This effect is important if the carburizing reaction produces carbon dioxide faster than plain charcoal can convert it to carbon monoxide.

BIBLIOGRAPHY

1. F. Giolitti, "The Cementation of Iron and Steel," McGraw-Hill, 1915.

2. G. Takahashi, "On the Mechanism of Carbon Penetration in the Cementation of Iron and Steel," Science Reports, Tohoku Imperial University, Vol. 17, 1928, p. 761.

3. G. Takahashi, "On the Energizing Action of Carbonates Contained in Carburizing Mixtures," Science Reports, Tohoku Imperial University, Vol. 17, 1928, p. 883.

4. R. A. Ragatz and O. L. Kowalke, "Energizing Action of Various Chemicals in the Carburization of Steel with Solid Carburizing Agents," Metals and Alloys, Vol. 2, 1931, p. 290; "Mechanism of Energizer Action in Carburization," Metals and Alloys, Vol. 2, 1931, p. 343.

5. G. M. Enos, "The Role of Energizers in Carburizing Compounds," Transactions, American Society for Steel Treating, Vol. 20, 1932, p. 27.

6. E. G. Mahin, discussion of paper by H. W. McQuaid, Transactions, American Society for Metals, Vol. 26, 1938, p. 453.

7. T. C. Fong and R. A. Ragatz, "The Action of Carbonate Catalysts in the Carburization of Steel," Transactions, American Society for Metals, Vol. 32, 1944, p. 162.

8. "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand, 5th edition, 1939.

9. S. Marshall and J. Chipman, "The Carbon-Oxygen Equilibrium in Liquid Iron,"Transactions, American Society for Metals, Vol. 30, 1942, p. 695.

10. M. P. Matuszak, "Unitized Gas-Analysis Apparatus," Industrial and Engineering Chemistry, Anal. Ed., Vol. 6, 1934, p. 72.

11. A. Bramley and A. J. Jinkings, "The Gaseous Cementation of Iron and Steel. Part I.- Cementation by Carbon Monoxide," Iron and Steel Institute, Carnigie Scholarship Memoirs, Vol. 15, 1926, p. 17.

12. J. B. Austin and M. J. Day, "Chemical Equilibrium as a Guide in the Control of Furnace Atmospheres- A Review of Equilibrium Data," "Controlled Atmospheres,"

published by the American Society for Metals, 1942, p. 20.

13. E. G. Mahin, discussion of paper by T. C. Fong and R. A. Ragatz, Transactions, American Society for Metals, Vol. 32, 1944, p. 189.

14. G. Sachs and K. R. Van Horn, "Practical Metallurgy," published by the American Society for Metals, 1940, p. 442.

15. H. W. Gillett and B. W. Gonser, "Fundamental Features of Controlled Atmospheres, Particularly for the Heat Treatment of Steel," "Controlled Atmospheres," published by the American Society for Metals, 1942, p. 1.

16. M. A. Grossmann, "A Review of Some Fundamentals of Carburizing," Transactions, American Society for Metals, Vol. 26, 1938, p. 427.

17. W. E. Day, "Carburization by Solid Cements," Transactions, American Society for Steel Treating, Vol. 9, 1926, p. 240.

18. G. Takahashi, "On the Equilibrium Between Austenite and the Carbon Oxides," Science Reports, Tohoku Imperial University, Vol. 15, 1926, p. 157.

19. A. Johansson and R. Von Seth, "The Carburisation and Decarburisation of Iron and Some Investigations on the Surface Decarburisation of Steel." Journal, Iron and Steel Institute, Vol. 114, 1926, p. 295.

20. M. L. Becker, "Carburising and Graphitising Reactions Between Iron-Carbon Alloys, Carbon Monoxide and Carbon Dioxide," Journal, Iron and Steel Institute, Vol. 121, 1930, p. 337.

21. A. Bramley and H. D. Lord, "The Equilibria Between Mixtures of Carbon Monoxide and Carbon Dioxide at Various Pressures in Contact with Steels of Different Carbon Concentrations at 750-1100°," Journal, Chemical Society, Vol. 135, 1932, 1641.